Study of Recombination Characteristics Under Light and Elevated Temperature in Silicon Solar Cells

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

by

Resmi E. (Roll no.174073004)

under the guidance of

Prof. Anil Kottantharayil



Department of Electrical Engineering

IIT BOMBAY

2024

Approval Sheet

This thesis/dissertation/report entitled **Study of Recombination Characteristics Under Light and Elevated Temperature in Silicon Solar Cells** by Mr. Resmi E. is approved for the degree of <u>Doctor of</u> **Philosophy (PhD)**.

Examiners

Predma Deanvel

Supervisor (s)

AH

Chairperson

Date : 16 Angust 2024 Place : IT Bombey

Robertan

Declaration

I declare that this written submission represents my ideas in my own words, and where other's ideas or words have been included, I have adequately cited and referenced the sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated, or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will cause disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

Certain segments of the thesis are already published or under review in journals as listed below.

Chapter 6: E Resmi, K. P. Sreejith, Anil Kottantharayil, "Characterization of Light Induced Degradation in PECVD Silicon Nitride Passivated Cz Silicon Wafers Using Spectroscopic Techniques" Surfaces and Interfaces, vol.38, 2023.

Chapter 7: E. Resmi, K. P. Sreejith, A. Kottantharayil, "Comprehensive Analysis of Recombination Characteristics of due to Illumination under Elevated Temperature in Monocrystalline and Multicrystalline Wafers" under review in Journal Silicon.

Chapter 8: E. Resmi, K.P. Sreejith, A. Kottantharayil, "Analysis of variation in recombination characteristics due to light and heat in industrial silicon solar cells", Solar Energy, vol.252, pp.127-133, 2023.

Chapter 8: E. Resmi, K. P. Sreejith, A. Kottantharayil, "Characterization of Bulk Degradation due to Light and Elevated Temperature in Industrial Solar Cells", XXIst International Workshop on the Physics of Semiconductor Devices (IWPSD) 2021, Dec. 13-15, IIT Delhi.

Appendix B: E. Resmi, K. P. Sreejith, A. Kottantharayil, 2D distribution of Fe concentration in mc-Si wafers using optoelectrical characterization", International Conference

on Purification and Recycling of Materials (ICPREM) 2020, March 8-10, organized by C-MET Hyderabad, Govt of India.

Resmile

Resmi E. Roll No.174073004

16 August 2024.

Abstract

Light-induced and light and elevated temperature-induced degradation are major concerns during the initial operation of silicon solar cells in the field. This thesis contributes to the development of a better understanding of these degradation mechanisms. The chemical species involved in the light-induced degradation of plasma-enhanced chemical vapor deposited (PECVD) hydrogenated silicon nitride $(SiN_X : H)$ passivated p-type and n-type wafers under normal outdoor ambient conditions were investigated. The electrical characterization measurements, along with Fourier transform infrared (FTIR) and photoluminescence (PL) spectroscopic techniques, were utilized in this study. Significant reductions in effective minority carrier lifetime values and band-to-band PL intensities were noticed for both p-type and n-type samples after outdoor light soaking. The apparent defect density increased from 3.39 \times $10^{-3}~\mu s^{-1}$ to 1.68 \times $10^{-2}~\mu s^{-1}$ and $3.42 \times 10^{-4} \ \mu s^{-1}$ to $3.46 \times 10^{-3} \ \mu s^{-1}$, respectively, for p-type and n-type samples after light soaking of 111 hours corresponding to cumulative solar insolation of 95.7 kWh/m². The changes in FTIR absorbance intensities of chemical species such as SiNxHy, SiHm, SiO2i and SiO_n after light soaking confirmed the role of oxygen in addition to hydrogen in both p-type and n-type samples. Spectroscopic PL analysis further validated the decrease in concentration of silicon-oxygen species and reduction in effective lifetime for n-type samples.

The recombination characteristics of the surface and bulk of diffused industrial grade monocrystalline (c-Si) and multi-crystalline (mc-Si) silicon wafers passivated with PECVD SiN_X : H layer are investigated in detail by subjecting the samples to illuminated annealing at 75°C, closer to outdoor operating condition. Open circuit PL intensity variations suggest an extended growth of defective regions with increased light soaking duration in both c-Si and mc-Si samples. Regeneration in PL intensity and effective minority carrier lifetime is relatively lower in mc-Si samples than in c-Si samples due to the high density of crystallographic defects and metallic impurities. Further, the analysis of surface and bulk recombination characteristics reveals that emitter surface and bulk response are different during illuminated annealing. The bulk component dominates overall recombination characteristics and shows an initial degradation within 24 h followed by regeneration as light soaking duration increases. In contrast, the emitter surface shows an improved response for both c-Si and mc-Si as compared to the initial condition due to hydrogen diffusion. Light soaking beyond 24 h resulted in higher surface recombination in c-Si samples, indicating the possible formation of light and elevated temperature-induced degradation (LeTID) defects. However, no such degradation in the emitter surface is observed in mc-Si beyond 24 h, even after light soaking for 125 h. This suggests the absence of LeTID-related defect formation at the emitter surface. Our study shows that an emitter not only helps regenerate bulk but also determines the behavior of the surface when exposed to light and heat.

An in-depth examination of the changes in performance parameters of industrial monocrystalline and multicrystalline silicon solar cells is explored under exposure to light and heat. Higher degradation and better regeneration in performance parameters, namely open circuit voltage (V_{OC}), short circuit current density (J_{SC}), and fill factor (FF), are observed for monocrystalline solar cells. Suns-V_{OC} measurement indicates that the recombination current densities within the space charge region (J_{02}) and the rest of the solar cells (J_{01}) together play an important role in LeTID and subsequent regeneration characteristics. Both J_{01} and J_{02} changed significantly for monocrystalline and multicrystalline solar cells during the degradation phase. Even though J₀₁ was improved for both types of solar cells during regeneration, a notable reduction in J_{02} was observed only for monocrystalline solar cells. FF loss analysis shows that the recombination in the space charge region is majorly responsible for degradation and regeneration in FF. In contrast to most of the previous studies, we report similar reductions in external quantum efficiency (EQE) at 984 nm, 877 nm, and 658 nm and propose that the formation of defects related to LeTID are not only in the deep bulk but are distributed throughout the bulk. The absence of any improvement in EQE after prolonged exposure to light and heat suggests that defect transformation and gettering are not sufficient enough to regenerate J_{SC} in multicrystalline solar cells. EQE maps at 407 nm suggest that the LeTID behavior of the emitter is different from that of bulk.

Since most high-efficiency solar cells utilize hydrogen-rich dielectric layers and are prone

to defects triggered by light and elevated temperatures, the analysis presented in the thesis offers valuable insights into the chemical species affecting performance degradation, recombination characteristics, and factors influencing the performance parameters. This examination assists in comprehending the fundamental degradation mechanisms and developing models for the degradation processes in high-efficiency solar cells functioning under typical ambient conditions. Consequently, it actively contributes to the continuous improvement of the efficiency of these solar cells.

Contents

Al	bstract v			V	
Li	List of Figures xi List of Tables xvii				
Li					
No	omeno	clature			xviii
1	Intr	oductio	n		1
	1.1	Motiva	ation		3
	1.2	Organi	ization of the Thesis		6
2	Silic	on Sola	ar Cells and Recombination Mechanisms		9
	2.1	Perfor	mance parameters of solar Cells		9
	2.2	Two di	iode model of solar cells		11
	2.3	Carrie	r recombination in solar cells		13
		2.3.1	Radiative recombination		14
		2.3.2	Auger recombination		16
		2.3.3	Shockley - Read - Hall- recombination		19
			2.3.3.1 SRH statistics		20
		2.3.4	Surface recombination		23
			2.3.4.1 Silicon dioxide passivation		26
			2.3.4.2 Silicon nitride dielectric passivation		27
			2.3.4.3 Hydrogenated amorphous silicon passivation		28
			2.3.4.4 Aluminium oxide dielectric passivation		28
		2.3.5	Effective lifetime of charge carriers		29

	2.4	Detail	ed analysis of defect-related lifetime degradation using simulation	30
		2.4.1	Effect of defect parameters and doping concentration	30
		2.4.2	Effect of injection level on SRH recombination activity	33
	2.5	Conclu	usion	35
3	SRH	I recom	bination characteristics of defects in Si solar cells	36
	3.1	Recon	bination properties of defects in Si wafers	36
		3.1.1	Iron related defects in Si	37
		3.1.2	Copper related defects in Si	38
		3.1.3	Nickel related defects in Si	39
		3.1.4	Oxygen related defect in Si	40
			3.1.4.1 Boron-Oxygen complex	41
	3.2	Mitiga	tion of SRH defects	43
	3.3	Hydro	gen-related defects in Si	46
	3.4	Conclu	usion	50
4	TI J	onstand	ling of light and elevated temperature-induced degradation in silicon	
4	Una	erstanu		
4	ond sola	r cells	ing of right and elevated temperature-induced degradation in sincon	51
4	solar 4.1	r cells	in Si solar cells	51 52
4	sola 4.1 4.2	r cells LeTID Factor	in Si solar cells	51 52 53
4	sola 4.1 4.2	r cells LeTID Factor 4.2.1	in Si solar cells	51 52 53 54
4	sola 4.1 4.2	r cells LeTID Factor 4.2.1 4.2.2	in Si solar cells	51 52 53 54 55
4	sola 4.1 4.2	r cells LeTID Factor 4.2.1 4.2.2 4.2.3	in Si solar cells	51 52 53 54 55 57
4	sola 4.1 4.2	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4	in Si solar cells	51 52 53 54 55 57 58
4	sola 4.1 4.2 4.3	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4 Kinetic	Image of right and elevated temperature-induced degradation in sincon In Si solar cells Is influencing LeTID Firing process parameters Dielectric film properties Emitter diffusion profile Wafer thickness Cs of degradation and regeneration	51 52 53 54 55 57 58 59
4	sola 4.1 4.2 4.3	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4 Kinetic 4.3.1	9 in Si solar cells	51 52 53 54 55 57 58 59 60
4	sola 4.1 4.2 4.3	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4 Kinetic 4.3.1 4.3.2	9 in Si solar cells	 51 52 53 54 55 57 58 59 60 63
4	sola 4.1 4.2 4.3	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4 Kinetic 4.3.1 4.3.2 Root c	9 in Si solar cells	 51 52 53 54 55 57 58 59 60 63 64
4	sola 4.1 4.2 4.3 4.3	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4 Kinetia 4.3.1 4.3.2 Root c 4.4.1	Pin Si solar cells Si solar cells Si influencing LeTID Si solar cells Firing process parameters Si solar cells Dielectric film properties Si solar cells Emitter diffusion profile Si solar cells Wafer thickness Si solar cells Injection and regeneration Si solar cells Defect Modeling Si solar cells Metallic impurities as a cause for LeTID Si solar cells	 51 52 53 54 55 57 58 59 60 63 64 64
4	sola 4.1 4.2 4.3 4.4	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4 Kinetic 4.3.1 4.3.2 Root c 4.4.1 4.4.2	Principal and elevated temperature-induced degradation in sincon Principal Structure degradation in sincon Sinfluencing LeTID Firing process parameters Dielectric film properties Emitter diffusion profile Wafer thickness Cs of degradation and regeneration Injection and temperature dependency of LeTID kinetics Defect Modeling ause of LeTID Metallic impurities as a cause for LeTID Hydrogen as a prime suspect for LeTID	51 52 53 54 55 57 58 59 60 63 64 64 64
4	sola 4.1 4.2 4.3 4.4	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4 Kinetic 4.3.1 4.3.2 Root c 4.4.1 4.4.2 4.4.3	P in Si solar cells	51 52 53 54 55 57 58 59 60 63 64 64 64 66
4	sola 4.1 4.2 4.3 4.4 4.4	r cells LeTID Factor 4.2.1 4.2.2 4.2.3 4.2.4 Kinetic 4.3.1 4.3.2 Root c 4.4.1 4.4.2 4.4.3 Metho	Pin Si solar cells	51 52 53 54 55 57 58 59 60 63 64 64 64 66 67 68

	4.7	Summ	ary	70
5	Cha	racteriz	zation Techniques	71
	5.1	Lifetin	ne characterization	71
	5.2	Photol	uminescence imaging	73
	5.3	Photol	uminescence Spectroscopy	74
	5.4	FTIR S	Spectroscopy	75
	5.5	Curren	nt-voltage characteristics	76
	5.6	Quanti	um efficiency measurement	78
6	Cha	racteriz	zation of Degradation in PECVD Silicon Nitride Passivated Cz Silicon	
	Waf	ers at N	Jormal Ambient Outdoor Conditions	81
	6.1	Experi	imental methods	82
		6.1.1	Sample preparation and characterization	82
	6.2	Resul	ts and discussion	83
		6.2.1	Electrical characterization	83
			6.2.1.1 Estimation of apparent defect density	86
			6.2.1.2 Estimation of surface recombination current density and bulk	
			lifetime	86
		6.2.2	Optical characterization	88
			6.2.2.1 FTIR Spectroscopy	88
			6.2.2.2 Luminescence spectroscopy	92
		6.2.3	Influence of SiN_X : H deposition on hydrogen and oxygen related defect	
			in Si wafers	94
		6.2.4	Defect analysis using linearized SRH statistics	95
		6.2.5	Comparison of Results in this work with existing literature	99
	6.3	Summ	ary	100
7	Con	nprehen	isive Analysis of Recombination Characteristics due to Illumination Un-	
	der	Elevate	d Temperature in Monocrystalline and Multicrystalline Wafers	102
	7.1	Experi	imental Methods	103
		7.1.1	Sample preparation and characterization	103
	7.2	Result	s and discussion	106

		7.2.1	Photoluminescence imaging	106
		7.2.2	Lifetime characterization	108
			7.2.2.1 Significance of emitter in determining LeTID and subsequent	
			regeneration	112
		7.2.3	Quantum Efficiency	113
		7.2.4	Comparison of Results in This Work with Existing Literature	114
	7.3	Summ	ary	116
8	Ana	lysis of	Variation in Recombination Characteristics due to Light and Heat in	L
	Indu	istrial S	Silicon Solar Cells	117
	8.1	Experi	mental methods and characterization	118
	8.2	Experi	mental results and discussion	119
		8.2.1	Variation in performance parameters	119
		8.2.2	Variation in two model parameters	122
		8.2.3	Fill Factor loss analysis	123
		8.2.4	LBIC for short circuit current analysis	125
		8.2.5	PL imaging for uniformity analysis	127
		8.2.6	Comparison of Results in This Work with Existing Literature	129
	8.3	Summ	ary	130
9	Con	clusion	and Future Work	131
	9.1	Conclu	usion	131
	9.2	Future	scope of the thesis	133
A	Vari	ation ir	n solar irradiance, temperature, humidity and wind speed	135
B	Qua	ntificat	ion of defects in Si wafers	137
	B .1	Estima	ation of oxygen concentration in Si wafers	137
	B.2	Estima	ation of hydrogen concentration in Si wafers	138
	B.3	Estima	ation of electrically active iron concentration in multicrystalline Si wafers	138
Bi	bliog	raphy		168
Li	st of l	Publicat	tions	169

Acknowledgments

List of Figures

1.1	Recombination current in p-type material and its future trend [12]	2
1.2	Normalized effective lifetime variations in asymmetrically diffused n-type Cz	
	samples as a function of annealing duration in dark (diamond) and under 1	
	kW/m ² illumination (triangles) [22]	4
1.3	Cross sectional view of PERC and TOPcon solar cell	4
2.1	(a) The basic structure of a p-n junction solar cell. (b) The current density-	
	voltage (J-V) characteristics of a typical solar cell and the corresponding power-	
	voltage (P-V) characteristics are represented in black and red solid lines, respec-	
	tively	10
2.2	The electrical equivalent of a p-n junction solar cell	12
2.3	Schematic diagram showing radiative recombination process	15
2.4	Schematic diagram showing Auger recombination consisting of "eeh" process	
	and "ehh" process.	16
2.5	Schematic diagram showing (a) Electron emission, (b). Electron capture (c)	
	Hole capture (d) Hole emission [56]	19
2.6	Schematic diagram showing (a) Electron emission, (b) Electron capture (c) Hole	
	capture (d) Hole emission [56]	23
2.7	Variation effective lifetime, radiative lifetime, Auger recombination, and SRH	
	lifetime as a function of excess carrier density in p-type Si material with defect	
	level located at the mid of band gap	30
2.8	Variation in SRH lifetime of p-type samples as a function of defect energy level	
	for different doping concentrations keeping Q fixed	31
2.9	Variation in SRH lifetime of p-type samples as a function doping concentration	
	for different defect energy levels keeping Q fixed	32

2.10	Variation in SRH lifetime of p-type samples as a function doping concentration	
	for Q = 0.1, Q=1 and Q=10 keeping energy level fixed at $E_T = E_V + 0.8eV$	32
2.11	Variation in SRH lifetime in a p-type sample as a function of normalized injec-	
	tion level for different defect energy levels keeping Q fixed	34
2.12	Variation in SRH lifetime in a p-type sample as a function of normalized injec-	
	tion level for Q = 0.1, Q=1 and Q=10 keeping energy level fixed at $E_T = E_V + 0.6$	
	eV	34
3.1	iV_{OC} maps calibrated at one sun of a diffused multi-crystalline silicon wafer;	
	(a) after the deposition of PECVD SiNx: H and (b) after the subsequent belt	
	furnace firing process [152].	43
3.2	Defect concentration in SiN_X passivated samples with different SiH_4 : NH_3 ra-	
	tios during deposition process [149]	44
3.3	Variation of defect concentration as a function of time in SiN_X : H passivated	
	samples with different SiH_4 : NH_3 ratios before and after the firing process [149].	45
3.4	Variation in defect concentration with annealing time in Si samples passivated	
	with a dielectric stack of Al_2O_3/SiN_X : H [149]	46
4.1	Effective minority carrier lifetime of fired (415°C to 740°C) and non-fired (NF)	
	multicrystalline samples as a function of light soaking duration at 140°C, 44.8	
	$kW m^{-2}$ (left). The maximum extent of degradation (black circles) and effective	
	lifetime at the maximum degradation (red squares) as a function of peak firing	
	temperature (right) [32]	54
4.2	(a) Measured temperature profiles of the firing processes. (b) Normalized defect	
	concentration as a function of degradation time averaged over the whole wafer	
	area [27]	55
4.3	Variation in normalized defect density as a function of light soaking duration	
	for samples passivated with SiN_X : H films with optical properties given Table	
	4.1 (left). Normalized defect concentration as a function of SiN_X : H (right) [34].	56
4.4	(a) Effective lifetime and (b) maximum effective defect density as a function	
	of refractive index n measured at a wavelength of 633 nm (lower axis) and the	
	corresponding silicon-to-nitrogen ratio (upper axis) of the silicon nitride layer	
	keeping silicon nitride film thickness constant [29].	57

4.5	(a) Effective lifetime corresponds to $\Delta n = 7.5 \times 10^{14} \text{ cm}^{-3}$ as function of light	
	soaking duration, (b) normalized defect density of effective lifetime and (c)	
	total emitter saturation current density of double side diffused multicrystalline	
	Si passivated with SiO ₂ /SiN _X : H on both sides [30]	58
4.6	Effective defect density measured from lifetime data at $\Delta n = 1 \times 10^{15} \text{ cm}^{-3}$	
	for p-type multicrystalline samples with thickness varying from 128 μ m to	
	159µm versus light soaking duration (left). Maximum defect density versus	
	wafer thickness of conventional and high-performance multicrystalline samples	
	(right) [13]	59
4.7	LeTID defect transition model adapted from [169].	60
4.8	The relative dark current (semi-logarithmic scale) of p-type high-performance	
	multicrystalline PERC solar cells versus degradation time at different injection	
	conditions (left). The dashed and dotted lines indicate the best fit of the data	
	points used for estimating the degradation rate constant. Degradation rate con-	
	stant plotted as a function of excess carrier density (right) [42]	61
4.9	Measured normalized defect densities N* as a function of the exposure time t	
	in hours after exposure to 0.5 suns illumination and temperature ranging from	
	75 to 120° C (left). Degradation rate constants of the fast and slow degradation	
	components versus the inverse temperature 1/T according to the Arrhenius law	
	(right) [170]	62
4.10	Maximum normalized defect density as a function of hydrogen fraction released	
	from SiN _X films deposited at 400°C (left) and 420°C (right) in multicrystalline	
	wafers with resistivities of 1.6 Ω cm and 1.9 Ω cm [33]	67
5.1	PL spectra of a silicon sample passivated with SiN _x at 300K	75
5.2	J-V (black solid line) and P-V (red solid line) characteristics of a sample solar	
	cell fabricated at NCPRE measured using a AAA class solar simulator from	
	Abet Technologies.	76
5.3	The electrical equivalent of a p-n junction solar cell used for FF loss analysis.	77
5.4	EQE (black solid line) and Reflection (red solid line) curve of a sample solar	
	cell fabricated at NCPRE measured using Bentham PVE300 tool	79
5.5	Penetration depth in a silicon sample as a function of wavelength at 300 K [197].	80

6.1	(a). A schematic of the test structure used in the experiment. (b). A photograph	
	of the experimental setup during the light soaking in outdoor conditions	82
6.2	Variation in average solar insolation between 10.00 am and 4.00 pm measured	
	at Mumbai, India, during the period from 29 January 2020 to 06 March 2020.	83
6.3	Effective minority carrier lifetime variation in p-type (top) and n-type (bottom)	
	samples after light soaking with a cumulative solar insolation up to 95.7 kWh/m^2 .	84
6.4	Si band to band PL intensity of p-type (top) and n-type (bottom) sample before	
	(left) and after (right) light soaking with a cumulative solar insolation of 95.7	
	kWh/m^2	85
6.5	Apparent normalized defect density variation in p-type and n-type samples as a	
	function of cumulative solar insolation.	87
6.6	Variation of surface recombination current density, J_{0s} and bulk lifetime, τ_B	
	in n-type samples as function of cumulative solar insolation. Inset shows a	
	representative inverse Auger corrected lifetime curve of the light-soaked sample	
	when subjected to solar insolation of 95.75 kWh/m ² . The slope of the green line	
	(linear fit generated for high injection regime and extrapolated to the y-axis) was	
	used to estimate the $J_{0s}.$	88
6.7	FTIR spectra of p-type (left) and n-type (right) samples before and after light	
	soaking for 63 kWh/m ²	89
6.8	Measured and deconvoluted FTIR spectra for p-type before (left) and after	
	(right) light soaking for 63 kWh/m 2	90
6.9	Measured and deconvoluted FTIR spectra for n-type before (left) and after	
	(right) light soaking for 63 kWh/m ²	90
6.10	Measured FTIR spectra Si-H bond for p-type (left) and n-type (right) sample	
	before and after light soaking for 63 kWh/m ²	91
6.11	Normalized PL spectra (denoised) before and after light soaking for n-type sam-	
	ples. The inset shows the measured PL spectra of the sample	93
6.12	Normalized absorbance spectra showing Si_H vibrational peak at 2160 cm ⁻¹ (a)	
	in p-type (a) and (b) in n-type Si wafers before and after PECVD $\text{SiN}_X: H$	
	dielectric film deposition process.	94
6.13	Normalized absorbance spectra showing oxygen related vibrational peak in p-	
	type Si wafer before and after PECVD SiN_X : H dielectric film deposition process.	95

6.14	Normalized absorbance spectra showing oxygen related vibrational peak in n-
	type Si wafer before and after PECVD SiN_X : H dielectric film deposition process 96
6.15	SRH lifetime versus X=n/p for p-type samples after light soaking of 111 h 98
6.16	SRH lifetime versus $Y = p/n$ for n-type samples after light soaking of 111 h 98
7.1	Process flow for the fabrication of test structures used for studying the LeTID
	and regeneration effects in diffused and non-diffused silicon wafers 104
7.2	Schematics of the test structure used in the analysis
7.3	Schematic diagram of Xenon test chamber (Q-SUN Xe-3) used for effective
	reproduction of environmental conditions
7.4	The spatial variation in PL intensity as a function of light soaking duration for
	the representative lifetime samples from c-Si and mc-Si groups. The histograms
	at different light soaking durations $t = 00$ h, $t = 24$ h, and $t = 88$ h are shown
	below the PL images
7.5	Variation in iV_{OC} as a function of light soaking at five different regions for (a)
	c-Si and (b) mc-Si samples. The schematic diagram given in Figure 7.5 (c)
	shows the five different locations where iV_{OC} is measured
7.6	The variation in excess minority carrier lifetime (measured at $\Delta n = 10^{15} \text{ cm}^{-3}$)
	of c-Si samples as a function of light soaking duration. Inset shows the effective
	lifetime of minority carriers measured as a function of Δn at the center of the
77	sample
1.1	The variation in excess minority carrier filetime (measured at $\Delta n = 10^{10}$ cm ⁻¹)
	time-SI samples as a function of right soaking duration. Inset shows the effec-
	tive lifetime of minority carriers measured as a function of Δn at the center of
7.0	
/.8	The variation in $\tau_{\rm B}$ and $J_{\rm 0s}$ as a function of light soaking duration of c-Si and
	mc-Si samples.
7.9	(a) Variation in minority carrier lifetime characteristics as a function of excess
	carrier density in non-diffused Cz samples at different light soaking durations.
	(b) The corresponding changes in surface component J_{0s} and bulk lifetime τ_B
	as a function of light soaking duration
7.10	QE variation in c-Si and mc-Si solar cells at $t = 00$ h, $t = 24$ h and $t = 88$ h of
	light soaking

8.1	Schematic cross-section of the device used in the study	119
8.2	Variation of efficiency of mono and multi solar cells as a function of light soak-	
	ing time	120
8.3	Variation in normalized performance parameters of mono and multi solar cells	
	as a function of light soaking time	121
8.4	J_{01} and J_{02} , R_s and R_{sh} variation with light soaking for both mono and multi	
	solar cells.	123
8.5	Variation in FF loss due to J_{01} and J_{02} , R_s , R_{sh} of both mono and multi solar	
	cells after light soaking.	124
8.6	EQE map of representative solar cells from mono at 984 nm, 877 nm, 658 nm	
	and 407 nm for $t = 00 h$, $t = 24 h$ and $t = 67 h$.	126
8.7	EQE map of representative solar cells from multi at 984 nm, 877 nm, 658 nm	
	and 407 nm for $t = 00 h$, $t = 24 h$ and $t = 67 h$.	126
8.8	PL images of representative solar cells from mono and multi before and after	
	light soaking. Histograms of PL intensity for initial ($t = 00$ h), degraded ($t = 24$	
	h) and regenerated (t = 67 h) are shown beneath PL images. $\dots \dots \dots \dots$	128
A.1	Variation in solar irradiance from 10.00 am to 4.00 pm for the days on which	
	light soaking is carried out. Both these sets of data are reordered at the site of	
	the experiment using a PV module monitoring station.	135
A.2	Variation in the maximum, average, and minimum value of ambient humidity	
	and windspeed for the days on which light soaking is carried out. The humidity	
	and wind data are recorded at a site 7.55 km away from the experiment site. \therefore	136
B.1	Effective lifetime variations in a p-type multicrystalline Si sample as a function	
	of excess carrier density before and after light dissociation of FeB	140
B.2	Estimated electrically active average Fe concentration in multicrystalline Si	
	samples	140
B.3	PL image showing the distribution of electrically active Fe concentration across	
	the multicrystalline Si sample.	141

List of Tables

2.1	The normalized SRH lifetime under low-level injection based on the position of	
	defect energy level	33
3.1	Recombination properties of Fe defects in Si [68]	37
3.2	Recombination properties of Cu defects in Si [3, 125, 126]	39
3.3	Recombination properties of Ni in Si [3, 133, 135]	40
3.4	Recombination properties of oxide precipitate in Si [140]	40
3.5	Recombination properties BO defect in Si [70, 148].	43
3.6	Recombination properties of hydrogen-related defects in Si [157]	47
3.7	Summary of recombination characteristics of light-sensitive defects in Si	48
4.1	SiN_X : H dielectric film properties [34]	56
6.1	Integrated absorbance intensities for the Gaussian components before and after	
	light soaking for p-type and n-type samples.	91
6.2	Defect parameters for p-type and n-type samples.	99
7.1	Extent of LeTID reported in diffused samples passivated with PECVD SiN_X : H in the literature and in this work.	115
8.1	Relative reduction in efficiency of solar cells associated with LeTID under a	
	wide range of operational conditions [157].	129

Nomenclature

List of Abbreviations

a–Si : H	Hydrogenated Amorphous Silicon
Al_2O_3	Aluminium Oxide
AlO_X : H	Hydrogenated Aluminum Oxide
AlO _X	Aluminum Oxide (non-stoichiometric)
B_iO_i	Interstitial Boron- Interstitial Oxygen Complex
B _i VO _{2i}	Interstitial Boron- Vacancy- Interstitial Oxygen Complex
B _s O _{2i}	Substitutional Boron Interstitial Oxygen Complex
B _i	Interstitial Boron
Cu ₃ Si	Interstitial Copper Silicon Complex
Cu _i	Interstitial Copper
Cu _s Cu _i	Substitutional Copper - Interstitial Copper Complex
Cu _s Cu _s	Substitutional Copper Complex
Cu _s	Substitutional Copper
Fei	Interstitial Iron
NH ₃	Ammonia
Ni _i	Interstitial Nickel

Nis	Substitutional Nickel
Ni _X Si _Y	Nickel Silicide Complex
O _{2i}	Interstitial Oxygen Dimer
POCl ₃	Phosphorus Oxychloride
Si _x H _y N _z	Silicon-Hydrogen-Nitrogen Complex
SiH ₄	Silane
SiN_X : H	Hydrogenated Silicon Nitride
SiO ₂	Silicon Dioxide
SiOX	Silicon Oxide (non- stoichiometric)
B _s	Substitutional Boron
O _i	Interstitial Oxygen
SiNX	Silicon Nitride (non- stoichiometric)
SiO _i	Silicon Interstitial Oxygen Complex
SiO _X	Silicon Oxdie (non- stoichiometric)
ALD	Atomic Layer Deposition
ARC	Anti-Reflection Coating
Au	Gold
В	Boron
BO	Boron-Oxygen Complex
BSF	Back Surface Field
c-Si	Crystalline Silicon
CID	Carrier Induced Degradation

Cu	Copper
Cu LID	Copper related Light Induced Degradation
DSP	double-side polished
EDX	Energy-Dispersive X-ray analysis
EQE	External Quantum Efficiency
Fe	Iron
FFP	Fast Firing Profile
FGA	Forming Gas Annealing
FRC	Fast Recombination Centre
FTIR	Fourier Transform Infrared
FZ	Float Zone
Н	Hydrogen
HID	Hydrogen Induced Degradation
HIR	Hydrogen Induced Recombination
HIT	Heterojunction with Intrinsic Thin layer
IBC	Interdigitated Back Contact
InGaAs	Indium-Gallium Arsenide
IQE	Internal Quantum Efficiency
IR	Infrared
ITRPV	International Technology Roadmap for Photovoltaics
J-V	Current density-Voltage
LBIC	Light Beam Induced Current

LC	Latent Complex
LeTID	Light and elevated Temperature Induced Degradation
LID	Light Induced Degradation
LID	Light Induced Degradation
LTO	low-temperature thermal oxide
mc-CID	Multicrystalline Carrier Induced Degradation
mc-Si	Multicrystalline Silicon
Ν	Nitrogen
NAOS	Nitric Acid Oxidation of Silicon
NCPRE	National Center for Photovoltaic Research and Education
Ni	Nickel
0	Oxygen
O P-V	Oxygen Power-Voltage
O P-V PECVD	Oxygen Power-Voltage Plasma Enhanced Chemical Vapor Deposition
O P-V PECVD PERC	Oxygen Power-Voltage Plasma Enhanced Chemical Vapor Deposition Passivated Emitter Rear Contact
O P-V PECVD PERC PL	Oxygen Power-Voltage Plasma Enhanced Chemical Vapor Deposition Passivated Emitter Rear Contact Photoluminescence
O P-V PECVD PERC PL PSG	OxygenPower-VoltagePlasma Enhanced Chemical Vapor DepositionPassivated Emitter Rear ContactPhotoluminescencePhosphosilicate Glass
O P-V PECVD PERC PL PSG PV	OxygenPower-VoltagePlasma Enhanced Chemical Vapor DepositionPassivated Emitter Rear ContactPhotoluminescencePhotophosilicate GlassPhotovoltaic
O P-V PECVD PERC PL PSG PV QE	OxygenPower-VoltagePlasma Enhanced Chemical Vapor DepositionPassivated Emitter Rear ContactPhotoluminescencePhotophosilicate GlassPhotovoltaicQuantum Efficiency
O P-V PECVD PERC PL PSG PV QE QSSPC	OxygenPower-VoltagePlasma Enhanced Chemical Vapor DepositionPassivated Emitter Rear ContactPhotoluminescencePhotophosilicate GlassPhotovoltaicQuantum EfficiencyQuasi-Steady-State Photoconductance
O P-V PECVD PERC PL PSG PV QE QSSPC RTP	OxygenPower-VoltagePlasma Enhanced Chemical Vapor DepositionPassivated Emitter Rear ContactPhotoluminescencePhotosphosilicate GlassPhotovoltaicQuantum EfficiencyQuasi-Steady-State PhotoconductanceRapid Thermal Processing

Si	Silicon
SRC	Slow Recombination Centre
SRH	Shockley - Read - Hall
STC	Standard Test Condition
STEM	Scanning Transmission Electron Microscopy
TD	Thermal Donors
Ti	Titanium
TOPCon	Tunnel Oxide Passivated Contact

List of Symbols

α_{n}	Capture coefficient for electron, $\text{cm}^3 \text{ s}^{-1}$
$lpha_{ m p}$	Capture coefficient for hole, $\text{ cm}^3 \text{ s}^{-1}$
η	Efficiency
v	frequency, s ⁻¹
$\sigma_{\rm n}$	Capture cross section for electron, cm^2
$\sigma_{ m p}$	Capture cross section for hole, cm^2
τ	Charge carrier lifetime, s
$ au_{ m Aug}$	Auger lifetime, s
$ au_{ m eff}$	Effective lifetime, s
$\tau_{\rm n0}$	Capture time constant for electrons, s
$ au_{\mathrm{p0}}$	Capture time constant for holes, s
$ au_{ m rad}$	Radiative lifetime, s
$ au_{ m SRH}$	Shockley - Read - Hall- lifetime, s
Δn	Excess electron concentration, cm ⁻³
Δp	Excess hole concentration, cm^{-3}
В	Radiative recombination coefficient, $\text{ cm}^3 \text{ s}^{-1}$
C _n	Auger coefficients for "eeh" process, $cm^6 s^{-1}$
c _n	Capture rate for electrons, s^{-1}
Cp	Auger coefficients for "ehh" process, $cm^6 s^{-1}$
cp	Capture rate for holes, s^{-1}
D _{it}	Interfacial defect density, $cm^{-2} eV^{-1}$

E	Solar Insolation, KWh m ^{-2}
en	Emission rate for electrons, s^{-1}
ep	Emission rate for holes, s^{-1}
E _T	Defect energy level, eV
ft	Probability that defect energy level is filled
FF	Fill factor
g _{eeh}	Coulomb enhancement factors for "eeh" process
g _{ehh}	Coulomb enhancement factors for "ehh" process
h	Planck's constant, eV s
iV _{OC}	Implied open circuit voltage, V
J ₀₁	Recombination current density component in bulk, $A \text{ cm}^{-2}$
J ₀₂	Recombination current density component in the depletion region, $A \text{ cm}^{-2}$
J _{max}	Maximum power point current density, $A \text{ cm}^{-2}$
J _{ph}	Photogenerated current density, $A \text{ cm}^{-2}$
J _{SC}	Short circuit current density, $A \text{ cm}^{-2}$
k	Boltzmann constant, $eV K^{-1}$
K _{ij}	Rate constant for the transition from state i to the state j, s^{-1}
n	Total concentration of electrons, cm^{-3}
n ₀	Equilibrium concentration of electrons, cm^{-3}
N _A	Precursor concentration, cm^{-3}
NB	Recombination active defect concentration, cm^{-3}
N _C	Passivated defect concentration, cm^{-3}

n _s	Total electron concentration at the surface, cm^{-3}
N_T^*	Normalized defect density, s^{-1}
N _{0eeh}	Empherical constant for Coulomb enhanced "eeh" process, cm ⁻³
N _{0ehh}	Empherical constant for Coulomb enhanced "ehh" process, cm ⁻³
n _{Os}	Equilibrium concentration of electrons at the surface, cm^{-3}
N _C	Effective density of states in the conduction band, $eV^{-1}cm^{-3}$
N _{dop}	Bulk Doping concentration, cm^{-3}
N _{Ts}	Defect concentration at the surface, cm^{-2}
N _T	Defect concentration, cm^{-3}
N _V	Effective density of states in the valance band, $eV^{-1}cm^{-3}$
р	Total concentration of holes, cm^{-3}
p ₀	Equilibrium concentration of holes, cm^{-3}
p _s	Total hole concentration at the surface, cm^{-3}
p _{0s}	Equilibrium concentration of holes at the surface, cm^{-3}
P _{in}	Incident Power, W cm ⁻²
P _{max}	Maximum power point, W cm ⁻²
Q	Ratio of capture cross section for electrons and holes
R _{Aug}	Auger recombination rate, $\text{cm}^{-3} \text{ s}^{-1}$
R _{Aug}	SRH recombination rate, $cm^{-3} s^{-1}$
R _{deg}	Degradation rate, s
R _{eeh}	Auger recombination rate for "eeh" process, $cm^{-3} s^{-1}$
R _{eff}	Radiative recombination rate, $cm^{-3} s^{-1}$

R _{ehh}	Auger recombination rate for "ehh" process, $cm^{-3} s^{-1}$
R _{reg}	Regradation rate, s
R _{sh}	Shunt resistance, $\Omega \text{ cm}^2$
R _s	Series resistance, $\Omega \text{ cm}^2$
RI	Refractive index
S _{eff}	Effective surface recombination velocity of holes, cm s^{-1}
Т	Temperature, K
V _{max}	Maximum power point Voltage, V
V _{OC}	Open circuit voltage, V
W	Thickness of the Si wafer, cm

Chapter 1

Introduction

Silicon wafer based solar cells persist as the prevailing photovoltaic technology, playing a crucial role in electricity generation across numerous regions. Expanding the adoption of this technology necessitates implementing processing methods that effectively mitigate losses in device performance. A variety of solar cell structures have been developed using different semiconductor materials, including passivated emitter rear contact (PERC) solar cells, heterojunction with intrinsic thin layer (HIT) solar cells, interdigitated back-contact (IBC) solar cells, heterojunction with interdigitated back-contact solar cells, and tunnel oxide passivated contact (TOPCon) solar cells. The highest recorded efficiency of a monocrystalline solar cell stands at 26.8 ± 0.4 % with a cell area of 274.4 cm² while that of a monocrystalline module is 24.7 ± 0.3 % with a module area of 17806 cm² [1]. In the case of multicrystalline Si solar cells, the record efficiency is 23.81% with a cell area of 246.44 cm² [2] and for module-level, it is 20.4% with a module area of 14818 cm² [1]. One of the fundamental impediments to achieving better efficiency is the recombination of photo-generated charge carriers within the bulk of solar cells.

In multicrystalline solar cells, metallic impurities and extended crystallographic defects such as grain boundaries, dislocations, etc., in the Si bulk act as recombination centers of charge carriers [3, 4]. These metallic impurities come from silicon feedstock used for making multicrystalline Si wafers by direct solidification method [3]. The impurities include Fe, Cu, Ni, etc. They are fast diffusing in Si and highly recombination active, hence limiting the solar cells' electrical performance [5–7]. They can exist either in the elemental form, complexes, or as a precipitate [8, 9]. While metalizing solar cells with Cu and Ni, it is possible for defects associated with these elements to also develop within the device [10, 11]. The efficiency of monocrystalline

Si solar cells, especially p-type cells, is limited due to impurities such as boron-oxygen (BO) complexes, interstitial oxygen, oxide precipitate, hydrogen-related defects, and others in the bulk of Si wafer, even when employing the best-known surface passivation techniques. These defects act as lifetime killers of charge carriers and cause an increase in the device recombination current. The trend of recombination current in p-type monocrystalline Si solar cells as per the international technology roadmap for photovoltaics (ITRPV) 2024 report is shown in Figure 1.1 [12]. The report says that the bulk recombination current of p-type monocrystalline Si is about 50 fA cm⁻². In the future, with the advancement in processing technology, it is expected that recombination current can be reduced to a level of 20 fA cm⁻² for monocrystalline p-Si wafer-based solar cells.



Figure 1.1: Recombination current in p-type material and its future trend [12].

Metallic and non-metallic impurities in Si can act as defects or defect precursors. Defect precursors can be recombination inactive initially but can undergo structural transformation and become recombination active defects upon exposure to light and heat [13, 14]. Hence, the recombination characteristics of the device change on exposure to light and heat. This, in turn, causes performance degradation of the device under normal operating conditions [13, 14]. To achieve high-efficiency solar cells, it is imperative to decrease recombination losses occurring on both the front and rear sides of the cell, along with those within the bulk material of Si solar

cells.

1.1 Motivation

Light and elevated temperature induced Degradation (LeTID) is one of the primary degradations that adversely impact the performance of solar cells [15, 16]. Petter et. al. [17] has reported more than 10% relative decrease in efficiency in PERC solar cells when subjected to light and heat. LeTID is reported in all types of silicon wafers irrespective of the type of doping (n-type or p-type), growth technique (casting, Czochralski or float zone) or crystal structure (monocrystalline or multicrystalline) [15], [18-23]. Accurate defect physics of LeTID is still unknown; however, various studies have proposed the presence of hydrogen in silicon could be the major cause [24–26]. Hydrogen is incorporated into solar cells from the hydrogenated silicon nitride (SiN_X : H) anti-reflective coating (ARC) during the co-firing process [27, 28]. Plasma-enhanced chemical vapor deposition (PECVD) is the preferred method of SiN_X : H deposition in the industrial production of solar cells. When subjected to light and heat, PECVD SiN_X : H passivated silicon samples also show a recovery in performance after the degradation [18–23, 27, 29, 30]. This recovery is attributed to improved bulk lifetime by transforming defect configurations and internal gettering [13, 14]. Figure 1.2 provides an insight into the impact of light and heat on the effective lifetime of charge carriers in asymmetrically distributed n-type samples passivated with PECVD : SiN_X : H layer. The samples show initial degradation in the effective lifetime during illuminated annealing at 1 kW/m² and 140°C for up to 50 minutes and begin to recover as the light soaking duration increases, eventually regaining their initial value after 8 hours.

The impact of various fabrication process parameters such as firing process [19, 27, 31, 32], SiN_X : H film deposition [29, 33–35] and emitter diffusion [28, 30] on LeTID have been studied by many research groups. Previous studies show that LeTID behavior is severe in silicon samples for peak firing temperature greater than 700°C [19, 27, 31, 32]. Several groups demonstrated that LeTID is proportional to the thickness and atomic bond (Si-H and N-H) density of SiN_X : H films [29, 33–35]. In addition, LeTID is reported in samples with hydrogenated aluminum oxide (AlO_X : H) films deposited by the PECVD technique as well [36]. This confirms the strong dependence of LeTID on the deposition technique. Hence, it is extremely important



Figure 1.2: Normalized effective lifetime variations in asymmetrically diffused n-type Cz samples as a function of annealing duration in dark (diamond) and under 1 kW/m² illumination (triangles) [22].

to study the characteristics of LeTID, as most of the current architectures such as PERC cells and upcoming architectures such as TOPCon cells in the solar photovoltaic industry use the PECVD technique for dielectric deposition. The crossectional view of PERC and TOPcon solar cells are shown in Figure 1.3.



Figure 1.3: Cross sectional view of PERC and TOPcon solar cell

Additionally, research by Sen et al. [30] emphasized that emitter sheet resistance plays a crucial role in degradation and regeneration behavior, affecting both the bulk and surface of solar cells. Their findings suggested that emitters with high sheet resistance profiles result in lower bulk degradation but higher surface degradation [30]. Furthermore, it is important to note that transition metals found in multicrystalline silicon may play a role in LeTID and its subsequent regeneration behavior. Therefore, the impurity-gettering process also has an impact on LeTID behavior. Schmidt et al. [14] and Zuschlag et al. [28] reported that wafers without effective impurity gettering are more susceptible to LeTID compared to wafers with gettering processes in place. All the above studies indicate that the industry processes significantly influence the LeTID behavior of silicon solar cells.

Initially, LeTID was reported in boron-doped multicrystalline silicon solar cell structures [13, 19, 27–29, 31–33, 35, 37–40]. Later studies revealed that solar cell structures fabricated on float zone and Czochralski (Cz) grown monocrystalline silicon wafers also exhibit LeTID characteristics [18, 22, 23, 41]. However, LeTID behavior in those test structures are different from one another, and the variation is based on the position of Fermi level [42], the intensity of illumination, and annealing temperature [43, 44]. Recently, Chen et al. investigated LeTID-related variation in minority carrier lifetime characteristics in diffused and non-diffused p-type and ntype Cz-grown silicon solar cell structures [21, 22]. They reported degradation in both diffused and non-diffused samples. However, they observed a recovery in effective carrier lifetime after degradation in diffused samples. Their studies also revealed that effective lifetime variation in both n-type and p-type samples is mainly due to the defects formed in the bulk with no significant changes in the emitter. In contrast, Sen et al. [30] reported that defects are formed mainly at the emitter surface when subjected to illuminated annealing at 130°C for 100 h and that the emitter doping profile plays a significant role in determining the degradation characteristics. Since the response of the emitter surface determines the overall performance of high-efficiency solar cell architectures, it is essential to characterize and analyze the LeTID behavior of the emitter surface along with bulk. To the best of our knowledge, no published research has investigated the recombination characteristics associated with LeTID in the emitter surface and bulk of commercially viable silicon solar cell structures with varying bulk qualities. Moreover, there are no reported studies on the presence of any chemical species other than hydrogen or their involvement in either bulk or surface degradation in PECVD SiN_X : H passivated samples. Most of the work related to LeTID is reported on partially processed silicon wafers, and only

limited literature is available for finished solar cells. The available literature mainly focuses on performance stability analysis of cells and modules [15, 45] comparison of performance parameters for different cell architectures [46, 47], the impact of process parameter variations [32, 39, 40, 46, 48] estimation of defect formation and transformation activation energies [39, 42, 43] and the mitigation measures [39, 40, 42–44, 48]. Even though the variations in cell performance parameters were presented previously, no characterization or in-depth analysis

was reported on the factors contributing to it. Apart from the current-voltage analysis, spectral response measurements have been commonly used for characterizing the LeTID behavior in silicon solar cells[40, 46-49]. Cho et al. [47] reported a variation in the external quantum efficiency (EQE) for the wavelength range of 700 nm to 1000 nm after light soaking. Maischner et al. [40] and Hu et al. [48] also proposed that deep bulk defects are responsible for LeTID by comparing the EQE in the long wavelength range. Padmanabhan et al.[46] recorded variation in spectral response in the wavelength range from 500 nm onwards for one sun-illuminated annealing at 90°C. In addition, Xiao et al. [49] recently reported long-term degradation at the surface and subsurface region based on the light beam-induced current (LBIC) variation at 406 nm and 658 nm wavelengths for light soaking duration beyond 280 hours (h). These studies suggest that correlating LeTID only to deep bulk defects may not be appropriate for all light soaking conditions, and hence, detailed investigations are required in this direction. In addition, as hydrogen is considered the main culprit for LeTID, it can impact the silicon - SiN_X : H interface, diffused emitter, space charge region, bulk, and rear of the solar cells. There are no reported studies on recombination within the space charge region due to illuminated annealing and its influence on the performance parameters of solar cells. Moreover, the discussions related to variations in open circuit voltage were always restricted to either deep bulk defects [40, 47] or LeTID and subsequent regeneration kinetics [32, 46–48]. Although LeTID and regeneration in fill factor were reported elsewhere [40, 46, 47], no detailed discussions about factors contributing to fill factor variation are available. Hence, there is a requirement to classify the factors contributing to LeTID and subsequent regeneration in silicon solar cells.

1.2 Organization of the Thesis

The thesis is organized into nine chapters. **Chapter 1** introduces the research's significance, current development in the specified area of interest, and motivation behind studying the recombination characteristics of light and elevated temperature-induced degradation in industrial silicon solar cells. **Chapter 2** describes the solar cell's structure, performance parameters, two-diode electrical equivalent model, and physics of various recombination mechanisms that limit the electrical performance of Si semiconductor devices. A detailed analysis of the dependency of Shockley - Read- Hall (SRH) recombination characteristics on the electrical properties of defects and injection conditions is also presented. The **Chapter 3** reviews the recombination

properties of common light-sensitive SRH defects in Si wafers and methodologies used to mitigate the SRH defects. In **Chapter 4**, a literature review for understanding the LeTID behavior in silicon solar cells, factors influencing degradation mechanism, modeling of degradation and regeneration kinetics, its root cause, and methods for mitigating the impact of LeTID are presented. **Chapter 5** describes the basic principle and characterization techniques used in the thesis.

Chapter 6 investigates the degradation behavior of PECVD SiN_X : H passivated Cz-grown silicon samples after light soaking under normal outdoor conditions. The degradation behavior of both p-type and n-type samples characterized by lifetime measurements and spectroscopic techniques is detailed in the chapter. Further, the estimation of the amount of defect generated in the samples and the corresponding behavioral changes are also presented. The chapter also gives an insight into the importance of emitter in determining the regeneration behavior of solar cells after degradation during the normal operating conditions of light and elevated temperature.

Chapter 7 comprehensively analyzes recombination characteristics due to illumination under elevated temperature in Si wafers. The chapter presents a study of band-to-band photoluminescence (PL) emission from the test structures fabricated on industrial monocrystalline and multicrystalline Si wafers to analyze the spatial variation of LeTID and regeneration behavior. An investigation of the impact of LeTID on the emitter surface and bulk separately as a function of annealing duration using lifetime characterization is also presented in the chapter. The last section of the chapter describes validating the LeTID behavior of surface and bulk in the test structures with quantum efficiency (QE) measurements in crystalline and multicrystalline Si solar cells.

Chapter 8 explores the recombination characteristics resulting from LeTID in industrial silicon solar cells. This chapter commences by investigating the variations in performance parameters attributed to LeTID in both monocrystalline and multicrystalline silicon solar cells featuring an aluminum back surface field (Al-BSF). A comprehensive analysis of the two-diode model parameters is conducted to discern the factors contributing to the observed fluctuations in performance parameters. Furthermore, the chapter delves into a detailed examination of the behavior of different regions within the solar cells. This examination encompasses the emitter, space charge, and bulk regions, scrutinizing their responses during LeTID and the subsequent regeneration processes.

Chapter 9 summarizes the thesis and provides a glimpse into the future potential for extending

the research.
Chapter 2

Silicon Solar Cells and Recombination Mechanisms

The thesis explores the decline in the performance of both monocrystalline and multicrystalline Si solar cells under the influence of light and heat. An essential aspect of this investigation involves scrutinizing the performance parameters of solar cells and the factors that influence these parameters. The key factors that impact the performance parameters of solar cells include recombination processes, light-induced current, series resistance, and shunt resistance [50]. This chapter provides an overview of the p-n junction solar cell's structure, performance parameters, and the underlying physics of various recombination mechanisms that affect the cell's performance characteristics.

2.1 Performance parameters of solar Cells

A typical solar cell is a semiconductor device that converts light energy from the sun into electrical energy. For the efficient conversion of light energy to electrical energy, the solar cell has to perform four important functions: light trapping, generation of charge carriers, separation of charge carriers, and finally, collection of charge carriers [50]. A solar cell device's basic structure must perform all these functions. The schematic diagram of a p-n junction solar cell is shown in Figure 2.1 (a). It comprises a thick, lightly doped p-type base material with a thin, heavily doped n-type emitter. Amble charge carriers are generated within the cells' base and separated by the electric field at the junction. The emitter's surface is textured and coated with an ARC to enhance the cell's light trapping. ARC also reduces surface recombination by passivating the dangling bonds. The metal contacts are provided on the front and back surfaces to maximize the charge carrier collection probability. The output characteristics of the cell are



Figure 2.1: (a) The basic structure of a p-n junction solar cell. (b) The current density-voltage (J-V) characteristics of a typical solar cell and the corresponding power-voltage (P-V) characteristics are represented in black and red solid lines, respectively.

shown in Figure 2.1 (b). The cell's current density-voltage (J-V) characteristics and the corresponding power density-voltage (P-V) characteristics are represented in black and red solid lines, respectively. On the P-V curve, the maximum power point (P_{max}) in W cm⁻² and corresponding point on the J-V curve is the maximum power point current density (J_{max} , A cm⁻²) and maximum power point voltage (V_{max} , V). The solar cell must operate at its maximum power point to get maximum power output. The most important and commonly used performance parameter is the solar cell's efficiency, which measures how much power output can be generated from a cell for a given solar irradiance. It is defined as the ratio of maximum output power to the input power as given in Eq.2.1 [50].

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{V_{\text{max}} \times J_{\text{max}}}{P_{\text{in}}}$$
(2.1)

Where P_{in} is the solar irradiance, which is equal to 0.1 W cm⁻² under standard test condition (STC) of AM 1.5G spectra and 25°C.

The other performance parameters include short circuit current density (J_{SC} , A cm⁻²), open circuit voltage (V_{OC} , V), and fill factor (FF) [50]. J_{SC} is the maximum current flowing through the solar cell when the output voltage across the solar cell is zero (i.e., when the solar cell is

short-circuited). It is determined by various factors such as solar irradiance, light absorption and reflection properties of the cell, number of charge carriers generated, and collection probability. V_{OC} is the maximum output voltage across the cell (i.e. when the cell is open circuit). V_{OC} is determined by the various recombination mechanisms within the solar cell, photo-generated current, and J_{SC} dependency on photo-generated current. However, the cell's power is zero at both operating conditions corresponding to J_{SC} and V_{OC} . The performance parameter FF, a measure of squareness of the J-V characteristics of the cell, can be used to relate the V_{OC} , J_{SC} , and P_{max} of the cell. FF is defined as the ratio of maximum output power to the product of V_{OC} and J_{SC} .

$$FF = \frac{P_{max}}{V_{OC} \times J_{SC}} = \frac{V_{max} \times J_{max}}{V_{OC} \times J_{SC}}$$
(2.2)

FF is determined by various internal mechanisms, such as the cell's recombination parameters and restive components. By combining Eq.2.1 and 2.2, efficiency can be related to the performance parameters of the solar cells as given in Eq.2.3

$$\eta = \frac{FF \times V_{OC} \times J_{SC}}{P_{in}}$$
(2.3)

2.2 Two diode model of solar cells

The two-diode model is used to analyze the performance parameter variations in solar cells [51–54]. This model offers several advantages in describing the electrical characteristics of solar cells. It provides a more accurate representation of a solar cell's current-voltage characteristics, particularly in regions where the one-diode model is less effective, such as at low and high current densities. The two-diode model enables more precise estimation of parameters like series resistance, shunt resistance, and diode ideality factors. By distinguishing recombination effects at the junction from those in the rest of the solar cell, it enhances the understanding of loss mechanisms. It better accommodates leakage currents, especially under high reverse bias conditions, where junction and bulk recombination mechanisms contribute significantly. This separation of recombination mechanisms facilitates a more precise assessment of the impacts of shunt and series resistances on the overall performance of the PV cell. Moreover, the two-diode model provides a more detailed description of cell behavior under low illumination conditions, emphasizing the increased significance of junction recombination relative to bulk recombination.

The two-diode model represents the electrical equivalent of a p-n junction solar cell, as shown in shown in Figure 2.2. The circuit contains two diodes, D_1 and D_2 . D_1 accounts for the



Figure 2.2: The electrical equivalent of a p-n junction solar cell.

recombination within the bulk of the solar cells and two cell surfaces. The D_2 accounts for the depletion region recombination. The current source J_{ph} represents the photo-generated diffusion current density (A cm⁻²). The series resistances (R_s, Ω cm²) and shunt resistance (R_{sh}, Ω cm²) account for ohmic resistances offered by the series and shunt current paths respectively. Based on the diode model, the J-V characteristics of the solar cell can be modeled as follows

$$J_{ph} = J_{01}e^{(V+JR_s)/kT} + J_{02}e^{(V+JR_s)/2kT} + \frac{V+JR_s}{R_{sh}}$$
(2.4)

where J_{01} is the recombination current density of the bulk, front and rear surfaces (A cm⁻²), J_{02} is the recombination current density in the depletion region (A cm⁻²), J is the output current density in (A cm⁻²), V is the output voltage (V), k is Boltzmann constant (eV K⁻¹), and T is the temperature (K).

The degradation in the electrical performance of the solar cells can be due to recombination losses and ohmic losses. The ohmic losses are due to the resistive components R_s and R_{sh} . In addition to the above electrical losses, there can be optical losses, too. It is due to the reflection of incident light by the device and the shadowing effect of the metal contact grid. The optical losses can be minimized by texturing the silicon surface with pyramidal structures and optimizing the dielectric properties and thickness of the ARC layer. The metal lines in the contact grid also cause optical loss by limiting the amount of light trapped in the solar cell. However, minimizing the optical loss by reducing the number and thickness of metal lines is not optimum. Reducing the metal lines' number and size will affect the device's current collection capabil-

ity and increase ohmic losses. So, industrial Si solar cells use optimum design to decide the metal line's number and thickness to maximize efficiency. The major loss in solar cells is due to recombination loss. The recombination of the charge carriers, which limits the performance of solar cells, can occur throughout the device. Recombination at the emitter, within the bulk, at the Si-dielectric layer interface, and at the Si-metal interface will decide the conversion efficiency of the solar cell. Various mechanisms responsible for carrier recombination within the solar cell are described in the following section.

2.3 Carrier recombination in solar cells

Large amounts of free charge carriers are generated when semiconductors are subjected to external excitation such as light, heat, or by applying an external voltage. The bounded charge carriers in the valance band will absorb energy from external sources and undergo the transition from the valance band to the conduction band. This process is referred to as generation. The generation of excess carriers will disturb the equilibrium condition of the system. Hence, the system will try to bring back the system to its equilibrium condition by an inverse process known as recombination. The excited charge carriers return to the minimum energy level by releasing absorbed energy. In other words, during the recombination process, the electrons in the conduction band undergo a downward transition to the empty state in the valance band and annihilate the electron-hole pair. The change in concentration of excess charge carriers with time is known as the recombination rate. The recombination rate depends upon the carrier densities and the probability of a downward transition from the conduction band to the valance band. Both energy and change in momentum are conserved during the recombination process, releasing photons and phonons and transferring the energy to another free-charge carrier within the system [55, 56]. The recombination and generation can occur throughout the semiconductor at any time, even under equilibrium conditions. However, under thermal equilibrium conditions, the generation is balanced by the reverse processes of recombination. This process determines the equilibrium concentration of electrons $(n_0, \text{ cm}^{-3})$ and equilibrium concentration of holes (p_0, cm^{-3}) . Upon external excitation, the increase in generation rate is counterbalanced by an increase in the recombination rate. The net generation or recombination rate determines the non-equilibrium electron concentration $n = n_0 + \Delta n$ and hole concentration $p = p_0 + \Delta p$. Here, Δn and Δp are the semiconductor's excess electron and excess hole concentration (cm⁻³). Since excess charge carriers are generated or recombined in pairs $\Delta n = \Delta p$. When the recombination rate exceeds the generation rate, the concentration of charge carriers decreases with time. The following rate equation R represents the decay of charge carriers (cm⁻³ s⁻¹) [55, 56].

$$R = \frac{dn(t)}{dt}$$
(2.5)

The time constant associated with the decay of charge carriers during the recombination process is known as recombination lifetime or carrier lifetime (τ , s). Mathematically, the carrier lifetime is represented as follows

$$\tau = \frac{\Delta n}{R} \tag{2.6}$$

Several physical mechanisms have been suggested to account for the recombination of electrons and holes in semiconductors [55, 56]. Based on the physical mechanisms by which the excess charge carriers undergo recombination, the recombination mechanisms are classified as band-to-band recombination, Auger recombination, SRH recombination, and surface recombination. The surface recombination is considered as an extension of SRH recombination within the bulk. The individual recombination mechanisms are characterized by their respective recombination rates. The effective recombination rate in the semiconductor is determined by the recombination rates associated with each of these individual mechanisms.

2.3.1 Radiative recombination

Radiative recombination is one of the prominent intrinsic recombination mechanisms in direct band gap semiconductors. This type of recombination occurs due to the direct transition of electrons from the conduction band energy state to the empty (hole) state in the valance band [57–59]. In radiative recombination, the energy is released during the downward transition of the electron from the conduction band to the valance band in the form of photons whose energy (hv) is equal to the band gap of the semiconductors, as shown in Figure 2.3. In Figure 2.3, E_C represents the lower end of the conduction band energy level (eV), E_V represents the upper end of the valance band energy level (eV), h is the planks constant (eV s), and v is the frequency (s⁻¹) of the emitted photons. The radiative recombination rate is proportional to the number of electron concentrations in the conduction band and holes in the valance band.The following



Figure 2.3: Schematic diagram showing radiative recombination process

expression represents the net radiative recombination rate $(R_{rad}, cm^{-3}s^{-1})$

$$\mathbf{R}_{\mathrm{rad}} = \mathbf{B}(\mathbf{n}\mathbf{p} - \mathbf{n}_{\mathrm{i}}^2) \tag{2.7}$$

where B is the coefficient of radiative recombination (cm^3s^{-1}) and is determined by the band structure of the material. Substituting $n = n_0 + \Delta_n$ and $p = p_0 + \Delta_p$ and $n_0p_0 = n_i^2$ the recombination rate in Eq.2.7 can be modeled as follows

$$\mathbf{R}_{\text{rad}} = \mathbf{B}(\mathbf{n}_0 + \mathbf{p}_0 + \Delta \mathbf{n})\Delta \mathbf{n} \tag{2.8}$$

Being an indirect band gap material, radiative recombination in Si requires the participation of phonons of the right momentum for momentum conservation [56]. This extra requirement reduces the probability of radiative recombination. It is reflected in the value of B. and is around 4.73×10^{-15} cm³ s⁻¹ in Si [60]. The value of B for GaAs, which is a direct band gap material, is around 7.2×10^{-10} cm³ s⁻¹ at 300 K [61]. The lifetime of charge carriers due to radiative recombination (τ_{rad} , s) is given by [57]

$$\tau_{\rm rad} = \frac{\Delta n}{R_{\rm rad}} = \frac{1}{B(n_0 + p_0 + \Delta n)}$$
(2.9)

For low level injection condition $\Delta n \ll n_0 + p_0$, the radiative lifetime of charge carriers becomes

$$\tau_{\rm rad} = \frac{1}{B(n_0 + p_0)} \tag{2.10}$$

For high level injection condition $\Delta n \gg n_0 + p_0$, the radiative lifetime of charge carriers becomes

$$\tau_{\rm rad} = \frac{1}{B(\Delta n)} \tag{2.11}$$

2.3.2 Auger recombination

Auger recombination is an intrinsic mechanism involving three charge carriers based on the Auger effect [55, 56]. In this process, electrons directly transit from the available conduction band state to an empty state in the valance band and annihilate the electron-hole pair. The excess energy released during the recombination of the electron-hole pair is not in the form of photons; rather, the energy is transferred to another free charge carrier in the system. Hence, Auger recombination is a non-radiative recombination process. The excess energy released during the Auger recombination can be transferred to an electron or a hole. If the energy is exchanged with an electron, it is known as the "eeh" process. If the energy is exchanged with a hole, it is known as the "ehh" process. The newly excited charge carrier exchanges its energy with the surrounding semiconductor lattice. Hence, the rate of Auger recombination due to both the "eeh" and "ehh" processes is proportional to the concentration of respective charge carriers involved. Hence, the recombination rate due to the "eeh" process (R_{eeh} , cm⁻³) and the recombination rate due to the "ehh" process (R_{eeh} , cm⁻³) becomes

$$R_{eeh} = C_n n^2 p$$

$$R_{ehh} = C_p n p^2$$
(2.12)

where C_n and C_p are the Auger coefficients associated with the "eeh" and "ehh" processes (cm⁶ s⁻¹), respectively. The schematic diagram showing Auger recombination is shown in Figure 2.4. Net Auger recombination rate (R_{Aug} , cm⁻³ s⁻¹) can be modeled as follows



Figure 2.4: Schematic diagram showing Auger recombination consisting of "eeh" process and "ehh" process.

$$R_{Aug} = C_n(n^2p - n_0^2p_0) + C_p(np^2 - n_0p_0^2))$$
(2.13)

The values of the Auger coefficients are $C_n = 2.8 \times 10^{-31} \text{ cm}^6 \text{s}^{-1}$ and $C_p = 9.9 \times 10^{-32} \text{ cm}^6 \text{s}^{-1}$ for Si [62]. Substituting $n = n_0 + \Delta n$ and $p = p_0 + \Delta n$ in Eq.2.13, R_{Aug} can be rewritten as

$$R_{Aug} = C_n((n_0 + \Delta n)^2(p_0 + \Delta n) - n_0^2 p_0) + C_p((n_0 + \Delta n)(p_0 + \Delta n)^2) - n_0 p_0^2)$$
(2.14)

The corresponding Auger lifetime of the charge carriers (τ_{Aug} , s) is

$$\tau_{Aug} = \frac{\Delta n}{R_{Aug}} = \frac{\Delta n}{C_n((n_0 + \Delta n)^2(p_0 + \Delta n) - n_0^2 p_0) + C_p((n_0 + \Delta n)(p_0 + \Delta n)^2) - n_0 p_0^2)}$$
(2.15)

In the case of high-level injection conditions $\Delta n \gg n_0 + p_0$, τ_{Aug} in Eq.2.15 becomes

$$\tau_{\text{Aug,high}} = \frac{1}{(C_n + C_p)\Delta n^2}$$
(2.16)

The above Eq.2.16 suggests the strong dependence of Auger recombination on excess carrier concentration at high injection conditions [63]. In the case of low-level injection conditions $\Delta n \ll n_0 + p_0$, τ_{Aug} in Eq.2.15 becomes

$$\tau_{\text{Aug,low}} = \frac{1}{C_{\text{n}} n_0^2} = \frac{1}{C_{\text{n}} N_{\text{dop}}^2} \qquad \text{for n-type Si}$$
(2.17)

$$\tau_{\text{Aug,low}} = \frac{1}{C_p p_0^2} = \frac{1}{C_p N_{\text{dop}}^2} \qquad \text{for p-type Si}$$
(2.18)

where N_{dop} the doping concentrations (cm⁻³). Eq.2.17 and 2.18 indicate the dependence of the Auger recombination on the doping concentration of the semiconductor material [63].

The traditional Auger recombination model described above will hold well with experimentally measured lifetime values only when the doping concentration of Si is greater 5×10^{18} cm³. However, for lightly and moderately doped Si, the modeled Auger lifetime values differ from measured values [63]. The deviation in lightly doped material is due to the Coulomb interaction of free charge carriers proposed by Hangleiter and Hacker [64]. According to the quantum mechanical theory of Hangleiter and Hacker, the spatial interaction of free charge carriers can form scattering states and bound states (exciton). Due to exciton formation, the electron density in the vicinity of holes increases, and Coulomb interaction increases. However, the exciton formation is suppressed when the majority carrier concentration or excess carrier density due to injection exceeds exciton Mott density of 10^8 cm^{-3} . Hence, the traditional Auger recombination model is modified, considering the Coloumb Enhanced Auger Recombination proposed by A. Hangleiter and R. Hacker [64]. To include Coulomb interaction in Auger recombination, the Auger coefficient C_n and C_p are multiplied with enhancement factors g_{eeh} and g_{ehh} [65]. Altermatt et al. [65] modeled Coulomb enhancement factors based on the lifetime measurements as given below

$$g_{eeh}(n_0) = 1 + 13.0[1 - \tanh(\frac{n_0}{N_{0,eeh}})^{0.66}]$$

$$g_{ehh}(p_0) = 1 + 7.5[1 - \tanh(\frac{p_0}{N_{0,ehh}})^{0.63}]$$
(2.19)

where g_{eeh} and g_{ehh} are enhancement factors that account for the coulomb enhancement under low-level injection conditions. The empirical values of the constants used are: $N_{0,eeh}$ = $3.3 \times 10^{17} \text{ cm}^{-3}$, $N_{0,ehh}$ = $7 \times 10^{17} \text{ cm}^{-3}$. Eq.2.20 represents a generalized model considering the dependency of Auger recombination on Coulomb interaction at low-level injection and the dependency on excess carrier density at high-level injection [66].

$$\tau_{Aug} = \frac{\Delta n}{R_{Aug}} = \frac{\Delta n}{np(g_{eeh}C_n n_0^{0.65} + g_{ehh}C_p p_0^{0.65} + C_a \Delta n^{0.8})}$$
(2.20)

The empirical values of the constants used are $C_n = 2.8 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$, $C_p = 9.9 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$, $C_a = 3.79 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ [66]. The third parameter, C_a , is required since the Coulomb interaction is reduced due to the screening effect based on the concentration of electrons and holes. C_a represents the injection-dependent ambipolar coefficient. The theoretical model for Auger recombination is essential to analyze its fundamentals and predict the values since Auger recombination cannot be measured, unlike radiative recombination. However, all the internal processes involved in the Auger process are not fully understood so far. It is reported that in addition to the Coulomb interaction, the Auger recombination can occur involving the impurities known as trap-assisted Auger recombination and involving photons. For silicon at 300 K, the parameterization proposed by Kerr and Cuevas [66] is widely used for describing Auger recombination. Further, Ritcher et al. [62] proposed an improved quantitative description for Auger recombination in crystalline Si. According to Richer et al., the modified empirical constants associated with Auger recombination are $C_n = 2.5 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$, $C_p = 8.5 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$, $C_a = 3.0 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$ [62]. In the case of Si solar cells, the emitter is heavily doped. Therefore,

the lifetime of charge carriers in the emitter region is limited by Auger recombination. Auger recombination in Si solar cells can also be significant when the devices are subjected to high level injection conditions, even though the substrate is lightly doped.

2.3.3 Shockley - Read - Hall- recombination

Shockley – Read – Hall (SRH) recombination dominates indirect band gap materials like Si and Ge. This type of recombination occurs due to defects in the bulk of semiconductor material. These defects act as recombination centers of charge carriers and significantly reduce the carrier lifetime within the bulk. The defects can be metallic impurities (Fe, Cu, Ni, Ti, Au) [5–7], meta-stable defects (FeB complex, BO complex) [67–71], precipitates [72, 73], crystallographic defects (grain boundaries, vacancies, interstitial), etc. The defect can disturb the periodicity of the semiconductor crystal structure and introduce defect energy levels in the forbidden band gap of the crystalline semiconductor. The defect energy level can capture the charge carriers from the conduction and valance bands. When the defect level is occupied with an electron, it can emit an electron to the conduction band or capture an electron from the conduction band or emit a hole into the valance band. The schematic diagram of these four processes is depicted in Figure 2.5 [56]. The defect levels act as either trap, generation, or recombination centers



Figure 2.5: Schematic diagram showing (a) Electron emission, (b). Electron capture (c) Hole capture (d) Hole emission [56].

of charge carriers. Trap centers capture charge carriers from the valance band and conduction band. Then, the charge carriers are re-emitted to the band from where it is captured. Defect levels act as generation centers when they emit electrons to the conduction band and hole to the valance band, or an electron is first excited to the defect level. Then, it is excited to the conduction band. In both cases, an electron-hole pair is created. Defect level acts as recombination center when the electron-hole pair is annihilated. During the recombination process, the excited charge carriers transit from the conduction band to the trap level and then transit from the trap level to the empty state in the valance band, annihilating electron-hole pair or the electron in the conduction band transit to the empty state in the trap level annihilating the electron-hole pair. Thus, defects in the semiconductor's bandgap enable a two-step process known as defect-assisted recombination. Hence, the rate of defect-assisted recombination depends upon defect density, the position of the defect energy level, and the ability of the defect level to trap and release charge carriers in addition to the charge carrier densities in the semiconductor [56]. Shockley, Read, and Hall modeled the defect-related recombination by statistical analysis of the fundamental processes of electron capture, electron emission, hole capture, and hole emission [74]. The predicted SRH model applies to non-degenerate semiconductors with a single defect level, and its concentration should be much less than the doping concentration.

2.3.3.1 SRH statistics

In defect-assisted recombination, the change in concentration of charge carriers with time is determined by the emission rate and capture rate of electrons and holes of the defect energy level [56]. The capture (emission) rate represents the rate at which the charge carriers are captured (emitted) from (to) the respective bands by the defect energy level. It depends upon the concentration of the charge carriers and the capture coefficient. The capture rate can be expressed as

$$c_{n} = \alpha_{n} * n$$

$$c_{p} = \alpha_{p} * p$$
(2.21)

where c_n and c_p are the capture rate for electron and hole (s^{-1}) respectively, α_n and α_p are capture coefficients of electron and hole $(cm^3 s^{-1})$ respectively. The capture coefficients are defined as follows

$$\alpha_{\rm n} = \sigma_{\rm n} * v_{\rm th}$$

$$\alpha_{\rm p} = \sigma_{\rm p} * v_{\rm th}$$
(2.22)

where σ_n and σ_p are capture cross-sections of the defect level for electron and hole (cm²), respectively. The capture cross-section measures the recombination centers' effectiveness in capturing the charge carriers. The higher the value of the capture cross-section, the higher will be the capture rate. v_{th} is the thermal velocity of charge carriers (cm s⁻¹).

Let N_T be the concentration of the defects in a semiconductor material in cm⁻³, and f_t be the probability that the defect energy level E_T is filled with electrons. Then, the change in concentration of charge carriers with time can be expressed as

$$\frac{dn}{dt} = e_n f_t N_T - \alpha_n n(1 - f_t) N_T$$

$$\frac{dp}{dt} = e_p f_t N_T - \alpha_p p(1 - f_t) N_T$$
(2.23)

where e_n and e_p are the emission rates for the electrons and holes (s⁻¹) respectively. Using the principle of detailed balancing, the emission rate can be determined. The principle of detailed balancing states that under thermal equilibrium process and its inverse process are balanced irrespective of any other process occurring within the system [56]. In other words dn/dt = dp/dt = 0. Then, the emission rate can be expressed as follows

$$e_n f_t N_T = \alpha_n n(1 - f_t) N_T$$

$$e_n = c_n n \frac{1 - f_t}{f_t} = \alpha_n n_1$$
(2.24)

and

$$e_{p}f_{t}N_{T} = \alpha_{p}p(1-f_{t})N_{T}$$

$$e_{p} = \alpha_{p}p\frac{1-f_{t}}{f_{t}} = \alpha_{p}p_{1}$$
(2.25)

where $n_1 = n \frac{1-f_t}{f_t} = N_C \exp{-\frac{(E_C - E_T)}{kT}}$ and $p_1 = p \frac{1-f_t}{f_t} = N_V \exp{-\frac{(E_T - E_V)}{kT}}$. N_C and N_V are the effective densities of states ($eV^{-1}cm^{-3}$), respectively, in the conduction band and valance band. The SRH density terms n_1 and p_1 can also relate with the intrinsic carrier concentration n_i (cm^{-3}) and intrinsic energy level E_i (eV) as given in the following Eq.2.26

$$n_1 = n_i \exp{-\frac{(E_T - E_i)}{kT}}$$
 $p_1 = n_i \exp{-\frac{(E_i - E_T)}{kT}}$
(2.26)

By substituting the expression of the emission rate in Eq.2.23 and equating dn/dt=dp/dt, occupation probability f_t of the defect center can be obtained. Inserting the expression for f_t in

either of the Eq.2.23, the net SRH recombination rate (R_{SRH} , $cm^{-3}s^{-1}$) can be expressed as

$$R_{SRH} = \frac{np - n_i^2}{\frac{1}{\alpha_p N_T}(n + n_1) + \frac{1}{\alpha_n N_T}(p + p_1)}$$
(2.27)

Eq.2.27 can also be written by replacing the $n = n_0 + \Delta n$ and $p = p_0 + \Delta n$ as follows

$$R_{SRH} = \frac{((n_0 + \Delta n)(p_0 + \Delta p) - n_i^2)\alpha_p \alpha_n N_T}{\alpha_n (n + n_1) + \alpha_p (p + p_1)}$$
(2.28)

The SRH lifetime of charge carriers (τ_{SRH}) in μs can be deduced from R_{SRH} , which is given by

$$\tau_{\rm SRH} = \frac{\frac{1}{\alpha_{\rm p}N_{\rm T}}(n_0 + n_1 + \Delta n) + \frac{1}{\alpha_{\rm n}N_{\rm T}}(p_0 + p_1 + \Delta n)}{n_0 + p_0 + \Delta n}$$
(2.29)

It is clear from Eq.2.29 that the SRH recombination depends on the dopant levels, injection level, defect concentration, and defect-specific properties, like the capture cross-section, defect concentration, and the defect energy level.

This expression can be simplified under high and low-level injection conditions for a p-type semiconductor as follows

Case 1: Low level injection $\Delta n \ll p_0$

$$\tau_{\text{SRH,low}} = \frac{\frac{1}{\alpha_{\text{p}} N_{\text{T}}}(n_{1})}{p_{0}} + \frac{\frac{1}{\alpha_{\text{n}} N_{\text{T}}}(p_{0} + p_{1})}{p_{0}}$$
(2.30)

The quantities $\frac{1}{\alpha_p N_T}$ and $\frac{1}{\alpha_n N_T}$ are replaced with capture time constants τ_{n0} and τ_{p0} for electrons and holes respectively in μ s.

$$\tau_{\text{SRH,low}} = \tau_{\text{p0}} \frac{n_1}{p_0} + \tau_{\text{n0}} \frac{(p_0 + p_1)}{p_0} = \tau_{\text{n0}} (1 + \frac{p_1}{p_0} + Q\frac{n_1}{p_0})$$
(2.31)

where $Q = \frac{\tau_{p0}}{\tau_{n0}} = \frac{\alpha_n}{\alpha_p} = \frac{\sigma_n}{\sigma_p}$

Under low-level injection conditions, SRH lifetime is independent of the density of excess carriers; rather, it is limited by doping concentration and characteristic parameters of the defect like defect energy level, defect concentration, and capture cross section of electrons and holes for the defect.

Case 2: High level injection $\Delta n \gg p_0, p_1, n_1$

$$\tau_{\text{SRH,high}} = \frac{\frac{1}{\alpha_{\text{p}}N_{\text{T}}}\Delta n + \frac{1}{\alpha_{\text{n}}N_{\text{T}}}\Delta n}{\Delta n}$$
$$= \frac{1}{\alpha_{\text{p}}N_{\text{T}}} + \frac{1}{\alpha_{\text{n}}N_{\text{T}}}$$
$$= \tau_{\text{p0}} + \tau_{n0}$$
$$= \tau_{n0}(Q+1)$$
(2.32)

Under high-level injection, SRH lifetime is limited defect concentration and the capture crosssection of electrons and holes for the defect. It is independent of defect energy level, doping concentration, and excess carrier density.

2.3.4 Surface recombination

Surface recombination refers to the recombination due to interfacial traps. The inter-facial traps are created due to the abrupt termination of the crystal structure at the surface or interface. Abrupt termination causes unsatisfied Si bonds called dangling bonds at the interface. So, the charge carriers are trapped at the surface by these dangling bonds, which annihilates the electron-hole pair, as shown in Figure 2.6.



Figure 2.6: Schematic diagram showing (a) Electron emission, (b) Electron capture (c) Hole capture (d) Hole emission [56]

The inter-facial trap centers have functionality similar to the SRH recombination centers. Therefore, the recombination at the surface due to interfacial defects can be formulated as an extension of SRH recombination proposed by Shockley et al. [74]. The surface recombination rate (R_S , cm⁻² s⁻¹) due to a single trap level can be expressed similarly to the SRH recombina-

tion rate specified in Eq.2.28 [56] as given below

$$R_{S} = \frac{n_{s}p_{s} - n_{i}^{2}}{\frac{1}{\alpha_{ps}N_{Ts}}(n_{s} + n_{1s}) + \frac{1}{\alpha_{ns}N_{Ts}}(p_{s} + p_{1s})}$$
(2.33)

Where n_s and p_s are the electron and hole density at the surface (cm⁻³), n_{1s} and p_{1s} are SRH densities defined in Eq.2.26. N_{Ts} is the defect density (cm⁻²) due to a single trap level at the surface. α_{ns} and α_{ps} are capture coefficients of the electrons and holes at the surface (cm³ s⁻¹). The terms $\alpha_{ns}N_{Ts}$ and $\alpha_{ps}N_{Ts}$ have dimensions of cm s⁻¹.

Unlike bulk defects, dangling bonds can give rise to the recombination active defect levels distributed throughout the band gap of the semiconductor surface. The net surface recombination rate due to non-interacting inter-facial trap levels can be obtained by integrating the recombination rate due to a single trap level over the entire band gap range. Let D_{it} be the interfacial trap density (cm² eV⁻¹) in a small energy level dE. Then D_{it} dE, which represents the number of interfacial traps per cm² with energy between E and E+dE. D_{it} dE is equivalent to N_{Ts} in Eq.2.33. Hence, the net surface recombination rate can be obtained from Eq.2.33 by replacing N_T with D_{it} dE and integrating over the entire bandgap [56].

$$R_{S} = n_{s}p_{s} - n_{i}^{2} \int_{E_{V}}^{E_{C}} \frac{D_{it}(E)}{\frac{1}{\alpha_{ps}}(n_{s} + n_{1s}) + \frac{1}{\alpha_{ns}}(p_{s} + p_{1s})} dE$$
(2.34)

The expression for surface recombination can be further simplified for p-type and n-type materials depending upon the injection condition. For a p-type semiconductor under low-level injection conditions, the recombination at the surface can be deducted from Eq.2.34 by rewriting $n_s = n_{0s} + \Delta n_s$ and $p_s = p_{0s} + \Delta n_s$. Here, n_{0s} and p_{0s} are the equilibrium concentration of electrons and holes at the surface (cm⁻³), respectively. Δn_s is the excess carrier density at the surface in cm⁻³. Under the low level injection condition the term in $n_s p_s - n_i^2$ reduces to $p_{0s} \Delta n_s$. The denominator $\frac{1}{\alpha_{ps}}(n_s + n_{1s}) + \frac{1}{\alpha_{ns}}(p_s + p_{1s})$ reduces to $\frac{1}{\alpha_{ps}}n_{1s} + \frac{1}{\alpha_{ns}}(p_{0s} + p_{1s})$. The surface recombination rate can be expressed as

$$R_{S} = p_{0s}\Delta n_{s} \int_{E_{V}}^{E_{C}} \frac{D_{it}(E)}{\frac{1}{\alpha_{ps}}n_{1s} + \frac{1}{\alpha_{ns}}(p_{0s} + p_{1s})} dE = S_{eff}\Delta n_{s}$$
(2.35)

Where S_{eff} is the effective surface recombination velocity of electrons (cm s⁻¹).

$$S_{eff} = \int_{E_{V}}^{E_{C}} \frac{D_{it}(E)p_{0s}}{\frac{1}{\alpha_{ps}}n_{1s} + \frac{1}{\alpha_{ns}}(p_{0s} + p_{1s})} dE = \int_{E_{V}}^{E_{c}} \frac{D_{it}(E)\alpha_{n}(E)}{\frac{\alpha_{ns}}{\alpha_{ps}}\frac{n_{1s}}{p_{0s}} + 1 + \frac{p_{1s}}{p_{0s}}} dE$$
(2.36)

The denominator in the integral can be approximated as unity closer to the mid-band gap. For all other energy levels, the denominator can be approximated as infinite. The surface recombination velocity reduces to the form

$$S_{eff} = D_{it} \alpha_{ns} \Delta E$$
 (2.37)

where ΔE is the defect energy range closer to the mid-band gap of the material. Similarly, the effective surface recombination velocity of the n-type material can be deducted similar to Eq.2.37 as given as follows

$$S_{eff} = D_{it} \alpha_{ps} \Delta E$$
 (2.38)

It is clear from the above discussions that surface recombination in a semiconductor material is determined by the density of traps at the interface and the concentration of charge carriers. The inter-facial trap density and surface concentration of charge carriers must be reduced to reduce surface recombination. The interfacial trap density is reduced using chemical passivation of dangling bonds. This can be realized using PECVD SiN_X : H [75, 76] layer or by using oxide growth such as silicon dioxide (SiO₂) [77, 78], aluminum oxide (Al₂O₃) [79, 80] etc. The dangling bonds are passivated with hydrogen or oxygen atoms in these dielectric layers. In addition, liquid chemicals such as Quinhydrone in methanol, hydrogen fluoride (HF), super acids, etc., can also be used for temporary passivation of the surface defects [81-85]. The surface concentration of charge carriers is reduced using the field effect passivation. In field effect passivation, the dielectric layer's electric field created at the interface repels the minority charge carriers away from the surface, thereby reducing surface recombination. The electric field is created due to inherent charges associated with the dielectric layer or charge deposition using corona discharge [86, 87]. The minority carriers can be repelled away from the interface by creating a back surface field (BSF) using a $p-p^+$ or $n-n^+$ junction. Hence, surface recombination in a solar cell is determined by the effectiveness of chemical passivation, dielectric field passivation, and back surface field. The effectiveness of surface passivation is usually expressed in terms of effective surface recombination velocity, which is defined as the ratio of surface recombination rate to excess carrier density at the surface. $S_{eff} \equiv R_S / \Delta n_s$ for p-type material and $S_{eff} \equiv R_S / \Delta p_s$ for n-type material.

Now the lifetime of charge carriers at the surface (τ_s , s) is determined from the S_eff, the thickness (W, cm) of the sample as given in Eq.refEq.2.39 [78],

$$\tau_{\rm s} = \frac{\rm W}{\rm S_{eff,front}} + \frac{\rm W}{\rm S_{eff,back}}$$
(2.39)

where $S_{eff,front}$ and $S_{eff,front}$ are the effective surface recombination velocity of the front and back surfaces, respectively, in cms⁻¹. Eq.2.39 is valid when the sample surfaces are well passivated with a suitable dielectric of very low surface recombination velocity stratifying the condition $S_{eff}W/D < 0.25$. D is the diffusivity of the charge carriers. The surface recombination can be minimized using various passivation techniques discussed in the following section.

2.3.4.1 Silicon dioxide passivation

The dielectric film deposited by the thermal oxidation of silicon is considered the most effective method for Si surface passivation. The effectiveness of thermally grown SiO₂ is improved by post-deposition high-temperature treatment such as alneal process, forming gas annealing (FGA), corona charging of dielectric layer, and shielded ammonia plasma treatment, etc. Using alneal SiO₂, Kerr et al. [88] reported S_{eff} values of 1.72 cm s⁻¹ and 7 cm s⁻¹ in 1.5 Ω cm n-type and 1.0 Ω cm p-type material respectively. Bonilla et al. [89] reported S_{eff} of 0.24 cm $s^{-1},$ in an n-type Si with resistivity of 1.0 Ω cm after corona discharge. They observed an increase in S_{eff} up to 28 cm s⁻¹ for textured samples [89]. Using shielded ammonia plasma method, an S_{eff} of 0.17 cm s⁻¹ is reported in n-type Si with resistivity of 1.0 Ω cm [90]. The growth of thermal oxide of thickness about 100 nm at high temperatures is an expensive process from the point of view of the solar PV industry. Hence, low-temperature, cost-effective dielectric deposition methods such as PECVD deposited SiO_X, nitric acid oxidation of silicon (NAOS) techniques, etc., are used to grow the silicon oxide layer on the surface as dielectric cum passivation layer. Both of these processes require post-deposition annealing to improve passivation quality. Using PECVD SiO_X film deposition, S_{eff} of 1.5 cm s⁻¹ is reported in n-type Si with a resistivity of 1.0 Ω cm [91, 92]. With the NAOS technique, the S_{eff} in the range of 20 - 70 cm s^{-1} were reported [93, 94].

2.3.4.2 Silicon nitride dielectric passivation

PECVD silicon nitride dielectric layer is widely used as a passivation and dielectric layer in commercial Si solar cells. Wide acceptance of SiN_X : H film for the Si solar industry is due to the following reasons. 1. The refractive index of the PECVD SiN_X : H layer can be tuned to get the best anti-reflection property by controlling the deposition parameters and chamber conditions. 2. The PECVD deposited SiN_X : H layer is rich in hydrogen. The hydrogen released from the dielectric layer during the post-deposition annealing process helps to passivate the dangling bonds, thereby reducing the interfacial trap density. 3. PECVD SiN_X : H layer provides field effect reduction of minority carriers at the surface due to positive dielectric charges. Therefore, the dielectric coating is best suited to reducing the recombination rate in n-type surfaces like n⁺ diffused emitter regions in p-type Si solar cells. Si surfaces passivated with PECVD SiN_X : H layer is reported to have interfacial trap density of $10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$ and fixed dielectric charges in the range of 10^{11} cm⁻² to 10^{12} ecm⁻² [95]. Relatively lower S_{eff} values of less than 10 cm s^{-1} were reported by various research groups [62, 96, 97]. Kerr and Cuevas [96] reported S_{eff} value of 7 and 14 cm s⁻¹ respectively for n-type and p-type silicon samples with the resistivity of about 1.0 Ω cm. Chen et al.[97] reported S_{eff} value of 4.4 cm s⁻¹ in n-type silicon samples with 1 Ω cm whereas Richter et al., reported 1.6 cm s⁻¹ in n-type silicon samples [62]. The lowest reported S_{eff} value is 0.67 cm s⁻¹ in 0.87 Ω cm n-type Si samples passivated with PECVD SiN_X : H films [98].

The dielectric stack layer consisting of SiO₂ (15 nm)/SiN_X : H (75 nm) provides a low positive fixed charge density of about 10^{11} cm² and very low interface defect density of 3×10^{10} eV⁻¹ cm⁻² using inline deposition method [99]. Schmidt et al., reported S_{eff} of 5 – 10 cm s⁻¹ in p-type Si of resistivity 1 Ω cm passivated with dielectric stack of thermally grown SiO₂ and PECVD SiN_X : H layer [100]. In n-type samples, a much lower surface recombination velocity of about 1 - 2 cm s⁻¹ is reported in [101, 102] using thermally grown SiO₂ and PECVD SiN_X : H dielectric stack. The thermally grown SiO₂ provides chemical passivation, while fixed negative charges in the PECVD SiN_X : H layer provide field-effect passivation. The growth of oxide via PECVD is a rapid, low-temperature process compared to thermally grown SiO₂. Consequently, SiO₂ and SiN_X : H films can be deposited by the PECVD technique [103]. In addition, the PECVD process improves the chemical passivation property of the dielectric stack during the post-deposition annealing process. Using laboratory scale PECVD SiO_X/SiN_Y : H stack, a lowest S_{eff} of 7.6 cm s⁻¹ in n-type Si with resistivity of 3.5 Ω cm, and 11.2 cm s⁻¹ in p-type

Si with resistivity of 2 Ω cm is reported [104]. In the case of industrial grade SiO_X/SiN_Y : H stack, the best reported S_{eff} is 8.15 cm s⁻¹ on n-type Si with resistivity 1.5 Ω cm, and 35 cm s⁻¹ in p-type Si with resistivity of 1.5 Ω cm [105].

2.3.4.3 Hydrogenated amorphous silicon passivation

Hydrogenated amorphous silicon amorphous silicon a-Si : H films are used in heterojunction solar cells [106]. The disadvantage of a-Si : H films is the unwanted parasitic absorption and low thermal stability. This can be prevented by adding a capping layer of SiO_X/SiN_Y : H stack [107]. The field effect properties of such layers can be further improved by utilizing corona discharge [108, 109]. The best reported value S_{eff} for dielectric stack of $a-Si : H/SiO_X/SiN_Y$ with corona discharge is 0.086 cm s⁻¹ in n-type Si with resistivity 1.7 Ω cm and thickness 300 µm [108] and 0.06 cm s⁻¹ in 1 Ω cm n-type Si of thickness 200 µm [109]. The a-Si : H films deposited by the PECVD process have certain advantages over the other passivation schemes: The a-Si : H film deposited by the PECVD process is rich in hydrogen, thereby passivating the interfacial defects and the defect in the bulk. The energy band structure at the $a-Si_X : H/Si$ interface creates a step in the valance band and conduction band, which causes a larger barrier for holes than for electrons [110].

2.3.4.4 Aluminium oxide dielectric passivation

Exceptional surface passivation of Si can be obtained using an atomic layer deposited (ALD) aluminum oxide (AlO_X) dielectric layer. The passivation scheme requires 350 °C to 450 °C annealing for 10 to 30 min in an inert or forming gas environment to improve its effectiveness [62]. The dielectric film contains fixed negative charges and provides better field-effect passivation for p-type surfaces [111]. Hoex et al. reported S_{eff} of 2 cm s⁻¹ and 10 cm s⁻¹ respectively in low resistivity n-type and p-type Si passivated with AlO_X films deposited by ALD [80]. The best results for AlO_X passivation film are S_{eff} of 0.26 and 0.95 cm s⁻¹ respectively, for n-type and p-type Si of resistivity 1.0 Ω cm by Richter et al. [62] using plasma enhanced ALD. Because of the slow deposition process of the ALD technique, PECVD AlO_X deposition is more suited for industrial cell production. An additional capping layer using PECVD SiN_X or SiO_X layer provides improved anti-reflection properties, hydrogenation, and thermal stability of the underlying thin AlO_X layer during metallization. During the firing process, hydrogenation quality [112]. Using the inline PECVD technique, Duttagupta et al. [113] reported S_{eff} of 1.4 cm s⁻¹ in 3 Ω cm n-type Si, and 15 cm s⁻¹ in 3.5 Ω cm p-type Si. The atmospheric pressure chemical vapor deposition technique is also used for AlO_X deposition for higher throughput for industrial applications [114]. S_{eff} of less than 2.0 cm s⁻¹ on 1.2 Ω cm n-type Si, and less than 3 cm s⁻¹ on 1.35 Ω cm p-type Si are reported using inline manufacturing technique by Black et al.[114]

The analysis of various surface passivation methods indicates that surface recombination can be significantly decreased to a value less than 10 cms^{-1} by utilizing commercially feasible dielectric stack passivation techniques in both p-type and n-type Si wafers.

2.3.5 Effective lifetime of charge carriers

The recombination of charge carriers occurring at different regions of the semiconductor device simultaneously through various physical mechanisms is discussed in the previous subsection. The net recombination rate is determined by individual recombination mechanisms such as radiative recombination (R_{rad}), Auger recombination (R_{Aug}), and SRH recombination at the surface (R_S) and within the bulk (R_S). Hence, the effective lifetime of charge carriers τ_{eff} can be mathematically represented as [56]

$$\frac{1}{\tau_{\rm eff}} = \frac{1}{\tau_{\rm Rad}} + \frac{1}{\tau_{\rm Aug}} + \frac{1}{\tau_{\rm SRH}} + \frac{1}{\tau_{\rm S}}$$
(2.40)

Figure 2.7 shows the variation in τ_{eff} , τ_{rad} , τ_{Aug} and τ_{SRH} as a function of Δn in a well passivated p-type Si wafer with doping concentration of 10^{16} cm⁻³ and defect level located at the mid of band gap at T = 300 K. The sample's defect density is assumed to be 10^{12} cm⁻³. Parameterization used in the radiative and Auger recombination simulation is based on the model described in subsections 2.3.1 and 2.3.2. Being an indirect bandgap material, radiative recombination is not a limiting factor of the lifetime of charge carriers in Si devices ($\frac{1}{t_{rad}}$ is negligible in comparison with other recombination mechanisms. It is clear from Figure 2.7 that the effective lifetime at injection levels less than the doping concentration is limited by the SRH recombination. However, at a higher level of injection condition greater than 10^{17} cm⁻³, the Auger recombination process limits the effective lifetime. In the case of solar cells, under normal operating conditions with one sun illumination, the injection condition will be close to 10^{15} cm⁻³. Under the stated condition, SRH recombination will be the performance-limiting recombination in many device realizations, as indicated in Figure 2.7. The detailed analysis of



Figure 2.7: Variation effective lifetime, radiative lifetime, Auger recombination, and SRH lifetime as a function of excess carrier density in p-type Si material with defect level located at the mid of band gap.

defect-related lifetime degradation in silicon devices is discussed in section 2.4.

2.4 Detailed analysis of defect-related lifetime degradation using simulation

According to SRH statistics [74], the recombination characteristics depend on the electrical properties of the defects, such as defect energy level and capture cross-section of the defect for the electrons and holes. It also depends on the defect concentration, doping concentration, and injection conditions. A detailed analysis of variation in lifetime characteristics based on the electrical properties of the defect, doping concentration, and injection conditions is done using MATLAB simulation.

2.4.1 Effect of defect parameters and doping concentration

When the defect level is at the center of the bandgap at energy E_i , the probability of electron capture or electron emission and hole capture or hole emission are the same. For deep defect levels, SRH density terms defined in Eq.2.26 become $p_1 = n_1 = n_i$. Then $\tau_{SRH,low} = \tau_{n_0}$ under low level injection condition. Hence, for such defects, SRH lifetime equals the minority capture



Figure 2.8: Variation in SRH lifetime of p-type samples as a function of defect energy level for different doping concentrations keeping Q fixed.

time constant, determined only by the α_n and N_T . It is independent of the doping concentration and ratio of capture cross sections of electrons and holes. This indicates that the defects with energy levels close to mid-gap are the most dominant recombination centers, as evident from Figure 2.8. The defects in the lower and upper half of the band gap, which have the same energy distance from the mid-gap, show the same effectiveness for recombination. For shallow defects with energy levels, several kT away from mid-gap only contribute to recombination for high doping concentrations. SRH lifetimes are strongly doping-dependent, as indicated in Figure 2.8.

For a shallow defect closer to the conduction band edge, the probability of electron capture or electron emission from or to the conduction band is more than hole capture or hole emission from or to the valance band, $p_1 \ll n_1$ and $p_0 \ll n_1$. Then the normalized SRH lifetime $\frac{\tau_{\text{SRH}_1\text{ow}}}{\tau_{n_0}} = 1 + Q\frac{n_1}{p_0}$. The lifetime is limited by doping concentration and ratio of capture cross-section, as depicted in Figure 2.9. For an intermediate defect level between the shallow defect level and the mid-band gap, the probability of electron capture or electron emission from or to the conduction band is more than hole capture or hole emission from or to the valance band, $p_1 \ll n_1$. However, the doping concentration becomes comparable with the SRH defect density term n_1 . Hence, the normalized SRH lifetime is limited only by the capture cross-section ratio. For asymmetrical cross sections, a higher capture cross section for holes (Q<1) increases the recombination activity due to an increase in the capture probability of holes from the valance



Figure 2.9: Variation in SRH lifetime of p-type samples as a function doping concentration for different defect energy levels keeping Q fixed.

band [115], which is evident in Figure 2.10. Therefore, SRH lifetime will be smaller for smaller Q values [115]. For symmetrical capture cross section (Q=1) when the defect energy level lies



Figure 2.10: Variation in SRH lifetime of p-type samples as a function doping concentration for Q = 0.1, Q=1 and Q=10 keeping energy level fixed at $E_T = E_V + 0.8$ eV.

in between E_c and E_i , then SRH lifetime can be approximated as $\tau_{SRH,low} = 2\tau_{n_0}$. This indicates that the recombination activity is reduced by half compared with the recombination rate of deeplevel defect when the defect level lies in the upper band gap. When the defect level is closer to the edge of the valance band, the probability of hole capture/emission from/to the valance band is more than the probability of electron capture/emission from or to the conduction band, $n_1 \ll p_1$ and $p_0 \ll p_1$. Hence $\frac{\tau_{SRH,low}}{\tau_{n_0}} = 1 + \frac{p_1}{p_0}$. Here also, the normalized SRH recombination activity strongly depends on the doping concentration and is independent of Q. However, for an intermediate defect in the lower band gap of the material $n_1 \ll p_1$ and the doping density p_0 becomes comparable with p_1 . Therefore, the normalized SRH lifetime $\frac{\tau_{SRH,low}}{\tau_{n_0}} = 2$. Here also, the recombination rate is reduced by half concerning the recombination rate of the deep-level defect. The variation in normalized SRH lifetime under low-level injection depending upon the position of defect energy level is summarized in Table 2.1[115]

Table 2.1:	The normalized	SRH lifetime	e under	low-level	injection	based	on the	position	of
defect ener	gy level.								

Position of defect in the Energy band	Relative densities of	normalized SRH
gap	n_1 and p_1 in compar-	lifetime $\frac{\tau_{\text{SRH.low}}}{\tau_{n}0}$
	ison with p ₀	11
Deep defect Level $E_T \rightarrow E_i$	$p_1 = n_1 = n_i << p_0$	1
Shallow defect level $E_T \to E_C$	$p_1 << p_0 << n_1$	$1 + Q \frac{n_1}{p_0}$
Shallow defect level $E_T \to E_V$	n ₁ < <p<sub>0<<p<sub>1</p<sub></p<sub>	$1 + \frac{p_1}{p_0}$
Defect in the upper half of band gap	$p_1 << p_0 \approx n_1$	$1 + Q \frac{n_1}{n_0} = 1 + Q$
between deep and shallow defect level		FU
Defect in the lower half of band gap	n ₁ < <p<sub>0≈p₁</p<sub>	$1 + \frac{p_1}{p_0} = 2$
between deep and shallow defect level		۲U

2.4.2 Effect of injection level on SRH recombination activity

The injection dependency of SRH recombination is described using the normalized injection level $\frac{\Delta n}{n_0+p_0}$ [115]. SRH lifetime under low-level injection conditions is independent of excess carrier density. However, under high-level injection, SRH lifetime is limited to the sum of the capture time constants of electrons and holes as in Eq.2.32. For intermediate injection conditions, the injection-dependent SRH characteristics differ depending upon defect parameters such as the position of defect energy level and capture cross-section. According to Rein et al. [115], for deep levels and all defects in the upper half of the band gap, SRH lifetime decreases with injection level if $n_1 < p_0$ as depicted in Figure 2.11. However, the SRH lifetime decreases with injection band edge, $n_1 >> p_0$ for all injection conditions. As the electron concentration at the defect level increases with the injection level E_T , the injection dependence of the SRH lifetime is stronger for higher Q as shown in Figure 2.12. This



Figure 2.11: Variation in SRH lifetime in a p-type sample as a function of normalized injection level for different defect energy levels keeping Q fixed.

is because of the increased probability of hole capture by the defect level [115],



Figure 2.12: Variation in SRH lifetime in a p-type sample as a function of normalized injection level for Q = 0.1, Q=1 and Q=10 keeping energy level fixed at $E_T = E_V + 0.6$ eV.

2.5 Conclusion

Various physical mechanisms associated with the recombination of charge carriers in silicon solar cell devices are described in this chapter. It includes radiative recombination, Auger recombination, and SRH recombination at the surface and bulk. Being an indirect band gap material, radiative recombination is relatively very low in Si devices. Auger recombination is dominant in the heavily diffused emitter region. However, the thickness of the Auger dominant emitter region is too small compared to the bulk. The study of different surface passivation techniques points out that the recombination at the surface can be effectively reduced to some extent by employing industrially viable dielectric stack passivation techniques. Therefore, in well-passivated Si devices, defect-assisted SRH recombination is the dominant recombination mechanism.

Chapter 3

SRH recombination characteristics of defects in Si solar cells

The efficiency of c-Si solar cells with the best surface passivation techniques is limited because of the recombination of charge carriers within the bulk of crystalline silicon. The dominant defect-assisted recombination in the bulk of solar cells is characterized by the position of the defect energy level in the band gap of Si, the ability of the defect to capture the charge carriers, and the defect concentration. This chapter delves into the characteristics of different defects that can emerge in solar cells from the material used for fabricating Si wafers and the manufacturing processes of solar cells. These defects can undergo structural transformation on exposure to light and heat during normal operation of the solar cells under field conditions.

3.1 Recombination properties of defects in Si wafers

The silicon wafers used in the photovoltaic industry exhibit various defects originating from different sources. Some of these defects in silicon material trace their origins back to the use of metallurgical grade silicon for producing cost-effective multicrystalline wafers. The multicrystalline Si wafers contain metallic defects such as Fe, Cu, Ni, Ti, etc. [3, 4]. Conversely, oxygen-related anomalies are incorporated into monocrystalline wafers during their crystal growth process [4, 116]. Moreover, additional defects emerge during the various fabrication stages of solar cells. These process-induced defects encompass defects related to H, O, Cu, and Ni. Hydrogen-related defects, for instance, are generated during the post-deposition

firing of dielectric films utilizing the PECVD technique [19, 27, 31]. Oxygen defects may infiltrate the silicon during the POCl₃ diffusion process. Copper and nickel defects, on the other hand, are introduced during the contact formation process in solar cell fabrication [10, 11]. Importantly, many of these defects exhibit light-sensitive properties and undergo changes in their characteristics when exposed to light and heat. Consequently, the recombination behavior of the PV device varies depending on outdoor operating conditions. This section of the chapter delves into the electrical properties of these defects.

3.1.1 Iron related defects in Si

Iron (Fe) stands out as a prominent impurity, particularly in multicrystalline silicon solar cells employed for photovoltaic applications. Fe is classified as a transition metal with moderately rapid diffusion characteristics. In silicon, Fe manifests itself either in its elemental state or in the form of precipitates. When present in its elemental form, Fe contributes to a reduction in the device's carrier lifetime. Conversely, when it forms precipitates, it leads to an increase in leakage current and a decrease in breakdown resistance. Fe occupies interstitial sites (Fe_i) within the silicon lattice and exhibits the properties of an electron donor. In p-type silicon, Fe_i causes notable recombination activity. It interacts with dopants present in p-type silicon, forming a complex known as the Iron-Boron (FeB) pair [3]. Both Fe_i and FeB coexist at room temperature and dissociate under illumination [117]. Upon carrier injection resulting from illumination or heating, the FeB pair dissociates, and they recombine when placed in dark conditions. It is worth noting that the recombination properties of Fe and the FeB complexes differ. Table 3.1. illustrates the defect levels introduced by Fe_i and FeB [68].

Table 3.1: Recombination properties of Fe defects in Si [68].						
Defect	type	Energy level (eV)	Capture cross sections (cm ²)			
			$\sigma_{ m p}$	σ_{n}		
Fe _i	Donor	$E_{V} + 0.38$	$7.0 imes 10^{-17}$	4.0×10^{-14}		
FeB	Donor	$E_{V} + 0.10$	$2.0 imes 10^{-14}$	4.0×10^{-13}		
FeB	Acceptor	$E_{C} - 0.27$	$2.0 imes 10^{-15}$	1.6×10^{-15}		

The defect levels attributed to Fe defects are positioned near the mid-gap of the energy band diagram, rendering them potent recombination centers. Comparing the recombination activity between Fe_i and the FeB complex, Table 3.1 provides clear evidence that Fe_i exhibits greater

recombination activity. Consequently, silicon devices contaminated with Fe will experience more pronounced degradation when exposed to light and heat.

3.1.2 Copper related defects in Si

Copper (Cu) is also a transition metal with relatively high solubility and diffusivity in silicon, even at room temperature. It is also sensitive to light and causes light-induced degradation, commonly called Cu-LID. Copper occupies substitutional sites (Cu_s) and diffuses as interstitial (Cu_i). It can also forms complex Cu pairs like Cu_sCu_s, Cu_sCu_i and Cu₃Si in silicon [5]. The complex Cu₃Si is formed when exposed to light [118]. Silicon wafers can be contaminated with Cu during multiwire wafer sawing [119], chemical etching process [120], or Cu interconnects[10, 11]. Cu interconnects are used to improve conductivity and reduce the cost of silicon solar cells [10]. Even though the contamination from these sources occurs on the surface, it can easily diffuse into the bulk because of the high diffusivity of Cu, even at room temperature. The Cu defects will cause a reduction in the bulk lifetime of minority carriers by forming Cu precipitate and substitutional Cu. Cu complexes dissociate upon illumination or slightly elevated temperature and cause Cu LID. Cu-LID is observed in all types of silicon devices such as boron-doped mc-Si [118], boron-doped Cz [121], boron-doped FZ-Si [122], and phosphorous-doped FZ-Si [123]. Ramappa et al. [121] suggested that CuLID is due to the dissociation of $Cu_i - Cu_s$ complex and the subsequent transformation of Cu_i into Cu_s . The extended substitutional defects possess an energy level of $E_V + 0.44$ with a hole capture coefficient of 4×10^{-16} cm⁻². Sachdeva et al. observed that n-type silicon samples are also prone to Cu-LID and proposed that the degradation is due to the formation of Cu precipitate [123]. The growth of precipitate is hindered in p-type due to a reduction in diffusivity by repulsion of Cu_i⁺ by positively charged holes, resulting in out-diffusion and formation of Cu_i⁺ B⁻ complex. Vainola et al. [124] observed that high-intensity light reduces the electrostatic repulsion between positively charged interstitial copper ions and copper precipitates. This enables copper to precipitate in the wafer bulk even at a low concentration level. In addition to that, the oxygen precipitates provide effective heterogeneous nucleation sites for Cu. Cu_{3i}Si precipitate inside the bulk Si in a spherical shape, creating a band of energy levels from 0.1 to 0.4 eV below the conduction band edge [3]. Table 3.2 shows the energy level associated with Cu-related defects in Si [3, 125, 126].

The copper contamination in p-type Si samples can be eliminated by promoting the out-

Defect	Туре	Energy level (eV)	Capture cross sections (cm ²)	
			$\sigma_{ m p}$	$\sigma_{\rm n}$
Cui	Acceptor	E _C -(0.150.20)		
Cu ₃ Si	Acceptor	E _C -(0.150.20)		3×10^{-16}
		E_{C} -(0.400.58)		
Cu _s	Acceptor	$E_V + (0.410.46)$	$1.5 imes 10^{-14}$	
		$E_V + (0.200.23)$	$3.0 imes 10^{-14}$	
Cu _s Cu _{3i}	Acceptor	$E_{V} + 0.07$		

Table 3.2: Recombination properties of Cu defects in Si [3, 125, 126].

diffusion of Cu towards its surface. Fast-moving Cu_i^+ experiences electrostatic repulsion from positively charged holes. So, it diffuses from the bulk towards the surface and forms a haze at the surface [127]. The out-diffusion of Cu_i^+ can be enhanced by negative charge at the surface created by both corona charging and dielectric layer film deposition such as Al_2O_3 , SiO_2 [128]. It can also be promoted by annealing by increasing the temperature to $400^{\circ}C$. The Cu_i^+ haze developed on the top can be removed by the etching process [128].

3.1.3 Nickel related defects in Si

Nickel (Ni) is used as a diffusion barrier to prevent Cu's diffusion into silicon from metal interconnects [129]. It also helps to reduce the contact resistance of Cu metallization in solar cells by forming nickel silicide (NiSi₂) at the interface. However, it causes performance degradation in Si solar cells [130]. Electrically active Ni in Si acts as an acceptor and occupies substitutional sites. Ni diffuses by dissociative mechanism; the substitutional Ni (Ni_s) dissociates into an interstitial Ni (Ni_i) and a vacancy [131]. Like Cu, Ni is also a fast diffusing metal, even at low temperatures, with low solid solubility [132]. Ni is first diffused in the bulk and then segregated at the wafer surface because of relatively less solubility in Si. Most Ni forms precipitate at the wafer surface during the cooling period, and only a small portion remains in the bulk. It can also precipitate at the lattice defects within the crystal. Ni reacts with Si and forms nickel silicide complexes Ni₂Si, NiSi, NiSi₂, depending on the temperature conditions [133]. The nickel-related defects in Si cause both FF loss and recombination losses in Si solar cells [134, 135]. Table 3.3 shows the energy level associated with Ni defects in Si [3, 133, 135].

Defect	Туре	Energy level (eV)	Capture cross sections (cm ²)		
			$\sigma_{ m p}$	σ_{n}	
Nis	Double Ac- ceptor	$E_{C} - 0.07$		5.4×10^{-18}	
Nis	Acceptor	$E_{C} - 0.40 \pm 0.03$	$8.0 \pm 5.7 imes 10^{-17}$	5.6×10^{-17}	
Nis	Donor	E_V + 0.19 ±0.06	1.1×10^{-15}	3.9×10^{-12}	
NiSi ₂	Acceptor	E_V + 0.42 ±0.06	5.0×10^{-15}	5×10^{-14}	

Table 3.3: Recombination properties of Ni in Si [3, 133, 135].

3.1.4 Oxygen related defect in Si

Oxygen related defects are one major concern in the Si PV industry. Nowadays, 80% of the silicon semiconductor industry uses c-Si wafers grown by the Cz process due to high crystal purity and fewer crystal defects. During crystal growth, oxygen from the quartz crucible holding the molten Si dissolves into the molten silicon. The dissolved oxygen is diffused throughout the Si crystal. Dissolved oxygen concentration is in the range of about 5×10^{17} to 2×10^{18} cm⁻³. Oxygen atoms are mobile when the temperature is above 300°C. Oxygen in silicon forms small electrically active agglomerates known as thermal donors (TD) upon heat treatment in the range of 300°C to 500°C [136–138]. The formation rate of TDs depends on the fourth power of oxygen concentration, indicating that TDs are agglomerate of four oxygen atoms [137]. However, TDs can be eradicated at temperatures above 550°C due to the small binding energies of about 0.5 eV to 0.8 eV, depending on the number of oxygen atoms in the clusters. Oxygen TDs can act as recombination centers by introducing deep energy levels 0.2 eV to 0.3 eV below the conduction band [139]. Oxygen atoms can precipitate at dislocations within the Si at temperatures above 600°C. These precipitates act as intrinsic gettering centers for metallic impurities and recombination centers of charge carriers. The recombination properties of oxide precipitate are specified in Table 3.4 [140].

ab	le 3.4: Recom	ibination properties of o	foxide precipitate in Si [140]
	Defect	Energy level (eV)	Capture cross sec-
			tion ratio (Q)
	TD	$E_{V} + 0.22$	157
		E _C -0.08	8.33×10^{-4}

Table 3.4: Recombination properties of oxide precipitate in Si [140].

3.1.4.1 Boron-Oxygen complex

Performance degradation is observed in p-type Cz-grown silicon samples contaminated with oxygen on exposure to light [141–144]. The light-induced degradation is observed to increase with increasing boron and oxygen concentrations [144], so it is inferred that the degradation is due to the formation of boron-oxygen (BO) complex. The BO complex introduces defects in the silicon crystal, which acts as strong recombination centers. Two different BO recombination centers are found to be activated on exposure to light or forward bias [145]. One is called Fast Recombination Centre (FRC), which takes a few seconds to minutes to form. The other is called Slow Recombination Centres (SRC), the formation of which takes a few hours. SRC has a greater impact on device performance than FRC since FRC is observed only for a short time. Various defect models proposed for the boron-oxygen-related degradation in solar cells are discussed below.

Bothe et al. [142] studied the relation between defect concentration N_T^* , substitutional boron concentration (Bs), and interstitial oxygen concentration (Oi) and found that N^{*}_T increases proportionally with (B_s) and quadratically with (O_i) . They proposed an oxygen-dimer model for the defect reaction, where small oxygen agglomerates, especially the oxygen dimer O_{2i}, are extremely mobile. The immobile substitutional boron atoms catch Oi dimers to form BsO2i complex, which acts as a recombination center. As the tetrahedral covalent radius of boron atoms is smaller than that of silicon atoms, the O_{2i} tends to be accommodated near the atom. The defect formation is a thermally activated process as it is controlled by the diffusion of O_{2i}. Bothe et al. also suggest that B_iVO_{2i} as another possible structure for the metastable complex, where the boron gets shifted to an interstitial space during reaction with O2i creating a vacancy. The role of illumination is inferred to be in increasing diffusivity of O2i through a recombination-enhanced diffusion process. The dependence of BO defect concentration on substitutional boron concentration and interstitial oxygen concentration for samples doped only with boron proposed by Bothe et al. [142]. However, data from p-type silicon co-doped with phosphorus reveal the dependence on hole concentration p rather than boron concentration [146]. Hence, Voronokov et al. argue that the major degrading center SRC cannot be identified with a B_sO₂ complex. Instead, they suggested a defect configuration, a complex formed with interstitial boron and oxygen [146]. Oxygen precipitates nucleate at around 700°C during crystal cooling, emitting self-interstitial and pushing some of the boron atoms into the interstitial state (B_i). When the temperature is lower, most Bi precipitates as Bi clusters. Bi atoms migrate and form complexes such as B_iO_2 , B_iO and B_iB_s . These will be in equilibrium with dissolved B_i . Below-freezing temperature exchange between boron clusters and dissolved boron stops, and the frozen in B_iO_2 is considered a Latent Complex (LC). Degradation occurs when LC becomes a recombination active center. There can be two configurations for the single positive B_iO_2 defect, which can be identified with LC and SRC. In the dark, the free energy is minimal for LC. In the presence of excess electrons when subjected to light and heat, the charge state of the defect changes, and it moves from +1 state to neutral state. In the neutral state, SRC is at the lowest minimum free energy. As all LC is completely transformed, the SRC inherits its dependence on LC, which explains the dependence of SRC on the product of hole concentration and squared oxygen concentration. The nature of FRC needs to be clarified, but studies suggest that FRC can be thought of as another configuration of the same defect created by the transformation of LC through a different path. Oxygen has two different roles in the degradation in this model: one in producing oxygen dimers and the second in producing self-interstitial.

Voronokov et al. [147] reported the results of one more study in 2011, where they used n-type Cz-Si co-doped with phosphorus and boron. The recombination center was found to be identical to FRC. As the rate of FRC generation is proportional to squared hole concentration, the time scale is considerably longer in n-Si. Only FRC was generated within illumination time as the time scale for SRC becomes enormously long. FRC is identified to be a B_sO_2 complex involving substitutional boron and an oxygen dimer, unlike the SRC, which is dominant in p-Si. FRC was found to exist in three charge states having two energy levels. Both energy levels contribute to recombination in n-Si, but only the donor level is significant in p-Si. The generation process is suggested to be a reconstruction from an LC into FRC through an intermediate configuration. The saturated FRC concentration is reportedly independent of the majority carrier concentration in n-Si [147].

Recent studies of BO defect using injection-dependent lifetime analysis and advanced SRH statistics identified that FRC and SRC are characterized by two defect levels in the band gap and four capture coefficients [70, 148]. The observed defect energy levels and capture coefficients are given in Table 3.5.

The defect levels introduced by the BO complex are close to the mid-band gap in silicon, which acts as strong recombination centers. Hence, the BO complex formed on exposure to light acts as a lifetime killer of charge carriers.

The lifetime degradation due to BO defect can be recovered temporarily by annealing by in-

Si-type	Defect type	Defect energy level	Capture cross
		(eV)	section ratio (Q)
p-type	SRC Donor	$E_{C} - (0.41 \pm 0.02)$	10±1
		E_V + (0.26 ± 0.02)	> 215
		$E_C - (0.65 \pm 0.25 \)$	100 ± 10
Compensated n-type	FRC Donor	$E_C - (0.34 \pm 0.02)$	18.1
• •	FRC Acceptor	$E_V + (0.31 \pm 0.02)$	85.7

Table 3.5: Recombination properties BO defect in Si [70, 148].

creasing temperature to 200°C [149, 150]. It is due to the dissociation of the BO complex. However, the defect will reappear when the Si sample is returned to the room condition, showing a metastable behavior. Hydrogenation of Si samples also helps to passivate the BO defects [151].

3.2 Mitigation of SRH defects

Hydrogenation is an industrial technique for passivating bulk defects in multicrystalline and monocrystalline silicon solar cells. In multicrystalline cells, hydrogenation helps to reduce the recombination activity of grain boundary defects, dislocation clusters, and transition metal impurities. In monocrystalline solar cells, hydrogenation reduces the recombination activity of bulk defects by passivating BO defects and oxide precipitate [152, 153]. Various methods are



Figure 3.1: iV_{OC} maps calibrated at one sun of a diffused multi-crystalline silicon wafer; (a) after the deposition of PECVD SiNx: H and (b) after the subsequent belt furnace firing process [152].

used for hydrogen passivation, including hydrogen diffusion from the dielectric layer, form-

ing gas annealing, hydrogen plasma treatment, and hydrogen ion implantation. The commonly used method in the Si PV industry for hydrogenation is PECVD deposition of dielectric layers SiN_X : H and AlO_X : H followed by rapid thermal annealing. The anti-reflection cum passivation layer in Si solar cells deposited by the PECVD method is rich in hydrogen. The co-firing process after metallization helps to release hydrogen from the PECVD dielectric film and further enables the diffusion of atomic hydrogen into the bulk silicon material. Depending upon the charge, the mono-atomic hydrogen interacts with the impurities and helps to passivate the bulk defects. Hydrogenation occurs unintentionally in all PECVD passivated solar cells during the co-firing process. Hydrogen passivation of defects within Si increases the effective minority carrier lifetime. A relative increase in efficiency of about 10 to 15% is reported in solar cells after hydrogenation [152]. The improvement in implied open circuit voltage (iV_{OC}), which is a direct measure of the lifetime of a diffused SiNX : H passivated multi-crystalline after the co-firing process, is shown in Figure 3.1 [152]. It is clear from Figure 3.1 that the deposition of PECVD SiN_X : H alone will not be effective for passivating defects at the grain boundaries. However, after the co-firing process, iV_{OC} increases throughout the sample structure within grain and grain boundaries as observed in studies by Hallam et al. [152]. b. An increase in iV_{OC} observed indicates a defect concentration reduction during the co-firing process due to hydrogen passivation. The diffusion of hydrogen into the bulk of multicrystalline silicon sam-



Figure 3.2: Defect concentration in SiN_X passivated samples with different SiH_4 : NH_3 ratios during deposition process [149].
ples can also contribute to the passivation of the metallic defects. Diffusing hydrogen atoms can form complexes with transition metals during the firing process, thereby reducing the recombination activity of the interstitial transition metal defects. The effect of hydrogen on interstitial iron concentration in p-type multicrystalline silicon was studied by Karzel et al. [154]. Their studies show a five-fold decrease in average interstitial iron concentration observed in p-type multicrystalline samples with hydrogenation after dissociation of the FeB complex [154]. The decrease in average interstitial iron concentration before and after hydrogenation is shown in Figure 3.2. Studies also reveal that the cooling after the firing process does not affect the defect passivation by hydrogenation, as seen in Figure 3.2 [149]. Wilking et al. [151] studied the variation of BO defect concentration in Cz-grown crystalline silicon samples passivated with hydrogen-rich dielectric layer SiN_X : H. Their experimental results show that passivation with SiN_X : H and Al_2O_3 can reduce the BO defect density in a p-type silicon sample under elevated temperature, as shown in Figure 3.3. The passivation layer can release hydrogen during high-temperature processing, and it helps to reduce defects' recombination activity. Studies on the change in defect concentration as a function of Al₂O₃ thickness in samples passivated with stacks of Al_2O_3 and SiN_X : H layer reveals that the thicker Al_2O_3 layer presents a higher the barrier for the diffusion of atomic hydrogen and poor passivation of bulk defects. The lowest defect concentration is obtained when the thickness of the Al₂O₃ layer is small, as shown in Figure 3.4.



Figure 3.3: Variation of defect concentration as a function of time in SiN_X : H passivated samples with different SiH_4 : NH_3 ratios before and after the firing process [149].

Even though hydrogen diffusion during the solar cell manufacturing process helps to pas-



Figure 3.4: Variation in defect concentration with annealing time in Si samples passivated with a dielectric stack of Al_2O_3/SiN_X : H [149].

sivate the silicon's defects, it can introduce a strong hydrogen-related recombination center in Si.

3.3 Hydrogen-related defects in Si

The recombination characteristics of hydrogen-related defects rely on the charge state of hydrogen, which is determined by the position of the Fermi level within the Si device [25]. Additionally, it hinges on hydrogen's ability to function as a dopant. Hydrogen in silicon exhibits amphoteric behavior, meaning it can act as either a donor or an acceptor. In p-type materials, where holes are prevalent, hydrogen donates its electron, stabilizing itself in the positive charge state as H^+ . The H^+ ions can then associate with acceptor impurities within the silicon. Conversely, in n-type materials with an abundance of electrons, the favored charge state for hydrogen is H^- , allowing it to interact with positively charged acceptors. This duality demonstrates that hydrogen defects in silicon can modify the material's conductivity through counterdoping. The neutral state H^0 is relatively unstable in silicon and rapidly transitions to either H^+ or H^- form.

According to Wenham's theory of hydrogen induced recombination (HIR), recombination events occur during the transition of hydrogen's charge state, shifting from H^- to H^0 state by loss of an electron and from H^0 to H^+ by capturing a hole [25]. These charged hydrogen species introduce energy levels, with the donor energy level positioned 0.16 eV below the conduction band and the acceptor level residing 0.07 eV below the midgap. Because the donor energy level is situ-

ated below the acceptor energy level, hydrogen is classified as a negative U defect [155]. The formation of hydrogen induced structural defects, resulting from platelet formation in borondoped crystalline silicon, is attributed to the presence of both positively and negatively charged hydrogen atoms, as documented in the literature [156]. Nickel et al. [156] have indicated that platelet formation occurs when the Fermi level is positioned 0.3 eV below the conduction band edge. As the platelet concentration increases to $2x10^{17}$ cm⁻³ the energy difference E_C and E_F decreases. All of the aforementioned findings underscore the influence of the Fermi level on hydrogen-related defects, thus highlighting that recombination activity varies depending on the type of dopants present. A summary of recombination properties, as determined through injection-dependent spectroscopic methods, is presented in Table 3.6.

Туре	Defect level	Capture	Ref.
		cross sec-	
		tion ratio	
		(Q)	
p-type mc-Si	$-0.26 \text{ eV} < E_{\text{T}} - E_{\text{i}} < 0.24 \text{eV}$	28.5	[158]
	$-0.27 \text{ eV} < \text{E}_{\text{T}} - \text{E}_{\text{i}} < 0.13 \text{eV}$	26 - 36	[159]
	$E_T - E_i = 0.21 \pm 0.05 \text{ eV}$ (Upper	49±21	[159]
	bandgap)		
	$E_{\rm T} - E_{\rm i} = -0.32 \pm 0.05 \text{ eV}$ (Lower	56 ± 23	[160]
	bandgap)		
	$E_T - E_i = 0.1 \pm 0.07 \text{ eV}$ (Upper	$23.5{\pm}~5.6$	[161]
	bandgap)		
	$E_{\rm T} - E_{\rm i} = -0.21 \pm 0.06 \text{ eV}$ (Lower	$23.9{\pm}~5.5$	[161]
	bandgap)m		
	assumed $E_T = E_i$	$33.4{\pm}~1.5$	[19]
	assumed $E_T = E_i$	29 ± 4	[162]
p-type CZ-Si	assumed $E_T = E_i$	39± 4.9	[19]
	not stated	36 ± 2	[163]
n-type Cz-Si	assumed $E_T = E_i$	$0.028\pm$	[21]
		0.003	
	Not stated	20 ± 2	[164]
p-type FZ-Si	assumed $E_T = E_i$	35	[165]
	assumed $E_T = E_i$	20± 7	[166]

Table 3.6: Recombination properties of hydrogen-related defects in Si [157].

A summary of recombination characteristics of light-sensitive defects in Si used for the solar cell fabrication process is given in Table 3.7.

Defect	Energy level (eV)	Capture cross section	
		ratio (Q)	
Fe _i , Donor	E _V +0.38	571	[68]
FeB, Donor	$E_{V} + 0.10$	20	[68]
FeB, Acceptor	$E_{C} - 0.27$	0.8	[68]
Cu _i	E _C -(0.150.20)	[3]	
Cu ₃ Si	E _C -(0.150.20)	$\sigma_{\rm n}$ = 3× 10 ⁻¹⁶	[3]
	E _C -(0.400.58)		
Cu _s	E_V +(0.410.46)	$\sigma_{\rm p}$ = 1.5 $ imes$ 10 ⁻¹⁴	[3]
	E _V +(0.200.23)	$\sigma_{\rm p}$ = 3 × 10 ⁻¹⁴	
Cu _s Cu _{3i}	$E_{V} + 0.07$	[3]	
Ni _s , double ac-	E _C -0.07		[3, 133, 135]
ceptor			
Ni _s , Acceptor	$E_{C}\!-\!0.40\!\pm\!0.03$	1.4 ± 0.06	[3, 133, 135]
Ni _s , Acceptor	$E_V \! + \! 0.19 \pm \! 0.06$	354	[3, 133, 135]
NiSi ₂	E_V + 0.42 ±0.06	10	[3, 133, 135]
BO (p-type Cz	$E_{C} - (0.41 \pm 0.02)$	10±1	[70]
Si)			
	E_V + (0.26 \pm 0.02)	> 215	[70]
	$E_C - (0.65 \pm 0.25)$	100 ± 10	[70]
BO (Compen-	$E_{C} = (0.34 \pm 0.02)$	18.1	[148]
sated n-type Cz			[]
Si)			
,	$E_V + (0.31 \pm 0.02)$	85.7	[148]
SiOX	E _V +0.22	157	[140]
	E _C - 0.08	8.33 ×10 ⁻⁴	[140]

Table 3.7:Summary of recombination characteristics oflight-sensitive defects in Si.

H defects p-type	$-0.26 \text{ eV} < E_{\text{T}} - E_{\text{i}} < 0.24 \text{eV}$	28.5	[158]
mc-Si			
	-0.27 eV < $E_T - E_i < 0.13$ eV	26 - 36	[159]
	$E_T - E_i = 0.21 \pm 0.05 \text{ eV}$	49±21	[159]
	(Upper bandgap)		
	$E_T - E_i$ = -0.32 \pm 0.05 eV	56±23	[160]
	(Lower bandgap)		
	$E_T\!-\!E_i$ = 0.1 \pm 0.07 eV (Up-	$23.5{\pm}~5.6$	[161]
	per bandgap)		
	$E_T - E_i$ = -0.21 ± 0.06 eV	23.9± 5.5	[161]
	(Lower bandgap)		
	assumed $E_T = E_i$	33.4± 1.5 [19]	
	assumed $E_T = E_i$	29 ± 4	[162]
H defects p-type	assumed $E_T = E_i$	39 ± 4.9	[19]
CZ-Si			
	not stated	36 ± 2	[163]
H defects n-type	assumed $E_T = E_i$	$0.028 {\pm}~0.003$	[21]
Cz-Si			
	Not stated	20 ± 2	[164]
H defects p-type	assumed $E_T = E_i$	35	[165]
FZ-Si			
	assumed $E_T = E_i$	20±7	[166]

Since most of the high-efficiency solar cell architectures utilize PECVD SiN_X : H passivation layers and p-type bulk, hydrogen and oxygen-related defects are very significant in today's PV industry. Even though the SRH defect characteristics are well studied by various research groups, the exact nature, configuration, structure, and physical mechanisms of hydrogen and oxygen-related defects are still unknown. Additionally, the reported energy levels of hydrogenrelated defects are inconsistent, as shown in Table 3.6. Most researchers have assumed deep energy levels in the middle of the energy bandgap for their studies when analyzing defect characteristics and have reported different values for capture cross-section ratios, particularly in the case of n-type samples. An estimation of the capture cross-section ratio of defects in the PECVD SiNX : H passivated p-type and n-type samples after light soaking in normal ambient conditions is addressed in subsection 6.2.4.

Experimental evidence supports the involvement of hydrogen in the recently reported degradation of Si solar cells under normal outdoor operating conditions at temperatures above 50°C, even after the dissociation of BO defects. Due to the involvement of hydrogen, such degradation is referred to as hydrogen-induced degradation (HID) [25]. Since HID is prominent in Si solar cells exposed to light and elevated temperatures, it is also known as light and elevated temperature-induced degradation (LeTID) in Si solar cells . A detailed discussion of LeTID is presented in Chapter 4.

3.4 Conclusion

The chapter examines the recombination characteristics associated with prevalent defects in the silicon photovoltaic cells, including Fe, Cu, Ni, and O defects. Research findings indicate that these defects exhibit significant recombination activity, with their defect levels positioned near the mid-band gap. Furthermore, it is observed that exposure to light and heat can induce alterations in the recombination properties of these defects. Research outcomes demonstrate that surface recombination defects can be alleviated through hydrogenation, a process feasible within the industry-standard PECVD dielectric deposition method. Even though the hydrogenation may passivate some of the bulk defects, there are concerns about the hydrogen induced defects.

Chapter 4

Understanding of light and elevated temperature-induced degradation in silicon solar cells

Antireflection coatings play a pivotal role in photovoltaic cells, serving multiple functions: enhancing optical absorption, minimizing reflection losses, and reducing surface recombination. Various methods are employed in the production of antireflection coatings. Among these, antireflection coating deposited by PECVD SiN_X : H has gained widespread acceptance in highefficiency solar cell designs within the silicon PV sector. The extensive adoption of PECVD SiN_X : H can be attributed to its exceptional attributes, which encompass outstanding light transmission properties, superior surface passivation capabilities, the attainment of a surface recombination velocity of less than 10 cm/s, strong thermal stability, and the ability to be deposited at low temperatures. Additionally, it functions as a protective shield, safeguarding the underlying silicon against external contaminants. In addition, the hydrogenation from the PECVD dielectric SiN_X : H during high-temperature treatment contributes to the passivation of defects present in grain boundaries, metallic impurities, BO defects, and other dislocations within the bulk silicon. However, it is crucial to highlight that monoatomic hydrogen, upon diffusion into the bulk silicon, displays a high level of reactivity. It interacts with Si-Si bonds, strained bonds residing within vacancies, and dopant atoms within the silicon lattice. Furthermore, it can engage in self-interactions, creating passive defects such as H₂ and hydrogen

precipitates.

Several experimental findings validate that monoatomic hydrogen can impair the performance of silicon solar cells and modules when exposed to typical outdoor operating conditions involving light and elevated temperatures. In the upcoming sections, we will provide an overview of the degradation induced by light and elevated temperatures (LeTID) and explore its dependence on the solar cell manufacturing process.

4.1 LeTID in Si solar cells

Since 2001, LID caused by boron-oxygen (BO) defects has been identified as the primary performance-limiting factor in silicon solar cells when exposed to light. Initially, this problem was exclusively observed in boron-doped p-type Si wafers produced using the Cz process. The degradation begins with an initial decrease in efficiency, followed by a swift recovery, contingent upon the duration of light exposure and prevailing temperature conditions. However, the formation of BO defects can be mitigated through processes such as hydrogenation and elevating the temperature within the range of 55°C to 70°C. This temperature range corresponds to the outdoor operating conditions of Si solar modules.

In 2012, Ramspeck et al. reported performance degradation in oxygen-free multicrystalline solar cells under typical outdoor conditions [167]. However, the term "Light and elevated Temperature Induced Degradation" was coined by Kersten et al. in 2015 [15]. LeTID is a carrier-induced degradation (CID) because the degradation kinetics depend on the excess carriers generated in the samples due to external excitation from light, heat, and applied voltage. As it was initially observed in multicrystalline cells, LeTID is also referred to as mc-CID. Experimental evidence supports the idea that hydrogen released from the PECVD dielectric layer plays a significant role in the degradation mechanism, either as a defect or a precursor to the defect. Therefore, Wenham et al. introduced the term "Hydrogen-induced degradation" (HID) [25].

LeTID emerged as a substantial concern within the solar industry, given that over 60% of the Si PV market depended on multicrystalline cells. Further investigations into LeTID unveiled that lifetime degradation occurs in Si wafers grown through both the float zone and Cz processes, irrespective of doping conditions or crystal orientation. In contrast to BO LID observed in Cz-grown wafers, the manifestation of LeTID and its recovery in solar modules necessitates a

more prolonged exposure under normal operating temperature conditions. It remains uncertain whether the modules will fully recuperate from this degradation throughout their entire operational lifespan. Additionally, the behavior of LeTID and subsequent degradation is influenced by all the manufacturing processes involved in solar cell production, leading to variations in LeTID behavior based on the specific solar cell architecture.

Several research teams have conducted extensive investigations into the effects of LeTID on silicon wafers, solar cells, and modules. These investigations have provided insights into how elevated temperatures affect the degradation induced by light, unveiling a unique pattern characterized by an initial gradual deterioration phase, succeeded by a subsequent and comparatively more rapid phase of recovery. The extent of degradation and the subsequent regeneration process vary considerably depending on the specific fabrication processes employed for the samples and the conditions of excitation. Petter et al. [17] noted a decline in efficiency, with multicrystalline Si PERC solar cells showing a maximum decrease of as much as 16%. In contrast, modules consisting of multicrystalline Si PERC cells exhibited a more modest 7% decrease in efficiency over a three-year period [15]. Studies indicate LeTID-related defect formation and regeneration are much slower than BO LID. Hence, several decades are required to reach maximum degradation and complete regeneration of electrical behavior under field conditions. Through the application of various supplementary processing measures intended to reduce the impact of LeTID in practical operating conditions, the maximum extent of LeTID has been lowered to less than 5% for silicon solar cells produced after the year 2018 [37].

4.2 Factors influencing LeTID

Empirical findings from diverse research teams demonstrate that each step involved in the fabrication of solar cells affects the extent of LeTID and the subsequent regeneration characteristics. Investigations have specifically delved into the influence of processes such as the firing step [19, 27, 31, 32], SiN_X : H film deposition [29, 33–35] and emitter diffusion [30] on LeTID. The research indicates that LeTID tends to be more pronounced in silicon samples when peak firing temperatures exceed 700°C [19, 27, 31, 32]. Several research groups have demonstrated a direct correlation between thickness and atomic bond (Si-H and N-H) density of SiN_X : H films [29, 33–35]. Meanwhile, Sen et al. [30] observed that the degradation and regeneration behavior within both the bulk and the surface of silicon is influenced by the sheet resistance of the emitter. Their investigation indicated that emitters with high sheet resistance profiles exhibit lower degradation in the bulk and higher degradation at the surface [30]. Similarly, Zuschlag et al. [28] and Schmidt et al. [14] reported that non-gettered wafers are more prone to LeTID than gettered samples.

4.2.1 Firing process parameters

The post-metallization firing process influences the degree of LeTID behavior, and it becomes more pronounced as the peak firing temperature increases, as confirmed by multiple research studies [27, 31, 32]. Figure 4.1 shows the effective lifetime degradation of p-type multicrys-talline Si solar cell structures with and without the post-deposition firing process versus the light soaking duration (left) and the maximum extent of degradation in partially processed multicrys-talline solar cell structures as a function of peak firing temperatures (right) [32]. Research has



Figure 4.1: Effective minority carrier lifetime of fired (415° C to 740° C) and non-fired (NF) multicrystalline samples as a function of light soaking duration at 140° C, 44.8 kW m⁻² (left). The maximum extent of degradation (black circles) and effective lifetime at the maximum degradation (red squares) as a function of peak firing temperature (right) [32].

shown minimal to no degradation occurs when samples are not subjected to firing or when firing temperatures remain below 600°C. The maximum degradation in lifetime varies with the peak firing temperature, with higher peak temperatures resulting in increased degradation. Additionally, even when the peak firing temperature remains constant, variations in the firing profile can also impact LeTID behavior [27]. The commonly employed fast-firing profile (FFO) in industrial solar cell production, represented by the solid black line in Figure 4.2, results in a higher

density of defects in samples treated with rapid firing during post-metallization processes, implying a more significant degree of degradation in such samples. Conversely, a firing profile characterized by a relatively slow heating and cooling rate has a minimal influence on LeTID, as depicted in Figure 4.2.



Figure 4.2: (a) Measured temperature profiles of the firing processes. (b) Normalized defect concentration as a function of degradation time averaged over the whole wafer area [27].

4.2.2 Dielectric film properties

In addition to the firing process, the properties of the dielectric film used for light trapping and passivation also play a pivotal role in determining the extent of LeTID in solar cells. LeTID behavior is observed only in samples passivated with hydrogen-rich dielectric layers deposited by the PECVD technique [33, 36]. FTIR spectroscopic studies conducted by Vargas et al. [33] correlated the extent of degradation with the amount of hydrogen diffused into the bulk from the hydrogenated dielectric layer during the firing process. The PECVD process parameters and operating conditions determining the dielectric film's thickness and optical properties influence the LeTID behavior. Varshney et al. investigated SiN_X : H thickness variation and LeTID-related defect generated using diffused p-type multicrystalline samples with the same refractive index passivated with SiN_X : H [34]. The optical properties of the SiN_X : H films used in their study are given in Table 4.1 [34]. Figure 4.3 shows variation in LeTID-related defect density as a function of dielectric film thickness [34]. The defect density is maximum when the dielectric film thickness is maximum. Hence, lifetime degradation will be greater for samples with thick SiN_X : H dielectric film. According to Varshnay et al. [34], defect density increases linearly with dielectric film thickness. The higher defect density in thick SiN_X : H film is due to the

Sample	Thickness	Refractive	Extinction
	(nm)	index	Coefficient
$SiN_X : H - 1x$	50.1	2.02	1.01
$SiN_X : H - 2x$	101.3	2.02	1.06
$SiN_X : H - 3x$	149.4	2.02	1.01
$SiN_X : H - 4x$	201.1	2.02	0.97

Table 4.1: SiN_X : H dielectric film properties [34].

release of more hydrogen into the bulk during the firing process.



Figure 4.3: Variation in normalized defect density as a function of light soaking duration for samples passivated with SiN_X : H films with optical properties given Table 4.1 (left). Normalized defect concentration as a function of SiN_X : H (right) [34].

Bredemeier et al. [29] investigated the dependency of LeTID behavior on SiN_X : H dielectric film with varying refractive indices keeping thickness constant. The refractive index is varied by changing the silicon-to-nitrogen ratios in the dielectric film. Figure 4.4 shows the effective lifetime variation as a function of the film's refractive index with a constant film thickness of 131 ± 5 nm. The corresponding variations in the atomic ratio of Si and N are shown at the top of Figure 4.4. It is clear from the graph that samples passivated with low refractive index films are less prone to LeTID degradation than those with higher refractive index. However, the samples' defect density and lifetime degradation are maximum when n is between 2.33 and 2.5 at 633 nm. The extent of LeTID is decreased with a further increase in n values above 2.5. At the same time, the use of high-refractive SiN_X : H films will deteriorate the surface passivation quality.



Figure 4.4: (a) Effective lifetime and (b) maximum effective defect density as a function of refractive index n measured at a wavelength of 633 nm (lower axis) and the corresponding silicon-to-nitrogen ratio (upper axis) of the silicon nitride layer keeping silicon nitride film thickness constant [29].

4.2.3 Emitter diffusion profile

Sen et al. [30] investigated the dependency of LeTID behavior on the emitter diffusion profile. Their studies reveal that surface degradation due to light and heat varies with surface phosphorous doping conditions. Figure 4.5 (a), (b), and (c) shows the variation in effective lifetime, normalized defect density, and surface recombination current density as a function of light soaking duration in diffused p-type multicrystalline samples passivated with SiO₂/SiN_X : H dielectric film [30]. The emitter diffusion profile with sheet resistance values of 85 Ω / \Box , 140 Ω / \Box , 240 Ω / \Box , and > 870 Ω / \Box were used in their study. The graph shows an initial degradation independent of the sheet resistance and doping profile variations. The second degradation depends upon the doping profile. The trend followed by the degradation agrees with the surface recombination current shown in Figure 4.5(c) and confirms that the second degradation during light soaking is due to surface-related defects. During the initial degradation phase, no variation in surface recombination current is observed during the light soaking duration. However, there

is an increase in defect density, pointing out that the LeTID-related defects are not at the surface but within the bulk. Surface degradation is higher in samples with lightly doped emitters and is dominant only after a longer light soaking duration of about 60 h under elevated temperatures. Longer light soaking duration under elevated temperatures promotes the diffusion of recombination active defects from the bulk toward the surface. It gets trapped there, which increases the defect density at the surface.



Figure 4.5: (a) Effective lifetime corresponds to $\Delta n = 7.5 \times 10^{14} \text{ cm}^{-3}$ as function of light soaking duration, (b) normalized defect density of effective lifetime and (c) total emitter saturation current density of double side diffused multicrystalline Si passivated with SiO₂/ SiN_X : H on both sides [30].

4.2.4 Wafer thickness

Light-induced carrier lifetime degradation and regeneration at elevated temperatures in Si solar cells structures vary depending upon sample thickness. Experiment results show that less degradation and faster regeneration occur in thinner wafers than in thicker wafers [13, 168]. Figure 4.6 shows the defect density measured from lifetime data in a p-type multicrystalline sample measured at $\Delta n = 10^{15}$ cm⁻³ as a function of light soaking duration at an illumination intensity of 1sun and a temperature of 75°C. The figure indicates that the extent of LeTID increases with wafer thickness. Around six-fold increase in defect density is observed when the wafer thickness is increased from 128 µm to 150 µm. Decreasing the silicon wafer's thickness is expected to accelerate the diffusion of impurities toward the surface from the bulk, which reduces bulk degradation during LeTID [13]. Consistent with the research conducted by Bredemeier et al. [13], Varshney et al. also noted a decrease in the degree of degradation as the thickness of the wafer decreased [168]. The reduced level of degradation observed in thinner wafers may



Figure 4.6: Effective defect density measured from lifetime data at $\Delta n = 1 \times 10^{15}$ cm⁻³ for p-type multicrystalline samples with thickness varying from 128 µm to 159µm versus light soaking duration (left). Maximum defect density versus wafer thickness of conventional and high-performance multicrystalline samples (right) [13]

be linked to the possibility of hydrogen out-diffusing from the thin bulk during the firing process. Furthermore, the thinning process induces modifications in the surface morphology of the wafers, resulting in alterations to their optical and physical characteristics. These changes could also contribute to the observed decline in degradation [168].

4.3 Kinetics of degradation and regeneration

The rate at which the electrical performance characteristics of solar cells degrade and regenerate in normal outdoor operating conditions is significant for understanding the physical mechanism responsible for the defect and for developing measures to minimize the impact of the defect. The defect kinetics can be better understood using the four-state defect transition model proposed by Fung et al., shown in Figure 4.3 [169].

The defect precursor initial in state R transitions to the new state during the post-metallization firing process with fast heating and cooling ramps. Defect precursors are mostly recombination inactive. With carrier injection, upon light soaking under elevated temperature, recombination active defects are formed, degrading the system's electrical performance in state B. The transition from state A to state B occurs during carrier injection at a temperature above 50°C. Further,



Figure 4.7: LeTID defect transition model adapted from [169].

prolonged exposure to light and heat causes a reverse transition from recombination active state B to a recombination inactive state C, possibly due to defect transformation to recombination in active form.

4.3.1 Injection and temperature dependency of LeTID kinetics

Investigation of LeTID kinetics reveals that injected excess carrier density and temperature modulate the LeTID and regeneration kinetics [42, 170–175]. Kwapil et al. [42] used high-performance multicrystalline PERC solar cells with three different base resistivities (HPM1 with base resistivity of 1.7 Ω cm, HPM2 with base resistivity of 2.1 Ω cm, HPM3 with base resistivity of 1.9 Ω cm) from different manufacturers for the study of LeTID kinetics. The samples were subjected to light soaking at 75°C and at an illumination intensity of 1 sun. The excess carrier density is kept constant for estimating the rate constant by applying the fixed external bias. The variation in the normalized dark current (I) normalized to the initial current (I_{init}) as a function of degradation time is shown on the left side of Figure 4.8. As indicated in Figure



Figure 4.8: The relative dark current (semi-logarithmic scale) of p-type high-performance multicrystalline PERC solar cells versus degradation time at different injection conditions (left). The dashed and dotted lines indicate the best fit of the data points used for estimating the degradation rate constant. Degradation rate constant plotted as a function of excess carrier density (right) [42].

4.8, the current increases as the degradation time progresses. The rate constant was estimated from the slope of the best-fit lines of the data points. The dependency of degradation rate (R_{deg}) on Δn is shown on the right side of Figure 4.8, indicating that the formation rate of LeTID defects depends upon the excess electron injected into the sample. Furthermore, the exponential factor is almost close to unity for low and moderate injection, meaning a single electron's involvement in defect formation. In some cases, the degradation behavior showed fast and slow components, indicating the possibility of two defect configurations responsible for the degradation [170]. In addition, both defect components strongly depend on excess carrier density and temperature. Bredemeier et al. suggested that the total degradation rate is the sum of the degradation rates contributed by slow and fast components. The activation energies for the defect formation of both the components were estimated from LeTID studies on high-performance p-type multicrystalline Si solar structures with base resistivity of 1.7 Ω cm subjected to an illumination intensity of 0.5 suns and temperature range of 75°C to 120°C [170]. The estimated values of activation energies are 0.89 ± 0.04 eV and 0.94 ± 0.06 eV for slow and fast defect formation, respectively, from the Arrhenius plots, as shown in Figure 4.9 [170]. Kwapil et al. demonstrated that the rate constant associated with the temporary recovery during defect transformation from recombination active state B to recombination inactive state A depends on the excess carrier density to the power 1.71 [171]. The reverse transformation of the defect requires two electrons to form a recombination inactive precursor state [171]. However, studies show that both degradation and regeneration kinetics are material specific [18, 20]. Vargas et al. [172]



Figure 4.9: Measured normalized defect densities N^* as a function of the exposure time t in hours after exposure to 0.5 suns illumination and temperature ranging from 75 to $120^{\circ}C$ (left). Degradation rate constants of the fast and slow degradation components versus the inverse temperature 1/T according to the Arrhenius law (right) [170].

estimated the activation energies during the degradation and regeneration process in p-type multicrystalline structures after dark annealing as 1.08 ± 0.05 eV and 1.11 ± 0.04 eV, respectively. Chen et al. [22] reported slightly different activation energies of 0.70 ± 0.05 eV and 0.83 ± 0.15 eV for slow defect formation during the degradation and regeneration phases, respectively, in boron-diffused n-type Cz samples. However, previous studies conducted by Chen et al. [22], Bredemeier et al. [170], Kwapil et al. [171] and Vargas et al. [172], have not taken into account the injection dependency of reaction kinetics while estimating the reaction rates during both degradation and regeneration phases. Considering the injection dependency with suitable experimental modification, Graf et al. [173] reported better activation energy values (0.78 ± 0.09) eV and (0.62 ± 0.09) eV during the degradation and regeneration process, respectively, in FZ samples for a fixed Δn corresponding to 1 sun illumination intensity. In contrast, Wyller et al. [174] reported activation energy of 1.38 ± 0.14 eV in the degradation phase and 0.56 ± 0.12 eV in the regeneration phase considering the injection dependency of reaction kinetics in p-type in multicrystalline samples using spatially resolved photoluminescence imaging at 1 sun illumination condition. Recently, Cheng et al. [175] reported the square law dependency of both rate constants on excess carrier density during regeneration in cast p-type monocrystalline silicon lifetime samples when subjected to light soaking at 1 sun illumination intensity at a temperature of 75°C. This group reported activation energy of 0.48 ± 0.02 eV in the degradation phase and 0.70 ± 0.02 eV in the regeneration phase [175].

4.3.2 Defect Modeling

During the degradation phase, the precursor concentration N_A and recombination active defect concentration N_B change with time. During the regeneration phase, the defect concentration N_B and the passivated defect concentration N_C change with time (see Figure 4.3). The net rate of change in the recombination active defect concentration N_B can be written assuming a first-order relation between the state transition A, B, and C for involved chemical species. It is the sum rate of change in concentration of chemical species involved in the reaction during the degradation phase and regeneration phase as indicated in Eq.4.1.

$$\frac{\partial N_B}{\partial t} = K_{AB} N_A(t) - K_{BA} N_B(t) + K_{CB} N_C(t) - K_{BC} N_B(t)$$
(4.1)

Here, K_{ij} represents the reaction rate constants associated with the transition between the states A, B, and C. The degradation rate (R_{deg}) is determined by the term $K_{AB}N_A(t) - K_{BA}N_B(t)$ and regeneration rate (R_{reg}) by the term $K_{CB}N_C(t) - K_{BC}N_B(t)$. The reaction rate constants during the degradation and regeneration phase are determined by temperature and the excess charge carriers injected into the device [42, 170, 171]. The presence of excess charge carriers is responsible for transforming idle precursors to recombination active defects and its reverse transformation.

Since the physical and chemical nature of the defect (N_B) is unknown, estimating the actual defect concentration is difficult. An apparent defect density term measured from the electrical parameters is commonly used to indicate the defect concentration. The apparent defect density (N_T^* , s⁻¹) estimated from lifetime measurement at any time t is given as follows

$$N_{\rm T}^*(t) = \frac{1}{\tau_{\rm d}} - \frac{1}{\tau_0}$$
(4.2)

where τ_0 and τ_d represent the measured effective lifetime of the samples before and after degradation (s), respectively [176]. A model for time variation of $N_T^*(t)$ variation accounting for the fact that degradation and regeneration occur simultaneously is given in Eq.4.3. as proposed by Vargas et al. [172].

$$N_{T}^{*}(t) = N_{Tmax}^{*}((1 - e^{-R_{deg}t}) - (1 + A')(1 - e^{-R_{reg}t}))$$
(4.3)

where N_{Tmax}^* is the apparent defect density at the maximum extent of degradation. The constant A' accounts for the deviation between the regenerated and initial lifetime values. R_{deg} and R_{reg} are the rate of degradation and regeneration processes.

4.4 Root cause of LeTID

Numerous inquiries have aimed to uncover the SRH characteristics and the fundamental causes of defects linked to LeTID in silicon solar cells and wafers. Initially, LeTID was restricted to multicrystalline Si solar cells, leading to suspicions that metallic impurities within the bulk Si were the primary suspects. Nevertheless, Bredemeier et al. [31] introduced the idea that hydrogen might also serve as a potential contributor to the creation of LeTID defects.

4.4.1 Metallic impurities as a cause for LeTID

Bredemeier et al. [31] advanced a defect theory to elucidate the function of metallic impurities in the onset of LeTID and its subsequent restoration. In multicrystalline silicon as initially grown, the metallic precipitate dissolves, yielding highly mobile interstitial metal atoms during the rapid firing process. Given the notably low density of these metallic precipitates, they do not significantly impact the overall lifetime of the bulk material. During the cooling phase following the attainment of the peak firing temperature, the interstitial metal atoms combine with uniformly distributed impurities (referred to as X) within the silicon to create a metal impurity complex denoted as M_i -X. These impurities, denoted as X, can be hydrogen (H), nitrogen (N), boron (B), phosphorus (P), and so forth. The M_i -X complex can serve as a relatively weak recombination center, transitioning to M_i -X* on injection of excess carriers into the device when subjected to light and heat.

Prolonged exposure to sunlight and heat leads to the dissociation of the M_i -X complex into isolated M_i and X. The interstitial metal atoms are highly prone to create recombination centers, which is responsible for the degradation observed. However, as time passes and under the influence of continuous exposure to light and heat, the migrating M_i atoms become permanently

trapped at the heavily doped emitter surface. This entrapment, combined with crystallographic defects, results in the regeneration of the lifetime. The emitter surface and crystallographic defects serve as a reservoir for these defect species. The distribution of metallic impurities within the silicon device is uneven and depends on factors such as the distribution of crystallographic defects and the sample thickness. Consequently, the regeneration process is not uniform throughout the material.

Numerous research teams have explored the impact of transition metal impurities on LeTID behavior, supporting the defect model originally proposed by Bredemeier et al. [31]. Luka et al. [177], using elemental analysis techniques like scanning transmission electron microscopy (STEM) and highly sensitive energy-dispersive X-ray analysis (EDX), identified Cu precipitates as potential culprits for LeTID in solar cells. Meanwhile, Niewelt et al. [165] excluded the possibility of impurities like B, Ga, P, W, Ti, V, Zn, Cr, Mg, Co, Mo, and Na contributing to LeTID, as these impurities in their elemental state cannot disperse sufficiently during the usual time and temperature conditions of the firing process. In contrast, studies by Nakayashiki et al. [158] and Morishige et al. [159] proposed that LeTID could be initiated by either interstitial titanium or substitutional tungsten, as indicated by their analysis of defect characteristics utilizing SRH statistics. Based on a statistical analysis of experimental data, Wagner et al. [178] proposed that aluminum and oxygen precipitates enhance LeTID in solar cells. Wagner et al. also mentioned that impurities like Fe, Cu, Cr, Ni, and Ti have an impact on degradation [178]. Deniz et al. [179] and Jensen et al. [180] corroborated Bredemeier et al.'s observations using STEM and EDX techniques. Deniz et al. [179] suggested that nickel silicide precipitates are involved in degradation and regeneration processes. Jensen et al. [180] reported an enhancement of the LeTID effect with fast-diffusing and highly soluble point defects, such as Cu and Ni. Furthermore, Bredemeier et al. [29] conducted a comparison of the diffusion coefficient of the defect species during the regeneration process, estimated from thickness-dependent lifetime spectroscopy measurements, with data available in the literature. They concluded that the estimated diffusion coefficient, in the range of $5 \pm 2 \times 10^{11}$ cm²s⁻¹ reasonably agrees with that of chemical species like Co, Ni, and H.

Despite the previously mentioned observations, the similarities in the degradation patterns between transition metal-free FZ and Cz wafers, when compared to multicrystalline wafers, raise questions about whether metallic defects are the primary cause of LeTID. A common nonmetallic defect responsible for LeTID exists in Si wafers, regardless of the growth method used. By establishing links between experimental findings, the influence of the firing process on LeTID behavior, and the diffusion of hydrogen during the firing process in PECVD-passivated samples, several research groups have proposed that hydrogen, in conjunction with its interactions with impurities in Si, may serve as defects or precursors to defects associated with LeTID.

4.4.2 Hydrogen as a prime suspect for LeTID

Even though the exact defect physics is still unclear, several postulates support hydrogen as the defect or defect precursor responsible for LeTID. The firing process promotes hydrogen diffusion from the PECVD SiN_X : H layer into the silicon bulk at peak firing temperature above 700°C. As the material cools down, several mechanisms come into play to reduce the bulk recombination of active monoatomic hydrogen. These include the formation of hydrogen dimers, hydrogen-dopant complexes, and other processes [181], as well as the effusion of hydrogen out of the sample [31]. Both the hydrogen dimer and complex act as reservoirs of hydrogen [25]. When subjected to illumination under elevated temperatures, the injection of excess carriers alters the charge state of hydrogen within the defect complex, causing hydrogen to dissociate [181]. Monoatomic hydrogen, in its individual state, exhibits a high propensity for recombination, thus contributing to degradation [158]. Over prolonged periods of exposure to elevated temperatures and continuous light, hydrogen diffuses and becomes trapped at emitter surfaces and within crystallographic defects, ultimately leading to regeneration.

Accurately measuring the concentration of hydrogen in silicon presents a challenge due to limitations in available physical characterization tools. Hydrogen exhibits significant mobility in silicon, even at room temperature, and the presence of hydrogen in ambient conditions can introduce uncertainties in measurements. Nonetheless, numerous studies have explored the factors that influence the quantity of hydrogen diffusing into silicon during the firing process, including parameters such as PECVD dielectric thickness and firing process conditions in relation to the extent of degradation. Vargas et al. [33], Bredemieir et al. [29] and Varshney et al. [34] related hydrogen released from PECVD SiN_X : H film during the firing process with LeTID effect. Figure 4.10 shows the variation in maximum normalized defect density in two sets of multicrystalline samples with resistivity of 1.6 Ω cm and 1.9 Ω cm and the hydrogen fraction released from SiN_X : H layers deposited at 400°C (left) and 420°C (right) after light soaking under elevated temperature.

Jensen et al. [26] related the variation in bulk hydrogen content directly injected into the bulk



Figure 4.10: Maximum normalized defect density as a function of hydrogen fraction released from SiN_X films deposited at 400°C (left) and 420°C (right) in multicrystalline wafers with resistivities of 1.6 Ω cm and 1.9 Ω cm [33].

by microwave-induced hydrogen plasma treatment with the extent of LeTID in multicrystalline silicon samples. Sperber et al. [18] demonstrated that LeTID could occur without the firing process in undiffused p-type FZ samples with as-deposited SiN_X : H film by direct PECVD rather than remote PECVD technique. The degradation behavior is due to the bulk hydrogen injected by the direct PECVD deposition method. Schmidt et al. [14] correlated LeTID-related defect concentration with total bulk hydrogen concentration in FZ silicon wafers, which is in agreement with the observation of Vargas et al. [172] where they related the fraction of hydrogen released from surface SiN_X : H layer with apparent defect density formed during light soaking.

4.4.3 Hydrogen induced degradation

Hydrogen Induced Degradation (HID) occurs when hydrogen migrates between hydrogen reservoirs and gettering centers, passing through recombination-active states. Initially, HID can lead to increased recombination within the bulk [15]. Subsequently, it manifests as surface defects due to hydrogen's attraction to the emitter surface, as observed in previous studies [41, 182]. The defect characteristics of hydrogen-related defects are summarized in Table 3.6 of subsection 3.3. In addition to recombination loss, HID can cause additional resistive loss due to increased Si device's series resistance by modifying the device's contact resistivity [183, 184]. Consequently, the diffusion of hydrogen into Si devices can lead to performance degradation depending on the device's operating conditions and usage duration. The mechanisms concerning the deterioration of bulk, surface, and contact resistance are outlined as follows:

- 1. Bulk Degradation: Hydrogen can induce bulk degradation by interacting with impurities in silicon, forming recombination-active defects like hydrogen-vacancy complexes, carbon-hydrogen-oxygen complexes, metal-hydrogen complexes, and more. Hydrogen can also introduce crystallographic defects by creating hydrogen platelets. Interstitial hydrogen acts as a potent recombination center, introducing deep energy levels in silicon.
- 2. Surface Degradation: Hydrogen has the potential to degrade surface quality by interacting with dopants, which can lead to counter-doping effects. Additionally, it can induce crystallographic damage in the surface region by accumulating hydrogen.
- 3. Alteration of contact resistance: The accumulation of hydrogen beneath contact regions increases contact resistance and, consequently, sheet resistance. This occurs because hydrogen interacts with dopants, forming hydrogen-dopant complexes and acting as a dopant itself. This process generates hydrogen-related interfacial defects, impeding the tunneling of charge carriers.

4.5 Methods for mitigating the impact of LeTID

As LeTID impacts all types of silicon wafers and solar cell architectures used in the mainstream solar industry, several approaches have been put forward to reduce or mitigate its adverse effects. Considering LeTID's reliance on transition metal impurities, employing phosphorous diffusion gettering can play a crucial role in reducing the impact of LeTID [185, 186]. This implies that refining the emitter diffusion profile aids in diminishing the impact of LeTID. Strategies to reduce LeTID can also be crafted by optimizing processes that impact the concentration and diffusion of hydrogen within the sample. These processes encompass fine-tuning the stoichiometry and thickness of the passivation layer, as well as managing the firing profile and firing process parameters, as elaborated in section 4.1. However, it's worth noting that adjustment of these process parameters, as well as altering the thickness of the dielectric film, can impact the optical properties of the film. Increasing the thickness of the dielectric film extends the metal's penetration depth, which can lead to poor contact formation. Therefore, these approaches require process re-optimization when implementing measures to suppress LeTID. Moreover, reducing the thickness of the base material to mitigate LeTID can render cells brittle and negatively impact yield.

Research suggests that the LeTID effect can be effectively reduced by increasing illumination intensity or temperature at a constant ratio of illumination intensity and time or temperature and time [39, 187]. Maischner et al. proposed a method to mitigate LeTID by modifying the cooling ramp during the co-firing process [40]. This adjustment resulted in an improvement in average efficiency reduction from 5.5 % to 1.5% in high-performance multicrystalline Si solar cells and cast monocrystalline cells. Sen et al. suggested incorporating an additional firing step at a temperature of about 400°C to 500°C with a faster belt speed of 1.4 m/min to restore cell stability without affecting contact resistance when operating under light and elevated temperatures [37]. This approach led to a 5% increase in the relative efficiency of p-type mc-Si PERC solar cells. Yli-koski et al. proposed a technique to prevent the subsequent development of LeTID by utilizing extended annealing at a low-temperature range (between 200°C and 300°C) for a duration exceeding 18.5 hours [188]. More recently, Hu et al. proposed a post-processing step that includes a forward current injection method and annealing to suppress LeTID. This method resulted in a relative increase of approximately 0.4% in V_{OC} when current injection and annealing were employed as pre-processing steps in PERC cell fabrication [48].

4.6 Gaps Identified in the Research Related to LeTID

While research has progressed in understanding and mitigating LeTID, several unresolved issues persist in the literature.

- The involvement of hydrogen in LeTID is widely accepted, but the exact defect structure and the physics of the defect mechanism behind LeTID are not fully understood. There is ongoing debate about whether LeTID is primarily due to hydrogen-related defects, metal impurities, or other types of defect complexes.
- Although LeTID has been reported in various silicon materials based on doping and bulk material quality, the LeTID susceptibility of solar cells with differing bulk quality and doping types, fabricated under identical processing conditions, needs to be investigated in detail.
- 3. The impact of screen printing and firing processes on LeTID, particularly concerning hydrogen introduction and redistribution, requires further research. In addition, limited studies exist on on the effects of LeTID on solar cells with varying sheet resistance.

- 4. Since hydrogen diffused from PECVD SiN_X : H passivation layer into the bulk of Si solar cells during the firing process is considered a prime suspect for LeTID, the hydrogen-related defects can be formed at the emitter surface, at the junction, and within the bulk. A comprehensive investigation into the LeTID behavior of different regions within the solar cell architecture needs to be addressed.
- 5. Even though the performance parameter variation due to LeTID has been reported in the literature, the factors influencing the performances and their long-term stability analysis have to be studied.
- 6. While some mitigation techniques (e.g., optimized firing profiles and current injection techniques prior to annealing) have been proposed, their long-term effectiveness and scalability need more validation. In addition, an understanding of the trade off between LeTID mitigation and other performance metrics, such as initial efficiency and cost, is crucial for developing practical solutions.

4.7 Summary

This chapter provides a comprehensive review of the existing literature on the degradation behavior induced by light and elevated temperatures in silicon solar cell devices. The studies conducted have unveiled several factors capable of influencing the severity of LeTID. These factors encompass the firing profile, parameters of the firing process, the dielectric deposition process, the thickness of the dielectric film, and the wafer's thickness. However, it is important to note that the degradation and subsequent regeneration kinetics are primarily determined by injection conditions and temperature.

The chapter also delves into the experimental evidence that supports hydrogen as the underlying cause of LeTID. Additionally, it examines recombination properties and presents a four-state model depicting LeTID and the kinetics of its regeneration. Furthermore, the chapter provides an overview of various strategies devised to mitigate the impact of LeTID. These strategies encompass alterations to the cooling rate within the firing profile, the integration of current injection techniques with annealing processes, and the inclusion of an additional low-temperature firing step during the fabrication of solar cells.

Chapter 5

Characterization Techniques

The chapter covers the foundational operational principles of multiple characterization techniques and the strategies employed for extracting device parameters through these methods. We focus only on the methods used in the thesis.

5.1 Lifetime characterization

Characterizing lifetime is essential for assessing the recombination properties of minority carriers within both the bulk and surface of silicon devices. To determine the minority carrier lifetime values, we employed a Sinton Instruments lifetime tester (WCT 120) based on the QSSPC method. In this method, the test samples are briefly exposed to a Xenon light source, which leads to the generation of excess carriers. Upon deactivation of the light source, these excess carriers undergo recombination, and their concentration decreases exponentially over time. The dynamics of this recombination process can be mathematically represented using the following continuity equation.

$$\frac{\partial \Delta n}{\partial t} = G(t, x) - R(t, x) + \frac{1}{q} \frac{\partial J_n}{\partial x}$$
(5.1)

where G and R represent the generation and recombination rates $(cm^{-3} s^{-1})$ in the sample under test. Δn is the excess carrier density (cm^{-3}) . J_n is the electron current density (A cm⁻²), which can vary spatially due to variations in the generation rate across the sample. q is the electronic charge (C).

Under uniform illumination, $\frac{\partial J_n}{\partial x}$ reduces to zero. Then rewriting recombination rate in terms of

minority carrier lifetime R= $\frac{\Delta n}{\tau_{eff}}$, the continuity equation shown in Eq.5.2 can be expressed as

$$\tau_{\rm eff} = \frac{\Delta n}{G - \frac{\partial \Delta n}{\partial t}}$$
(5.2)

When the light source is turned off (G = 0), the Eq.5.2 gives the transient lifetime

$$\tau_{\text{eff,transient}} = \frac{\Delta n}{\frac{\partial \Delta n}{\partial t}}$$
(5.3)

Under steady-state conditions, $\frac{\partial \Delta n}{\partial t} = 0$, then Eq.5.2 is reduced to a quasi-steady state lifetime.

$$\tau_{\rm eff,QSS} = \frac{\Delta n}{G} \tag{5.4}$$

Eq.5.3 and 5.4 illustrate how the effective lifetime of charge carriers within the sample can be approximated by examining the rate of change in excess carrier concentration and generation rate. These changes in excess carrier concentration influence the sample's conductivity. Eq.5.5 quantifies the conductivity variation in the sample resulting from the fluctuations in excess carrier density.

$$\Delta \sigma = q(\mu_p + \mu_n) \Delta n W \tag{5.5}$$

where μ_n , μ_p represents the mobility of electron and hole in the sample (cm²/Vs), and W is the thickness of the sample (cm). The lifetime tester uses a tuned RF bridge to measure the conductivity change with illumination intensity variation. The tester also measures the illumination intensity using a calibrated reference cell to compute the photo generated current density (J_{ph}, A/cm²) represented by the Eq.5.6.

$$J_{\rm ph} = \frac{q\Delta nW}{\tau_{\rm eff}}$$
(5.6)

Combining Eq.5.5 and 5.6, the effective lifetime of charge carriers can be estimated from the following relation.

$$\tau_{\rm eff} = \frac{\Delta\sigma}{J_{\rm ph}(\mu_{\rm p} + \mu_{\rm n})}$$
(5.7)

The effective lifetime measured by the Sinton lifetime tester consists of bulk and surface components. The bulk lifetime include three components; radiative recombination (τ_{rad} , s), Auger recombination (τ_{Aug} , s) and SRH recombination (τ_{SRH} , s) as discussed in section 2.3. The measured effective lifetime can also be represented in terms of the bulk and surface recombination parameters, as shown in Eq.5.8 for symmetrically passivated samples.

$$\frac{1}{\tau_{\rm eff}} = \frac{1}{\tau_{\rm rad}} + \frac{1}{\tau_{\rm Aug}} + \frac{1}{\tau_{\rm SRH}} + \frac{2S_{\rm eff}}{W}$$
(5.8)

where τ_{rad} , τ_{Aug} , τ_{SRH} represent radiative lifetime, Auger lifetime, and SRH lifetime, respectively, for the sample under test (s). S_{eff} represents the effective surface recombination velocity (cm s⁻¹) and W is the thickness of the sample (cm).

Eq.5.8 can be rewritten by replacing S_{eff} in terms of surface recombination current density $(J_{0S}, A \text{ cm}^{-2})$ at the emitter surface as given in Eq.5.9.

$$\frac{1}{\tau_{\rm eff}} = \frac{1}{\tau_{\rm rad}} + \frac{1}{\tau_{\rm Aug}} + \frac{1}{\tau_{\rm SRH}} + \frac{2J_{0s}(N_{\rm dop} + \Delta n)}{qn_{\rm i}^2 W}$$
(5.9)

 N_{dop} is the doping concentration (cm⁻³), Δn is the excess carrier density (cm⁻³), n_i is the intrinsic carrier density (cm⁻³), and q is the elementary electronic charge (C).

5.2 Photoluminescence imaging

Photoluminescence (PL) imaging is a remarkably rapid non-contact technique for characterizing the spatial distribution of electronic parameters in semiconductor devices. Inside the semiconductors, electron-hole pairs generated through optical absorption can undergo recombination through either a radiative recombination mechanism, a non-radiative mechanism, or a combination of both. The radiative recombination results in the emission of photons equivalent to the bandgap energy known as photoluminescence. The relation in Eq.5.10 represents the PL efficiency.

$$\eta_{\rm PL} = \frac{R_{\rm rad}}{R_{\rm rad} + R_{\rm nrad}}$$
(5.10)

The radiative recombination rate R_{rad} and non radiative recombination rate R_{nrad} (cm⁻³ s⁻¹) are defined as,

$$R_{rad} = \frac{\Delta n}{\tau_{rad}}, R_{nrad} = \frac{\Delta n}{\tau_{nrad}}$$
(5.11)

where Δn is the excess carrier density (cm⁻³), τ_{rad} and τ_{nrad} are radiative and non-radiative lifetime of charge carriers (s). So, the effective lifetime can be written considering radiative and

non radiative recombination parameters, as shown in Eq.5.12.

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{nrad}}}$$
(5.12)

Although radiative recombination is not the predominant process in Si, PL emission through the radiative recombination process can be used to examine the electronic properties of solar cells. The emitted PL signal is captured using an imaging technique with a sensor array. The intensity variation across captured PL images indicates the lifetime variation across the device. The brighter regions in the PL image, exhibiting relatively higher PL intensity, indicate regions with lower recombination activity and relatively longer effective carrier lifetimes. Conversely, the darker regions, distinguished by relatively lower PL counts, correspond to areas with shorter carrier lifetimes. In this thesis, the Lumisolar system from Greateyes is employed for capturing PL images. This system utilizes a set of LED arrays operating at a 660 nm wavelength as an illumination source. To filter the luminescence signal from the illuminated sample, a 960 nm high-pass filter is employed. This filtering ensures that the Si CCD detectors only receive PL emission from the Si devices.

5.3 Photoluminescence Spectroscopy

Photoluminescence Spectroscopy captures photons emitted from a sample when the charge carriers transit from the excited state to the ground state when irradiated by a laser beam. The measured spectrum is used to analyze the characteristics of the material and the impurities present in it. In the thesis, the PL measurement was carried out at room temperature using a customized setup with a 780 nm, 20 mW laser source, and an indium-gallium arsenide (InGaAs) detector. The spectral resolution is obtained by placing a monochromator before the detector. The PL spectrum of a passivated Si sample is shown in Figure 5.3. The spectrum exhibits the PL band of Si centered around 1170 nm at room temperature. This band appears quite broad because of the thermal vibrations of the charge carriers. The sub-bandgap PL signal arises due to the defects within the sample. Specifically, the PL band below 1320 nm is attributed to the intrinsic dislocations within the bulk of the Si material [189]. Impurities such as iron and oxygen contribute to the PL bands observed at 1400 nm and 1500 nm, respectively [190–192].



Figure 5.1: PL spectra of a silicon sample passivated with SiN_X at 300K.

5.4 FTIR Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy is a technique employed to analyze the chemical composition of a sample by examining its vibrational frequencies. This characterization method is known for its ease of operation, speed, accuracy, and sensitivity. During FTIR spectroscopic measurements, the sample is subjected to infrared (IR) radiation, leading to energy absorption by various chemical species within the sample. Each chemical species exhibits atomic vibrations that selectively absorb specific frequencies and energies of IR radiation. The IR spectra transmitted through the sample are detected. Different chemical species have different vibrational characteristics and, hence, different FTIR spectra. Identifying chemical species within the sample is accomplished through the analysis of FTIR spectra, with a particular emphasis on the unique absorbance peaks linked to each chemical species. The data extracted from FTIR spectra, specifically the absorbance peaks and spectral bandwidth, serves as a valuable tool for estimating the concentration of chemical species. In this thesis, the Brucker Vertex 80 FTIR spectroscopic instrument is employed to perform measurements and acquire the FTIR spectra of the samples. For the FTIR analysis, double-side polished <100> Cz - Si wafers with resistivity ranging from 1 - 5 Ω cm and thickness 300 μ m were used. The measurements were conducted in transmission mode at room temperature, involving 64 scans for a single measurement of the FTIR spectra.

5.5 Current- voltage characteristics

The solar cell's performance parameters, such as V_{OC} , J_{SC} , FF, and η are derived from the illuminated J-V characteristics. These J-V measurements are carried out under standard test conditions, with the illumination source closely matching the AM 1.5G spectra and the cell operating at a temperature of 25°C. Figure 5.2 shows the J-V curve of a large area silicon solar cell fabricated at the National Center for Photovoltaic Research and Education (NCPRE) in black solid lines. The points corresponding to V_{OC} (V) and J_{SC} (mA cm⁻²) are marked in Figure 5.2. The power-voltage characteristic is also depicted in Figure 5.2, using a red solid line to show the cell's maximum power point P_{max} (W cm⁻²). η and FF values are computed from P_{max} using Eq.5.13 as discussed in section 2.2.

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}}$$
(5.13)

where P_{in} is the irradiance incident on the solar cell and is equal to 0.1 W cm⁻² under STC of AM 1,5G spectra and 25°C.

$$FF = \frac{P_{max}}{V_{OC}J_{SC}}$$
(5.14)

In this thesis, a class AAA solar simulator from Abet Technologies is used for measuring the



Figure 5.2: J-V (black solid line) and P-V (red solid line) characteristics of a sample solar cell fabricated at NCPRE measured using a AAA class solar simulator from Abet Technologies.

illuminated J-V characteristics of the solar cells. The solar cell's series resistance (R_s , Ω cm²) is extracted from the J-V curves measured at illumination intensity of 1 sun and 0.1 sun using the Bowden method [193]. The shunt resistance (R_{sh} , Ω cm²) is measured using dark IV characteristics in the voltage range -50mV to +50mV.

The Suns Voc measurement system from Sinton Instruments measures the illuminated J-V characteristics under open circuit conditions. The system uses two diode equivalent model of solar cells for extracting the recombination current density components J_{01} and J_{02} [194, 195]. J_{02} (A cm⁻²) accounts for the recombination within the depletion region. J_{01} (A cm⁻²) accounts for the recombination within the rest of the solar cell regions, which include bulk, front surface, and rear surface.

In this thesis, FF loss analysis due to recombination and resistive components is implemented using the method suggested by Khanna et al. [196]. The method iterates the two-diode model J-V equation for the known parameters like V_{OC}, J_{SC}, R_s, R_{sh}, V_{max} and J_{max}. It provides a quantitative estimate of the absolute loss in FF in due to recombination in space charge region (Δ FF(J₀₂)), recombination in the rest of solar cell (Δ FF(J₀₁)), series resistance (Δ FF(R_s)), and shunt resistance (Δ FF(R_{sh})) [196]. The electrical equivalent of a p-n junction solar cell used for FF loss analysis is shown in Figure 5.3,



Figure 5.3: The electrical equivalent of a p-n junction solar cell used for FF loss analysis.

$$V_{\text{max}} = V_0 - J_{\text{max}} R_s \tag{5.15}$$

$$J_{\text{max}} = J_0 - \frac{V_{\text{max}} + J_{\text{max}} R_s}{R_{\text{sh}}}$$
(5.16)

The V_0 and J_0 represent the output voltage (V) and current density (mA cm⁻²) without considering the R_s effect. The product V_0J_0 can be determined from Eq.5.15 and 5.16 and normalized

with $V_{OC}J_{SC}$ to obtain the Eq.5.17

$$\frac{V_0 J_0}{V_{SC} J_{SC}} = \frac{V_{max} J_{max}}{V_{SC} J_{SC}} + \frac{J_{max}^2 R_s}{V_{SC} J_{SC}} + \frac{(V_{max} + J_{max} R_s)^2}{R_{sh} V_{SC} J_{SC}}$$

$$FF_0 = FF + \frac{J_{max}^2 R_s}{V_{SC} J_{SC}} + \frac{(V_{max} + J_{max} R_s)^2}{R_{sh} V_{SC} J_{SC}}$$
(5.17)

Eq.5.17 gives the relation between the fill factor of the resistance-free cell (FF₀) and the fill factor of the real cell (FF). The second and third terms in Eq.5.17 represent FF loss due to R_s (ΔFF_{Rs}) and FF loss due to R_{sh} (ΔFF_{Rsh}) respectively.

The recombination current component J_{01} limited FF (FF_{J01}) can be computed using Lambert W-Function without considering R_s , R_{sh} and J_{02} [196].

$$FF_{J_{01}} = \frac{kT}{qV_{OC}} \frac{(W[z]-1)^2 exp(W[z]-1)}{exp(qV_{OC}/kT) - 1}$$

$$z = 1 + exp(qV_{OC}/kT)$$
(5.18)

The FF loss due to the recombination component J_{02} ($\Delta FF_{J_{02}}$) is calculated from the difference between the FF limit due to J_{01} , (FF_{J₀₁}) and resistance-free fill factor, (FF₀).

$$\Delta FF_{J_{02}} = FF_{J_{01}} - FF_0 \tag{5.19}$$

5.6 Quantum efficiency measurement

Quantum efficiency (QE) is the ratio of the number of carriers collected by the solar cell to the number of photons of a given energy incident on the solar cell. It is used to characterize recombination losses at different wavelength regions and optical losses of the solar cells. QE is usually expressed as external (EQE) or internal (IQE). EQE measurements consider all the photons incident on the sample, including optical local losses such as photons reflected by the front surface and transmitted through the sample. However, IQE measurements consider the actual number of photons absorbed by the sample surface instead of the total number of photons incident on the sample. Hence IQE measurement does not take into account optical losses. The EQE and IQE are related as follows

$$IQE = \frac{EQE}{1 - R' - T'}$$
 (5.20)

Where R' and T' represent the reflection and transmission losses in solar cells. The transmission loss is ≈ 0 , for the solar cells with full Al coverage on the back surface. Hence, Eq.5.20 can be modified as follows,

$$IQE = \frac{EQE}{1 - R'}$$
(5.21)

The EQE measurement is done by illuminating the solar cell with different wavelengths and measuring the short circuit current through the contacted cell region. The reflectance from the illuminated spot is also measured to calculate IQE.



Figure 5.4: EQE (black solid line) and Reflection (red solid line) curve of a sample solar cell fabricated at NCPRE measured using Bentham PVE300 tool.

In this thesis, EQE and reflectance were measured using the PVE 300 tool from Benthem Instruments. The system uses a dual light source (xenon and halogen) combined with a monochromator for illuminating the sample surface in the wavelength ranging from 300 nm to 1100 nm. The illuminated area of the sample's surface is 1mm x 5mm. Figure 5.4 shows EQE and R curves of a c-Si solar cell fabricated at NCPRE. The EQE curve shows a sudden fall in the wavelength range 300 nm to 500 nm and 900 nm to 1100 due to surface recombination of charge carriers at the front and rear surfaces, respectively. The reduction in EQE in the midwavelength range indicates the recombination loss within the bulk of the solar cell. The spot QE measurement may not effectively represent the solar cells, especially in the case of multicrystalline Si solar cells with spatial nonuniformities. Light-induced beam current (LBIC) method is used to characterize the spatial variations in EQE of the entire sample area at different penetration depths. LBIC system also provides the reflection map at the corresponding sample depth to estimate IQE as per Eq.5.21.



Figure 5.5: Penetration depth in a silicon sample as a function of wavelength at 300 K [197].

LBIC system from Semilab WT-2000PVN is used in this study. The system uses four operating wavelengths: 407 nm, 658 nm, 877 nm, and 986 nm., The absorption depth corresponding to the wavelength 407 nm, 658 nm, 877 nm, and 984 nm in silicon is about 120 nm, 3.5 μ m, 20 μ m, and 100 μ m at 300 K, as shown in Figure 5.5 [197]. The spectral response of the emitter (at 407 nm), near-to-space charge region (at 658 nm), bulk (at 877 nm), and deep bulk (at 984 nm) was covered during the LBIC analysis.
Chapter 6

Characterization of Degradation in PECVD Silicon Nitride Passivated Cz Silicon Wafers at Normal Ambient Outdoor Conditions

A thorough investigation was conducted to examine the degradation behavior of both p-type and n-type silicon samples produced using the Cz growth method and passivated with PECVD SiNx: H when exposed to outdoor light under typical ambient conditions. This study employed a combination of electrical and optical techniques to evaluate the degradation effects. Changes in minority carrier lifetime were assessed for both p-type and n-type samples before and after exposure to light using lifetime measurement and PL imaging. Furthermore, alterations in the number of defects present in both n-type and p-type samples were quantified based on variations in lifetime. The experimental results indicate that both p-type and n-type samples experience a decline in performance when subjected to light and heat in regular outdoor conditions. Additionally, FTIR and PL spectroscopic analyses were carried out to identify the chemical species responsible for this degradation. The spectroscopic investigation reveals that the degradation observed in PECVD SiN_X : H passivated p-type and n-type silicon samples is primarily linked to hydrogen and oxygen-related defects in typical outdoor ambient conditions.

6.1 Experimental methods

6.1.1 Sample preparation and characterization

Both p-type and n-type double-side polished wafers grown by the Cz process with a resistivity of 1-5 Ω cm and 300 µm thickness were used for all the experiments. Interstitial oxygen concentration in the samples was estimated as per ASTM F1188-00 standard using FTIR measurements as described in Appendix B. It was found to be 8 x 10¹⁷ cm⁻³ and 5 x 10¹⁷ cm⁻³ for p-type and n-type samples respectively. Before SiN_X : H passivation layer deposition, the samples were cleaned using the RCA cleaning procedure. SiN_X : H passivation layer is deposited on both samples' sides using the Oxford Instruments Plasmalab PECVD system. The deposited dielectric film's thickness and refractive index (RI) were measured using a spectroscopic ellipsometer SE 2000 from Semilab. The thickness and RI (at 630 nm) of the deposited film were 104 nm and 2.1 nm, respectively. Post-deposition annealing of the samples was carried out at a peak temperature of 770°C for 30 seconds using a rapid thermal processing (RTP) system from Allwin21 Corp. The schematic structure of the test structure is shown in Figure 6.1 (a).



Figure 6.1: (a). A schematic of the test structure used in the experiment. (b). A photograph of the experimental setup during the light soaking in outdoor conditions.

The samples were enclosed inside solar glasses to avoid environmental contamination during light-soaking experiments. photograph of the experimental setup for the light soaking is shown in Figure 6.1 (b). Light soaking was done outdoors at the NCPRE PV module monitoring station in Mumbai, India, in January, February, and March of 2020. Light intensity during light soaking was measured using a pyranometer from Eppley in the spectral range of 295 nm to 2800 nm. The effective minority carrier lifetime of the samples was measured using the QSSPC Sinton WCT 120 lifetime tester. Band-to-band photoluminescence emission from the samples was measured using the Lumisolar tool from Greateyes. Various chemical species in the samples before and after light soaking were analyzed using Brucker Vertex 80 FTIR spectroscopic instrument. Spectroscopic PL measurement was carried out at room temperature using a customized setup with a 780 nm laser source and an indium-gallium arsenide (InGaAs) detector.

6.2 Results and discussion

6.2.1 Electrical characterization



Figure 6.2: Variation in average solar insolation between 10.00 am and 4.00 pm measured at Mumbai, India, during the period from 29 January 2020 to 06 March 2020.

The samples were subjected to light soaking directly under the sun in outdoor conditions from 29 January 2020 to 06 March 2020, resulting in cumulative solar insolation of 95.7 kWh/m². Solar irradiance on the samples during each day (from 10.00 am to 4 .00 pm) of light soaking was measured, and the solar insolation was found to vary between 4.56 kWh/m² and 5.60 kWh/m² as shown in Figure 6.1. Daily average ambient temperature during 0.00 am to 4 .00 pm was in the range from 33°C to 39°C. Variation in solar irradiance and temperature from 10.00 am to 4.00 pm of each day of light soaking is provided in the supplementary information in Appendix A. The maximum, average, and minimum values of humidity at Mumbai, India, are also provided as supplementary information in Appendix A. Humidity data provided was not recorded at the experiment site but at a location 7.55 km away from the experiment site. The samples were kept inside a laboratory during the intervals between successive light-soaking periods. The samples were kept inside a laboratory during the intervals between successive light-soaking light-soaking periods. Light soaking was not done on some days due to certain adverse climatic conditions, as indicated by break lines in Figure 6.2.



Figure 6.3: Effective minority carrier lifetime variation in p-type (top) and n-type (bottom) samples after light soaking with a cumulative solar insolation up to 95.7 kWh/m².



Figure 6.4: Si band to band PL intensity of p-type (top) and n-type (bottom) sample before (left) and after (right) light soaking with a cumulative solar insolation of 95.7 kWh/m².

The variations in effective minority carrier lifetime for p-type and n-type samples during light soaking for a period (t) of up to 111 h with cumulative solar insolation (E) of up to 95.7 kWh/m² are shown in Figure 6.3. Decreases in minority carrier lifetime from 84 μ s to 35 μ s and from 135 μ s to 93 μ s were observed for p-type and n-type samples, respectively. These lifetime values refer to effective minority carrier lifetime measured at excess minority carrier injection density (Δ n) of 10 ¹⁵ cm ⁻³. The reduction in effective lifetime as seen in Figure 6.3 indicates that light soaking introduces defects in both n-type and p-type samples.

The effective lifetime of charge carriers is determined by various recombination mechanisms such as Auger recombination, radiative recombination, and SRH recombination. SRH recombination accounts for defect-assisted recombination in semiconductors. As defect concentration during light soaking increases, the SRH recombination rate increases and the effective lifetime of charge carriers reduces. Hence, the difference in the effective lifetime of charge carriers before and after light soaking is considered as a measure of the apparent density of defects formed during light soaking of the samples. It is reported that light soaking of p-type samples leads to the formation of BO defects [69–71, 143, 145, 198, 199]. Since degradation is observed in both n-type and p-type samples, we can infer that some other forms of defects are also present besides the boron oxygen defects.

The measured band-to-band PL intensity variations in p-type and n-type samples are shown in Figure 6.4. After light soaking, a significant reduction in PL intensity was observed throughout the sample area. The reduction in PL intensity inside the region marked by the blue circle (which corresponds to the sensor region of the Sinton lifetime tester) was consistent with the change in measured minority carrier lifetime for both types of samples.

6.2.1.1 Estimation of apparent defect density

The apparent light-induced defect concentration was calculated from the effective minority carrier lifetime curves of the samples. The apparent normalized defect density (N_T^*) was calculated using the following relation [176],

$$N_{\rm T}^* = \sigma_{\rm p/n} v_{\rm th} N_{\rm T} = \frac{1}{\tau_{\rm d}} - \frac{1}{\tau_0}$$
(6.1)

where $\sigma_{p/n}$ is the electron/hole capture cross sections of the defect in cm², v_{th} is the thermal velocity (cm s⁻¹), N_T is the defect density (cm⁻³), τ_0 is the initial effective minority carrier lifetime of the samples before light soaking (s) and τ_d is the effective minority carrier lifetime of the degraded samples after light soaking (s). The variation in N_T^{*} as a function of cumulative solar insolation on the sample is shown in Figure 6.5. The graph shows an increase in N_T^{*} in both p-type and n-type samples for cumulative solar insolation up to 95.7 kWh/m². After solar insolation of 95.7 kWh/m², N_T^{*} increased from $3.39 \times 10^{-3} \ \mu s^{-1}$ to $1.68 \times 10^{-2} \ \mu s^{-1}$ in p-type samples and from $3.42 \times 10^{-4} \ \mu s^{-1}$ to $3.46 \times 10^{-3} \ \mu s^{-1}$ in n-type samples. Interestingly, the maximum change in N_T^{*} was observed after light soaking for 73 h, which corresponds to cumulative incident energy of 63 kWh/m². This trend was consistent for both n-type and p-type samples. Further, beyond 73 h of light soaking, N_T^{*} showed a near-saturation trend.

6.2.1.2 Estimation of surface recombination current density and bulk lifetime

Further, the surface recombination current density $(J_{0s}, A/cm^2)$ and bulk lifetime (τ_B, s) of the non-diffused samples were estimated to separate surface and bulk degradation. J_{0s} was estimated from the inverse Auger corrected carrier lifetime $(\tau_{Aug_corrected}, s)$ obtained from Sinton lifetime tester using Eq.6.2 and 6.3 [62, 200, 201].

$$\frac{1}{\tau_{\text{Augercorrected}}} = \frac{1}{\tau_{\text{B}}} + \frac{2S_{\text{eff}}}{W}$$
(6.2)



Figure 6.5: Apparent normalized defect density variation in p-type and n-type samples as a function of cumulative solar insolation.

where W is the thickness of the sample (cm). For non-diffused samples, excess carrier injection dependent surface recombination velocity (S_{eff} , cm s⁻¹) given in Eq.6.2 can be expressed in terms of J_{0s} , as proposed by McIntosh and Black [202].

$$S_{\text{eff}} = \frac{J_{0s}(N_{\text{dop}} + \Delta n)}{qn_i^2}$$
(6.3)

where N_{dop} is the doping density (cm⁻³), n_i is the intrinsic carrier density (cm⁻³), and q is the elemental charge of carriers (C). However, the above analysis was limited to n-type samples as the inverse Auger corrected lifetime curves of p-type samples were not extending to linear high injection regime ($\Delta n > 4 \times 10^{15}$ cm⁻³) for all light soaking conditions. A representative inverse Auger corrected lifetime curve of light soaked (with solar insolation of 95.75 kWh/m²) n-type sample used for estimating J_{0s} was shown in the inset of Figure 6.6. Further, τ_B shown in Figure 6.6 was estimated using Eq.6.2 and 6.3 at $\Delta n = 10^{15}$ cm⁻³.

Both J_{0s} and τ_B were found to be degraded after light soaking as shown in Figure 6.6. The increase in J_{0s} was from 259 fA/cm² to 502 fA/cm² while the reduction in τ_B was from 136 µs to 93 µs in n-type samples for solar insolation of 95.7 kWh/m². The reduction in



Figure 6.6: Variation of surface recombination current density, J_{0s} and bulk lifetime, τ_B in n-type samples as function of cumulative solar insolation. Inset shows a representative inverse Auger corrected lifetime curve of the light-soaked sample when subjected to solar insolation of 95.75 kWh/m². The slope of the green line (linear fit generated for high injection regime and extrapolated to the y-axis) was used to estimate the J_{0s} .

bulk lifetime is in contradiction with the previous studies carried out on non-diffused Cz-grown n-type samples under controlled laboratory conditions. Chen et al.[21, 22] have reported an increase in defect concentration due to surface degradation in non-diffused n-type samples. They observed an increase in defect concentration during both light soaking at an elevated temperature of 75°C and dark annealing at 172°C but with a stable bulk lifetime. However, their studies were restricted to electrical characterization techniques such as minority carrier lifetime measurements for analyzing degradation in silicon samples. In this study, we further exploited the optical characterization techniques: FTIR and PL spectroscopy to identify various chemical species involved in light-induced degradation mechanisms.

6.2.2 Optical characterization

6.2.2.1 FTIR Spectroscopy

Chemical species responsible for the increase in defect concentration in samples after light soaking with solar insolation of 63 kWh/m² were characterized using FTIR in the spectral



Figure 6.7: FTIR spectra of p-type (left) and n-type (right) samples before and after light soaking for 63 kWh/m².

range of 400 cm^{-1} to 3500 cm^{-1} at the center of samples.

The normalized absorbance spectra for p-type and n-type, before and after light soaking, are shown in Figure 6.7. The normalization was done with respect to the vibrational peak of the Si-Si bond at 611 cm^{-1} . Deconvolution of FTIR spectra was done for the detailed investigation of compositional changes in various chemical species within the samples before and after light soaking. Deconvolution was carried out using OrginPro 2020. The peaks identified by the second derivative method were further smoothed by Savitsky–Golay filtering. The peak fitting was then performed using Gaussian Modelling and the fitting procedure was stopped when the reduced chi-square was less than 1×10^{-6} . Figures 6.8 and 6.9 show deconvoluted FTIR spectra of both p-type and n-type samples, respectively, in the wavenumber range from 700 cm⁻¹ to 1200 cm^{-1} .

Three absorbance peaks were observed in the range 750 cm⁻¹ to 1100 cm⁻¹ due to stretching vibrations of SiN bond [203–206]. The lowest peak v_1 corresponds to the asymmetrical stretching vibrations of the Si-N bond with low nitrogen content. It is formed when nitrogen atoms incorporated into the Si matrix are bonded to the neighboring Si atoms (SiN_x). The peak v_2 corresponds to the chemical bond when one of the Si in SiN_x bonds with vibrational frequency v_1 is replaced by hydrogen (SiN_yH_a). The third peak v_3 corresponds to the vibrations of the nitrogen-rich Si-N bond (SiN_zH_b). The vibrational frequency corresponding to v_3 can extend up to 1100 cm⁻¹ depending upon the nitrogen content of the chemical species [207].

The vibrational peak v_4 at 1108 cm⁻¹ is due to interstitial oxygen atoms in silicon (SiO_{2i})



Figure 6.8: Measured and deconvoluted FTIR spectra for p-type before (left) and after (right) light soaking for 63 kWh/m².



Figure 6.9: Measured and deconvoluted FTIR spectra for n-type before (left) and after (right) light soaking for 63 kWh/m².

[208, 209], which are incorporated into the silicon matrix during the crystal growth process. The peak v_5 at 732 cm⁻¹ is due to oxygen thermal donors (TD). TD is formed during temperature treatment of the Si samples in the range 350°C to 500°C and appears as small agglomerates of oxygen in Si matrix (SiO_n) [210, 211]. But annihilation of TD is reported when annealing of the samples is done at 700°C for a few minutes [212]. In this work, the existence of oxygen-related TD vibrational peak at 732 cm⁻¹ is observed even after 770°C peak temperature post-annealing for 30 seconds. In Figures 6.8 and 6.9, the measured data is shown in black dots, and the cumulative fit for Gaussian components is shown in solid black lines. Gaussian fit corresponding

to peaks v_1 , v_2 , v_3 , v_4 , and v_5 are represented in solid red, green, blue, purple, and orange lines, respectively. A peak v_6 at 2168 cm⁻¹ in PECVD deposited SiN_X : H samples as shown in Figure 6.10 is due to stretching vibration of Si-H bond [213]. Integrated absorbance as a measure of bond density is analyzed for various chemical species and is summarized in Table 6.2.2.1.



Figure 6.10: Measured FTIR spectra Si – H bond for p-type (left) and n-type (right) sample before and after light soaking for 63 kWh/m².

Table 6.1: Integrated absorbance intensities for the Gaussian components before and after light soaking for p-type and n-type samples.

Integrated	<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃	v_4	<i>v</i> ₅	v ₆
Absorbance	cm ⁻¹	cm^{-1}	cm ⁻¹	cm^{-1}	cm^{-1}	cm ⁻¹
	SiN _x	SiN _y H _a	SiN _z H _b	SiO _{2i}	SiOn	SiH _m
p-type before	104.2	124.2	103.4	16.4	13.9	13.8
p-type after	157.4	38.6	126.0	14.7	09.5	12.7
n-type before	107.3	144.0	172.0	12.2	13.7	13.5
n-type after	167.2	26.0	99.8	06.2	04.4	08.4

The integrated absorbance of Gaussian components corresponding to vibrational frequencies v_2 , v_3 , v_4 , v_5 , and v_6 were reduced after light soaking in n-type samples. The relative reduction (with respect to before light soaking) in integrated absorbance intensities were 81.92%, 41.97%, 49.34%, 67.8% and 37.78%, respectively for chemical species corresponding to v_2 , v_3 , v_4 , v_5 and v_6 . In the case of p-type samples, the absorbance intensities of the chemical species with vibrational peaks v_2 , v_4 , v_5 , and v_6 only were reduced. The relative reduction in integrated absorbance intensities were 68.9%, 10.3%, 31.6%, and 7.9%. This indicates that the relative reduction in integrated absorbance intensities of the chemical species SiN_yH_a , SiN_zH_b , SiO_{2i} , SiO_n and SiH_m is more in the case of n-type samples than in p-type samples. The reduction in chemical species such as SiN_x , SiN_yH_a , SiN_zH_b and SiH_m associated with PECVD SiN_x : H film correlates to the degradation in surface passivation as quantified by an increase in surface recombination current density. Similarly, decreases in the concentration of chemical species such as SiO_{2i} and SiO_n were related to changes in the bulk of the samples.

A reduction in the integrated absorbance intensity of a chemical species indicates a reduction in the concentration of that chemical species. The FTIR measurements of the samples reveal that the concentration of chemical species containing hydrogen and oxygen reduced after light soaking under outdoor conditions. For instance, the initial measured hydrogen concentration in the samples was $2 \pm 0.2 \times 10^{22}$ cm⁻³, which is in agreement with the previous report [206, 214, 215]. After light soaking, the hydrogen concentration in the samples was reduced to $1.4 \pm 0.42 \times 10^{22}$ cm⁻³. The reduction in the concentration of hydrogen and oxygen-related chemical species indicates that hydrogen and oxygen are released from the chemical bonds and then combined with other chemical species, forming new defect species during exposure to light and heat, especially for n-type samples. These findings were also supported by experimental studies carried out by Tokuda et al. [216] and Markevicha et al. [217]. Tokuda et al. [216] reported light-induced transformation of hydrogen-related electron traps in n-type Cz samples. Markevicha and Suezawa [217] reported the formation of oxygen-hydrogen (O-H) complex in Cz-grown silicon samples in the temperature range 30°C to 150°C. The configuration and the charge state of defects (which depends upon the position of the Fermi level) may change during illumination/heat by injection of minority carriers. The excess minority carriers generated by external excitation are captured by the defects. The defects are then transformed into a new defect state. After the removal of external excitation, the defects can come back to a minimum energy configuration. The charged defect species can also combine with other chemical species within the sample resulting in an increase in defect concentration and a reduction in minority carrier lifetime.

6.2.2.2 Luminescence spectroscopy

To the best of our knowledge, the light-induced degradation in the bulk of Cz-grown n-type wafers due to oxygen-related species has not been reported previously. Hence, PL spectroscopy was used to confirm the changes in oxygen-related species in n-type samples. Spectroscopic



Figure 6.11: Normalized PL spectra (denoised) before and after light soaking for n-type samples. The inset shows the measured PL spectra of the sample.

PL of n-type samples in the wavelength range from 950 nm to 1540 nm was studied before and after light soaking. Wavelet-based denoising followed by normalization with respect to the maximum PL intensity at 1200 nm was applied to the measured PL spectra (shown in the inset of Figure 6.11) to obtain the PL spectra shown in Figure 6.11. The defect-related PL band below 1320 nm is due to the intrinsic dislocations within Si bulk [189]. In contrast, the sub-bandgap PL in the range 1400 nm to 1570 nm is due to the defects and impurities around the dislocations [218]. One of the components contributing to the PL band nearer to 1500 nm is silicon-oxygen species in the sample [189–192, 218]. Figure 6.9 indicates that the concentration of silicon-oxygen species within the samples was reduced marginally, which is in agreement with the FTIR spectroscopic observations of change in silicon-oxygen bonds. Reduction in silicon-oxygen defect in the sample is transformed into some other form of defect after light soaking. These defects are responsible for bulk degradation, which resulted in the reduction of bulk lifetime, as shown in Figure 6.5.

6.2.3 Influence of SiN_X : H deposition on hydrogen and oxygen related defect in Si wafers

Since the defect precursors are developed in the Si samples during dielectric deposition, the chemical species variations, especially oxygen and hydrogen-related defects in Si samples during the dielectric film deposition process, were studied using FTIR spectroscopy. Hydrogen-related defect species introduced in the Si samples after SiN : H dielectric film deposition, as evident from the FTIR spectroscopic measurement, is shown in Figure 6.12. The FTIR peak at 2160 cm^{-1} corresponds to SiH defects in the sample.



Figure 6.12: Normalized absorbance spectra showing Si_H vibrational peak at 2160 cm⁻¹ (a) in p-type (a) and (b) in n-type Si wafers before and after PECVD SiN_X : H dielectric film deposition process.

The variation in the oxygen-related vibrational peak in the bulk of silicon samples before and after PECVD SiN_X : H film deposition is shown in Figure 6.13 and Figure 6.14 for p-type and n-type respectively. Prior to the measurement, the deposited SiN_X layer was etched using HF : HNO₃ Solution in order to analyze variation in oxygen peak in bulk Si. The native oxide formed on the sample surface after the etching process was removed by dipping in HF solution. An increase in the vibrational peaks of oxygen TD's at 746 cm⁻¹ (v5)and SiO_{2i} at 1107 cm⁻¹ (v4)is observed in both p-type and n-type samples passivated with SiN_X : H film as shown in Figure 6.13 and Figure 6.14. The increase in oxygen-related vibrational peaks can be due to the release of oxygen from substitutional sites and their diffusion to interstitial sites during dielectric deposition and subsequent annealing process.

In the case of n-type samples, a slight increase in vibrational peak at 818 cm⁻¹ ((v7)) corresponding to oxygen-vacancy complex is observed along with the vibrational peaks of TD at 736



Figure 6.13: Normalized absorbance spectra showing oxygen related vibrational peak in p-type Si wafer before and after PECVD SiN_X : H dielectric film deposition process.

 cm^{-1} and SiO_{2i} at 1107 cm^{-1} as evident from Figure 6.14. However, no such change is evident in p-type samples after SiN_X : H deposition, as depicted in Figure 6.13. In addition, the concentration of all of the oxygen-related chemical species, particularly SiO_{2i} , is higher in n-type samples, as inferred from the vibrational peaks in Figure 6.14. As a result of these variations, the behavior of n-type Si samples during light soaking differs from that of the p-type sample.

6.2.4 Defect analysis using linearized SRH statistics

The SRH statistics commonly depicted in Eq.2.28 correlate the minority carrier lifetime due to SRH with the excess concentration of minority carriers, denoted as Δn for electrons and Δp for holes. The equation for the minority carrier lifetime can expressed as a linear function of the ratio of excess carrier concentration to the total carrier concentrations. In p-type material, the electron lifetime τ_{eff} is expressed as a linear function of the ratio of the total electron



Figure 6.14: Normalized absorbance spectra showing oxygen related vibrational peak in n-type Si wafer before and after PECVD SiN_X : H dielectric film deposition process

concentration to the total hole concentration as shown in Eq.6.4.

$$\tau_{\rm SRH} = \frac{1}{\alpha_{\rm n} N_{\rm T}} \left(1 + Q \frac{n_1}{p_0} + \frac{p_1}{p_0} + X(Q - Q \frac{n_1}{p_0} - \frac{p_1}{p_0}) \right)$$
(6.4)

where $X = \frac{n}{p}$ and $Q = \frac{\sigma_n}{\sigma_p}$. σ_n and σ_p capture the cross-section of the defects for electrons and holes, respectively. p_1 and n_1 are the SRH density terms defined in Eq. ??.

An equation analogous to Eq.6.4 for the hole lifetime in n-type material can also be expressed as given in Eq.6.5.

$$\tau_{\rm SRH} = \frac{1}{\alpha_{\rm p} N_{\rm T}} \left(1 + \frac{n_1}{n_0} + \frac{p_1}{Qn_0} + Y(\frac{1}{Q} - \frac{n_1}{n_0} - \frac{p_1}{Qn_0}) \right)$$
(6.5)

where $Y = \frac{p}{n}$

The plot of carrier lifetime as a function of X in p-type (Y in n-type) is linear for a single defect level.

In the p-type case, SRH parameters can be extracted by taking the derivative of Eq.6.4 with respect to X and dividing this by the high injection limit SRH lifetime at $X \rightarrow 1$.

$$\tau_{\text{SRH}(X\to1)} = \frac{1+Q}{\alpha_{\text{n}}N_{\text{T}}}$$
(6.6)

$$\frac{d\tau_{SRH}}{dX} = \frac{1}{\alpha_{n}N_{T}}(Q - \frac{Qn_{1} + p_{1}}{p_{0}})$$
(6.7)

$$\frac{\frac{d\tau_{SRH}}{dX}}{\tau_{SRH(x\to1)}} = \frac{Q}{1+Q} - \frac{Qn_1 + p_1}{(Q+1)p_0}$$
(6.8)

In the n-type case, SRH parameters can be extracted by taking the derivative of Eq.6.4 with respect to Y and dividing this by the high injection limit SRH lifetime at Y-> 1.

$$\tau_{\text{SRH}(Y\to1)} = \frac{1}{\alpha_{\text{p}}N_{\text{T}}} \left(1 + \frac{1}{Q}\right)$$
(6.9)

$$\frac{\mathrm{d}\tau_{\mathrm{SRH}}}{\mathrm{dY}} = \frac{1}{\alpha_{\mathrm{p}}\mathrm{N}_{\mathrm{T}}} \left(\frac{1}{\mathrm{Q}} - \frac{\mathrm{n}_{1}}{\mathrm{n}_{0}} - \frac{\mathrm{p}_{1}}{\mathrm{Q}\mathrm{n}_{0}}\right) \tag{6.10}$$

$$\frac{\frac{d\tau_{\text{SRH}}}{dX}}{\tau_{\text{SRH}(Y\to1)}} = \frac{1}{1+Q} - \frac{Qn_1 + p_1}{(Q+1)n_0}$$
(6.11)

The SRH lifetime of the sample due to the defects created after the light soaking can be measured from the difference in lifetime before and after light soaking. The linearized τ_{SRH} plot for p-type and n-type samples is shown in Figures 6.15 and 6.16. The plots can be represented as a linear combination of two linearized SRH plots corresponding to two defects with different characteristics. This indicates the possibility that two types of defects (defect 1 and defect 2) are responsible for the degradation behavior of the sample after light soaking, as shown in Figure 6.15 and 6.16. The defect's characteristics, such as the capture cross-section ratio of the defects in both types of samples, are estimated using the linearized SRH statistics as given in Eq.6.11. Since BO LID is a well-known defect reported in p-type Si, the Q value for defects is estimated using the BO defect energy levels at $E_C - (0.41 \pm 0.02)$ eV and at $E_V + (0.26 \pm 0.02)$ eV as reported in Niewelt et al. [70, 71]. The Q value estimated for defect 2 (shown in Figure 6.15) when the defect level is at $E_C - (0.41 \pm 0.02)$ is 7.52 ± 0.18, which is comparable with that of BO defect [70, 71]. The Q values of defects, possibly due to hydrogen-related defects with unknown energy level positions, are estimated by assuming the defects are located at the mid-band gap in



Figure 6.15: SRH lifetime versus X=n/p for p-type samples after light soaking of 111 h.



Figure 6.16: SRH lifetime versus Y = p/n for n-type samples after light soaking of 111 h.

the p-type and n-type samples. The Q value for defect 1 in p-type samples is 2.12. In the case of n-type samples, the defects formed during light soaking have Q values different from those of p-type samples. The estimated Q value is 0.69 and 2.85 for defect 1 and defect 2, respectively, in n-type samples. Most of the research on HID has focused on p-type samples subjected

Samples	Defects	Defect Energy level	Ration of cap-
		(eV)	ture Cross sec-
			tion
p-type	Defect1	$E_T = E_i$	2.12
	Defect2	$E_{\rm T} = E_{\rm C} \pm 0.41[70, 71]$	7.79
n-type	Defect1	$E_T = E_i$	0.69
	Defect2	$E_{T} = E_{i}$	2.85

Table 6.2: Defect parameters for p-type and n-type samples.

to light soaking under controlled laboratory conditions, such as halogen lamps and hot plate annealing [10-21]. Consistent with these studies, the experimental results in this study also showed degradation when exposed to light and heat under normal ambient conditions. Chen et al. [22-23] recently investigated HID behavior in non-diffused Cz grown n-type samples with PECVD SiNx:H layers subjected to light soaking (0.96 kW/m² halogen lamp) at elevated temperatures (75°C and 172°C on a hot plate). They reported an increase in defect concentration due to surface degradation in non-diffused n-type samples, although the bulk lifetime remained stable. In contrast, studies by Kang et al. observed degradation followed by recovery behavior in n-type samples at 140°C. Previous studies were limited to electrical characterization techniques, such as minority carrier lifetime measurements, to analyze degradation in silicon samples due to light and heat.

6.2.5 Comparison of Results in this work with existing literature

Most of the research on hydrogen-induced degradation has focused on p-type samples subjected to light soaking under controlled laboratory conditions, using methods such as halogen lamps and hot plate annealing [18, 29, 33, 34, 36, 38, 41, 162, 163, 183]. These studies primarily employed only electrical characterization techniques, such as minority carrier lifetime measurements, to analyze the degradation in silicon samples due to light and heat. Consistent with previous studies, the experimental results in this study also showed degradation without any recovery when exposed to light and heat under normal ambient conditions. Chen et al. [21, 22]

recently investigated HID behavior in non-diffused Cz grown n-type samples with PECVD SiNx : H layers subjected to light soaking (0.96 kW/m² halogen lamp) at elevated temperatures (75°C and 172°C) on a hot plate). They reported an increase in defect concentration due to surface degradation in non-diffused n-type samples, although the bulk lifetime remained stable. In addition, these non-diffused samples didn't exhibit any recovery of electrical characteristics even after a prolonged light soaking duration for several hours. Later on, studies by Kang et al. observed degradation followed by recovery behavior in n-type samples at 140°C [23]. In this study, an increase in defect concentration was observed in SiN_X : H passivated n-type samples due to defects formed both at the surface and within the bulk, which contrasts with the findings of Chen et al [21, 22]. Additionally, unlike the results reported by Kang et al.[23], the light-soaked samples in our study did not exhibit any regeneration in electrical characteristics even after 110 hours of light soaking under normal ambient conditions. The spectroscopic studies indicate that the degradation of samples during light soaking under normal ambient conditions is due to oxygen and hydrogen-related species, particularly in n-type samples, which has not been previously reported.

We expanded our investigation to include industrial-grade diffused mono and multicrystalline silicon, commonly used in solar cell manufacturing, as opposed to VLSI-grade Si wafers. The study was conducted in a controlled laboratory environment with the help of equipment that can effectively reproduce environmental conditions. Our objective was to analyze the influence of the emitter on the degradation process. The recombination characteristics of variation due to light and heat in the SiN_X : H passivated diffused Si samples are discussed in Chapter 7.

6.3 Summary

In this work, we utilized FTIR and PL spectroscopic techniques for identifying the chemical species involved in the light-induced degradation of PECVD SiN_x : H deposited samples under outdoor conditions. FTIR analysis revealed a change in the concentration of chemical species such as SiN_x , SiN_yH_a , SiN_zH_b , SiH_m , SiO_{2i} and SiO_n . The change in SiN_x , SiN_yH_a , SiN_zH_b and SiH_m associated with PECVD SiN_X : H film correlates to surface degradation while the change in SiO_{2i} and SiO_n correlates to bulk degradation of both p-type and n-type samples. Furthermore, PL spectroscopic analysis confirmed the involvement of oxygen-related defects

in the degradation mechanism of n-type samples following light soaking. Although the precise chemical nature of the defect remains unknown, analysis using linearized SRH statistics suggests the possible emergence of two defects during light soaking in both p-type and n-type samples. Notably, within p-type samples, one of these defects is associated with the BO complex, a conclusion supported by the calculation of the capture cross-section ratio.

Chapter 7

Comprehensive Analysis of Recombination Characteristics due to Illumination Under Elevated Temperature in Monocrystalline and Multicrystalline Wafers

Previous studies indicate that LeTID was first observed in boron-doped multicrystalline silicon solar cell structures with initial degradation followed by regeneration [13, 19, 27–29, 31– 33, 35, 37–40]. Later on, similar behavior was observed in Cz-grown monocrystalline silicon samples also [18, 22, 23, 41]. However, the extent of LeTID varies significantly across these test structures, influenced by factors such as the position of the Fermi level, the intensity of illumination, and the annealing temperature [42–44]. Additionally, the extent of LeTID depends on fabrication process conditions, including the emitter diffusion profile [28, 30], dielectric passivation technique [29, 33–35], and firing profile [19, 27, 31, 32]. There are limited studies comparing the behavior of solar cells having different bulk characteristics, but fabricated using the same process technology under identical light soaking conditions.

This work presents a detailed analysis of the variation in recombination characteristics of Si

wafers with different bulk qualities when subjected to light and heat. The findings of this research are significant and contribute to the understanding of the LeTID behavior in industrial mono and multicrystalline Si wafers. Various characterization techniques, such as band-to-band PL imaging, lifetime measurements, and quantum efficiency measurement techniques, are used for analyzing the LeTID behavior of the test structures. The band-to-band PL imaging technique was used to study the spatial variation of light-induced degradation and regeneration behavior of the test structures. Further, the impact of light and heat on the emitter surface and bulk was investigated separately as a function of annealing duration using lifetime measurement. The results suggest that bulk lifetime determines the overall recombination characteristics. However, the surface also shows significant variation due to light and heat treatment. It is also evident that the LeTID behavior is different at the surface and bulk, which in turn differ based on the bulk quality. The variation in LeTID behavior of surface and bulk was further validated with quantum efficiency (QE) measurements in c-Si and mc-Si industrial solar cells. In addition, the importance of emitter in determining LeTID and subsequent regeneration characteristics is also presented.

7.1 Experimental Methods

7.1.1 Sample preparation and characterization

6-inch boron doped, 180 μm thick, industrial grade Cz grown c-Si and block cast mc-Si wafers with bulk resistivity of 1-3 Ωcm were used in this study. Symmetrically diffused and passivated test structures were fabricated on these wafers following the process flow shown in Figure 7.1. The processing conditions were identical for both c-Si and mc-Si samples except for the texturization process. Potassium hydroxide - potassium silicate - isopropyl alcohol (KOH - K₂SiO₃ -IPA) alkaline solution and hydrofluoric acid - nitric acid (HF-HNO₃) solution were employed to generate random upright pyramid and inverted scallop textures respectively on c-Si and mc-Si wafers. The exact process details are described in [219–221]. Subsequently, both groups of textured wafers underwent phosphorous diffusion on both sides. The diffusion was performed in a tube furnace (Pro- temp USA, Sirius PRO 200) using phosphorus oxychloride (POCl₃) as the dopant source at 830°C peak diffusion temperature. Further, the phosphosilicate glass (PSG) formed during the phosphorous diffusion was removed by soaking the wafers in 2% HF



Figure 7.1: Process flow for the fabrication of test structures used for studying the LeTID and regeneration effects in diffused and non-diffused silicon wafers.

solution. A stack of low-temperature thermal oxide (LTO) and PECVD SiN_X : H was used for passivating the double-side diffused wafers. LTO was grown in the same diffusion tube furnace at 600°C for one hour. Subsequently, SiNx:H film was deposited at a temperature of 380° C for 6 min using the PECVD system (Oxford Instruments, Plasmalab 100). Finally, firing at a peak temperature of 770°C for about 30 s was done to improve the effectiveness of passivation using a rapid thermal processing (RTP) tool (Allwin21 Corp., AW 610). In addition, double-side polished (DSP), Cz grown, <100> oriented, 300 µm thick, n-type wafers with a resistivity of 1-5 Ωcm were also used to study the LeTID and regeneration mechanisms in non-diffused silicon wafers. PECVD SiN_X : H film deposited with similar process conditions discussed above was used for passivating the surfaces of n-type polished wafers. The schematics of the test structures used in the study are shown in Figure 7.2. The thickness and refractive index (RI) at 630 nm of SiN_X : H film deposited on polished wafers were 104 nm and 2.1, respectively. A spectroscopic ellipsometer (Semilab SE 2000) was used for thickness and RI measurements. Representative industrial Al-BSF c-Si and mc-Si solar cells were also used for light-soaking experiments. The partially processed solar cell test structures were subjected to light soaking in a xenon test chamber under the elevated temperature of 75° C for up to 125 hours (h). The xenon test chamber (Q-SUN Xe-3) used in this study effectively reproduces the environmental



Figure 7.2: Schematics of the test structure used in the analysis.

conditions with the full spectrum of sunlight, heat, and moisture [222]. A schematic diagram of Xenon test chamber is shown in Figure 7.3. The light-soaked test structures were characterized regularly after cumulative light soaking durations of 24 h, 46 h, 67 h, 88 h, 112 h, and 125 h to study the degradation and regeneration behavior.



Figure 7.3: Schematic diagram of Xenon test chamber (Q-SUN Xe-3) used for effective reproduction of environmental conditions.

The LeTID and regeneration behavior of the samples were characterized using band-to-

band PL imaging, minority carrier lifetime measurements, and QE measurements. The samples were placed back into the xenon test chamber immediately after each set of characterization measurements. Band-to-band PL emission from the samples was measured using a 660 nm light-emitting diode source PL system (Greateyes Lumisolar tool). The effective minority carrier lifetime τ_{eff} of the samples was measured using a lifetime tester (QSSPC Sinton WCT 120). The changes in quantum in the wavelength range of 300 nm to 1200 nm of light-soaked c-Si and mc-Si solar cells were measured using the QE measurement system (Bentham PVE 300) to verify the degradation and regeneration behavior at the emitter and bulk of c-Si and mc-Si samples.

7.2 **Results and discussion**

7.2.1 Photoluminescence imaging

The spatial variation in PL intensity as a function of light soaking duration for the representative lifetime samples from the c-Si and mc-Si groups is shown in Figure 7.4. The histogram variations before light soaking (t = 00 h) and after light soaking for 24 h (t = 24 h) and 88 h (t = 88 h)are shown below the PL images. In the case of diffused c-Si wafers, the PL intensity degraded uniformly throughout the wafer within 24 h of light soaking. The corresponding reduction in average PL intensity count was from 3.8×10^4 to 2.6×10^4 . After 24 h of light soaking, the brighter region with relatively higher PL intensity showed a continuous improvement in the PL intensity till the entire 125 h of light soaking. The regeneration in c-Si samples after 88 h of light soaking is visible in the histograms. The PL count distribution after 88 h of light soaking lies between the degraded state (t = 24 h) and the initial state (t = 00 h). Interestingly, the defective regions with relatively lower PL intensity grew further and extended towards their nearby regions as light soaking duration increased, as indicated by rectangular regions marked in broken green and blue lines. Similar behavior is observed for mc-Si samples as well all over the sample area, where the growth of defective regions continuously increased for a longer light soaking duration. In contrast to c-Si samples, the presence of larger defective regions in mc-Si samples has resulted in the absence of any regeneration in overall PL count, as is evident from the histograms. PL intensity variations of c-Si and mc-Si samples indicate that samples with different bulk qualities behave differently in response to light and heat.



Relatively higher concentrations of metallic defects and crystallographic defects, such as grain

Figure 7.4: The spatial variation in PL intensity as a function of light soaking duration for the representative lifetime samples from c-Si and mc-Si groups. The histograms at different light soaking durations t = 00 h, t = 24 h, and t = 88 h are shown below the PL images.

boundaries, are present in mc-Si wafers. The behavior of LeTID-related defects and defect precursors is different in the grain and at the grain boundaries [14, 31]. The PL images indicate the extended growth of defective regions in both c-Si and mc-Si samples. The high density of defective regions and their extension towards nearby regions during light soaking in mc-Si together retarded the regeneration process by hindering the diffusion of defect species towards the gettering sites in mc-Si samples [223, 224]. The variation in implied open circuit voltage (iV_{OC}) of c-Si and mc-Si samples measured at five different regions as a function of light soaking duration is shown in Figure 7.5 (a) and (b) respectively. The regions A, B, C, D, and E correspond to the center, top right, top left, bottom left, and bottom right circular areas of 2-inch diameter within the 6-inch square sample, as shown in Figure 7.5 (c). The trend followed by iV_{OC} is similar at all five regions for c-Si samples, with an initial decrease of about 7 mV within 24 hours followed by gradual regain in iV_{OC} up to 5 mV for longer light soaking durations. However, in the case of mc-Si samples, the trend followed by iV_{OC} during light soaking differs from region to region as seen in Figure 7.5 (b). It also indicates that the change in magnitude of iV_{OC} and its kinetics during degradation and subsequent regeneration phase is significantly different at different locations within mc-Si wafers. Unlike in PL images, the regeneration trend is no-



Figure 7.5: Variation in iV_{OC} as a function of light soaking at five different regions for (a) c-Si and (b) mc-Si samples. The schematic diagram given in Figure 7.5 (c) shows the five different locations where iV_{OC} is measured.

ticed in iV_{OC} values at all five measured regions of mc-Si samples. The non-uniform behavior of samples during LeTID and subsequent regeneration was further analyzed using the lifetime measurements.

7.2.2 Lifetime characterization

The variation in τ_{eff} measured at excess carrier density (Δn) of 10¹⁵ cm⁻³ at five different locations of c-Si and mc-Si samples as a function of light soaking duration is shown in Figure 7.6 and 7.7 respectively. Effective lifetime curves as a function of injection level measured at the center of the samples are shown on the inset of Figure 7.6 and 7.7, respectively.

It is clear from these figures that for both c-Si and mc-Si samples, the maximum variation in τ_{eff} was noticed in the injection regimes, where SRH defects limits the lifetime. The variation



Figure 7.6: The variation in excess minority carrier lifetime (measured at $\Delta n = 10^{15} \text{ cm}^{-3}$) of c-Si samples as a function of light soaking duration. Inset shows the effective lifetime of minority carriers measured as a function of Δn at the center of the sample.



Figure 7.7: The variation in excess minority carrier lifetime (measured at $\Delta n = 10^{15} \text{ cm}^{-3}$) of mc-Si samples as a function of light soaking duration. Inset shows the effective lifetime of minority carriers measured as a function of Δn at the center of the sample.

in τ_{eff} was significant for both c-Si and mc-Si close to one sun injection condition. The average value of τ_{eff} measured at Δn of 10¹⁵ cm⁻³ was reduced from 75 µs to 59 µs and 58 µs to 49 µs, respectively for c-Si and mc-Si samples. Light soaking for 88 h resulted in a regain of τ_{eff} to 72 µs for c-Si samples. However, in the case of mc-Si samples, light soaking up to even 125 h did not result in any significant regeneration in τ_{eff} in agreement with the iV_{OC} trends. Figure 7.4 confirms that the extent of LeTID and subsequent regeneration effect was greater for c-Si samples. This also indicates the injection dependency of degradation and regeneration kinetics due to the difference in the bulk quality of c-Si and mc-Si wafers [42, 43]. Injection dependent τ_{eff} is a measure of the overall recombination characteristics, which include both surface and bulk recombination components. Some other recent studies also showed that LeTID-related defects can impact the surface as well [30, 49].

Hence, we estimated the emitter surface recombination current density (J_{0s}) and bulk lifetime (τ_B) components from the lifetime measurements to investigate the influence of LeTID on surface and bulk separately. J_{0s} term was estimated from the inverse Auger corrected carrier lifetime ($\tau_{AugerCorrected}$) curves obtained from the Sinton lifetime tester using Kane-Sawnson method following the equation represented in Eq.6.2 and Eq.6.3 [225];

Figures 7.8 show the variation in J_{0s} and τ_B as a function of light soaking duration for c-Si and mc-Si samples, respectively. For c-Si samples, $\tau_{\rm B}$ degraded from 158 µs to 97 µs within 24 h of light soaking. As the light soaking duration increased, bulk quality improved, as seen in Figure 7.8 (a), and stabilized beyond 88 h of light soaking. The increase in average $\tau_{\rm B}$ was about 40 µs after 88 h of light soaking. The regeneration in bulk lifetime is possibly due to the transformation of recombination active LeTID-related defects and their gettering at the emitter surface [14]. Interestingly, J_{0s} follows a trend opposite to that of τ_B during light soaking, as evident from Figure 7.8 (c). The surface component J_{0s} showed an initial decrease followed by a consistent increase as light soaking progressed. The initial decrease in the average value of J_{0s} was from 166 fA/cm² to 119 fA/cm² for the initial 24 h of light soaking. After 88 h of light soaking, the average value of J_{0s} increased by 22 fA/cm² and stabilized at 141 fA/cm². The initial reduction in J_{0s} implies that the emitter surface recombination was reduced in c-Si samples, possibly due to hydrogen diffusion towards the surface. Further, as light soaking progressed, emitter surface degradation increased due to the formation of LeTID-related defects at the emitter surface. mc-Si samples also showed a significant degradation in τ_B from 102 μs to 78 μ s during the first 24 h of light soaking. The change in average τ_B in mc-Si samples



Figure 7.8: The variation in τ_B and J_{0s} as a function of light soaking duration of c-Si and mc-Si samples.

was relatively lower than that of c-Si samples. As discussed earlier, this can be attributed to the difference in the behavior of defects and defect precursors with crystallographic and other defect locations in multicrystalline wafers [14, 31, 223, 224]. Unlike c-Si, mc-Si samples did not show significant improvement in average bulk lifetime with a further increase in light soaking duration, as seen in Figure 7.8 (b). However, the surface component showed a small but gradual improvement with light soaking, and the decrease in J_{0s} after light soaking of 125 h was only 21 fA/cm². The reduction in J_{0s} implies a reduction in surface recombination in mc-Si samples, possibly due to hydrogen diffusion towards the emitter surface. Figure 7.8 (d) also suggests that unlike in c-Si samples, there was no significant formation of LeTID-related defects at the emitter of mc-Si samples even after light soaking for up to 125 h. This can be correlated to studies by Xiao et al. [49], where surface degradation was observed only beyond 280 h of light soaking at 122°C. Hence, it can be concluded that LeTID at the emitter is much slower than in bulk. Moreover, the initial bulk quality of the wafer further determines the kinetics of degradation. It is evident that bulk degradation is marginal and limits the overall reduction in τ_{eff} irrespective of the decrease in J_{0s}. However, the role of J_{0s} can be very significant as the emitter response decides the overall performance of solar cells, especially for high-efficiency architectures like PERC and tunnel oxide passivated contact (TOPCon). The significance of emitter in the regeneration process was further confirmed by analyzing LeTID behavior in non-diffused samples, as discussed below.

7.2.2.1 Significance of emitter in determining LeTID and subsequent regeneration

Figure 7.9 (a) shows τ_{eff} variation in the passivated n-type sample without emitter diffusion as a function of Δn for different duration of light soaking. A gradual reduction in τ_{eff} from 250 µs to 20 µs measured at $\Delta n = 10^{15} \text{ cm}^{-3}$ is observed for non-diffused samples after 110 h of light soaking. The lifetime degradation in the non-diffused samples after light soaking is due



Figure 7.9: (a) Variation in minority carrier lifetime characteristics as a function of excess carrier density in non-diffused Cz samples at different light soaking durations. (b) The corresponding changes in surface component J_{0s} and bulk lifetime τ_B as a function of light soaking duration.

to the formation of defects with high recombination activity positioned closer to the mid-band gap energy levels. The surface and bulk recombination components related to LeTID were also estimated from Auger-corrected lifetime curves for this group of samples, and variations are shown in Figure. It is clear from Figure 7.9 (b) that both surface and bulk are consistently degraded due to prolonged illumination under elevated temperatures. The decrease in τ_{eff} is associated with an increase of about 350 fAcm² in J_{0s} and a decrease of 225 µs in τ_{B} . Unlike in diffused samples, severe degradation is observed at the surface in non-diffused samples. In addition, non-diffused samples did not show any recovery trend in τ_{eff} and J_{0S} till the end of light soaking. These results show that diffused emitter not only aids in regeneration in the bulk lifetime, but also in preventing the severe recombination loss at the surface. Unlike in diffused samples, severe degradation is observed in non-diffused samples. In addition, non-diffused samples did not show any recovery trend in τ_{eff} till the end of light soaking. This is in agreement with previous reports of [21, 22]. Comparing these results with diffused emitter samples shows that the presence of emitters aids in bulk lifetime regeneration by separating impurities from the bulk during illuminated annealing for a time greater than 24 hours. This is because heavily doped emitter structures act as gettering centers for defects.



7.2.3 Quantum Efficiency

Figure 7.10: QE variation in c-Si and mc-Si solar cells at t = 00 h, t = 24 h and t = 88 h of light soaking.

The extent of degradation and regeneration at the surface and bulk of c-Si and mc-Si lifetime samples were also analyzed by comparing the QE curves of c-Si and mc-Si solar cells. The variation in QE of c-Si and mc-Si solar cells at t = 00 h, t = 24 h, and t = 88 h of light soaking are shown in Figure 7.10. It is evident from Figures 7.10 (a - d) that the degradation and regeneration behavior of c-Si and mc-Si solar cells are different. For c-Si solar cells, there was a reduction in QE corresponding to the deep bulk (wavelength above 600 nm) after 24 h of light soaking but regained nearly back to the initial values after 88 h of light soaking (Figure 7.8 (b)). The QE corresponding to the surface (wavelength below 500 nm) shows a trend opposite to that of deep bulk. As seen in Figure 7.10 (a), the QE shows a marginal increase after 24 h of light soaking and then decreases towards the initial condition as light soaking progresses. This agrees with the J_{0s} trend in Figure 7.8 (b). Similar to c-Si solar cells, a reduction in QE is observed after 24 h of light soaking in mc-Si solar cells for the wavelength range above 600 nm. However, regain in QE is not as significant even after 88 h of light soaking, as seen in Figure 7.10 (d). The QE response in the lower wavelength range below 600 nm slightly increases for both t = 24 h and t = 88 h (Figure 7.10 (c)). These patterns of variation in QE at various light soaking conditions for both groups of cells agree with the recombination current density variations on the surface and in the bulk of the test structure given in Figure 7.8.

7.2.4 Comparison of Results in This Work with Existing Literature

Consistent with previous research, this study observed that c-Si silicon samples initially degraded and subsequently regenerated in their lifetime characteristics during light soaking at elevated temperatures. However, the maximum extent of degradation varies depending on factors such as emitter diffusion, passivation techniques, firing profile, bulk doping, light soaking, and annealing conditions. In line with previous studies, a higher degradation is observed in the c-Si samples compared to mc-Si samples. The extent of degradation reported in earlier studies is summarized in Table 7.1. In addition, monocrystalline samples showed more than 90% recovery in lifetime characteristics as reported in previous studies. In contrast, mc-Si samples exhibit limited recovery of electrical properties due to the high concentration of defects within the bulk.

There appear to be no studies on the LeTID-related recombination characteristics of the emitter surface and bulk in commercially viable silicon solar cell structures with varying bulk qualities. Therefore, in this work, we analyzed the recombination characteristics at the emitter

Test structure	Maximum extend of degrada- tion	Light soaking Conditions	Peak firing tempera- ture	Ref.
$SiN_{x} \cdot H/n^{+}/n - mc - Si/n^{+}/SiN_{x} \cdot H$	70%	75 ⁰ C 1 Sun	900°C	[31]
	25%	175°C, Dark An- nealing	720°C	[19]
	40%	175°C, 1 Sun	800°C	[19]
$SiN_X : H/n^+/p - Cz - Si/n^+/SiN_X : H$	50%	175°C, 1 Sun	800°C	[22]
SiN_X : H/n ⁺ /n-Cz-Si/n ⁺ /SiN _X : H	30%	175°C, 1 Sun	800°C	[21, 22]
SiN_X : H/mc – Si/SiN _X : H	30%	220°C, 2 Sun	800°C	[201]
SiN_X : H/n ⁺ /p-mc-Si/n ⁺ /SiN _X : H	14%	75°C, 1 Sun	770°C	This work
SiN_X : H/n ⁺ /p-Cz-Si/n ⁺ /SiN _X : H	24%	75°C, 1 Sun	770°C	This work

Table 7.1: Extent of LeTID reported in diffused samples passivated with PECVD SiN_X : H in the literature and in this work.

surface and within the bulk of both types of samples. Our study reveals that the emitter and bulk exhibit different recombination characteristics. However, the bulk determines the overall recombination behavior, consistent with previous studies [20, 23]. The surface recombination characteristics show no degradation even after 125 hours of light soaking. This behavior was further confirmed using quantum efficiency measurements.

Considering the impact of both light and heat on the lifetime of charge carriers and the quantum efficiency of sample test structures, it is evident that these factors play a crucial role in determining the performance parameters of finished solar cells. The upcoming chapter delves into the changes in performance parameters and recombination characteristics observed in industrial Si solar cells under the influence of light and heat.

7.3 Summary

This study explored the response of both bulk and emitter surfaces in c-Si and mc-Si wafers when subjected to illuminated annealing. The research revealed a degradation followed by regeneration in bulk lifetime for both diffused c-Si and mc-Si wafers. However, mc-Si exhibited lower degradation and regeneration, primarily due to a higher concentration of grain boundary defects and metallic impurities.

It was observed that the behavior of the bulk material played a significant role in determining the overall LeTID and regeneration kinetics in both c-Si and mc-Si samples. Even after 125 hours of light soaking, the recombination at the emitter surface remained lower than the initial levels in both c-Si and mc-Si samples, potentially due to hydrogen diffusion during light soaking. In the case of diffused c-Si samples, light soaking beyond 24 h increased surface recombination current density, likely attributed to the formation of surface LeTID defects. The presence of an emitter was found to be crucial not only in determining the behavior of the Si-SiNx: H interface but also in the regeneration of the bulk.
Chapter 8

Analysis of Variation in Recombination Characteristics due to Light and Heat in Industrial Silicon Solar Cells

The existing literature on finished solar cells mainly addresses performance stability analysis of cells and modules [15, 45], comparisons of performance parameters for different cell architectures [46, 47], the impact of process parameter variations [32, 39, 40, 46, 48], the estimation of defect formation and transformation activation energies [39, 42, 43], and mitigation measures [39, 40, 42–44, 48]. While variations in cell performance parameters have been reported, no in-depth characterization or analysis of the contributing factors has been reported.

In addition to current-voltage analysis, spectral response measurements are commonly used to characterize LeTID behavior in silicon solar cells [40, 46–49]. Cho et al. [47] observed variations in EQE in the wavelength range of 700 nm to 1000 nm after light soaking. Maischner et al. [40] and Hu et al. [48] attributed LeTID to deep bulk defects by comparing EQE in the long wavelength range. Padmanabhan et al. [46] noted variations in spectral response from 500 nm onwards during one-sun illuminated annealing at 90^OC. Additionally, Xiao et al. [49] recently reported long-term degradation in the surface and subsurface regions based on light beam-induced current variations at 406 nm and 658 nm wavelengths for light soaking durations

beyond 280 hours. These studies suggest that attributing LeTID solely to deep bulk defects may not be appropriate for all light soaking conditions, necessitating more detailed investigations. Since hydrogen is considered the main cause of LeTID, it potentially impacts the silicon-SiN_X : H interface, diffused emitter, space charge region, bulk, and rear of the solar cells. To our knowledge, there have been no studies examining recombination within the space charge region due to illuminated annealing and its influence on solar cell performance parameters. Discussions related to variations in open-circuit voltage have been limited to either deep bulk defects [40, 47] or LeTID and subsequent regeneration kinetics [32, 46–48]. Although LeTID and regeneration in fill factor have been discussed elsewhere [40, 46, 47], no detailed analyses of factors contributing to FF variation are available. Therefore, it is necessary to classify the factors contributing to LeTID and subsequent regeneration in silicon solar cells.

In this section, the characteristics of monocrystalline and multicrystalline silicon aluminum back surface field (Al-BSF) solar cells on exposure to light and heat are discussed. Al-BSF solar cells were selected over PERC cells as the former has only a single hydrogen source i.e. the SiN_X : H at the front side, which makes the analysis much simpler. This work utilizes the two diode model parameters for identifying the factors contributing to variations in performance parameters. The role of different regions, such as emitter space charge and the bulk of solar cells in LeTID and subsequent regeneration behavior, is discussed in this chapter. Furthermore, a detailed investigation of spatial nonuniform behavior of recombination characteristics of the cells during the degradation and regeneration phase is also described.

8.1 Experimental methods and characterization

In this study, we used boron-doped monocrystalline and multicrystalline (156.75 x 156.75 mm², thickness 180±20 μ , base resistivity 1-3 Ω cm) Al-BSF industrial solar cells. The schematic cross-section of the device is shown in Figure 8.1. These cells were subjected to light soaking using a xenon test chamber under the elevated temperature of 75°C for up to 125 hours (h). The light-soaked cells were characterized at various points in time during light soaking (the cumulative time period of 24 h, 46 h, 67 h, 88 h, and 125 h) to study the degradation and regeneration behavior. The cells were placed back in the xenon test chamber immediately after the measurement. The LeTID behavior of the cells was characterized using J-V, suns-V_{OC}, and LBIC measurements. The illuminated J-V characteristics of the solar cells were measured



Figure 8.1: Schematic cross-section of the device used in the study.

under standard test conditions of 100 mW/cm² intensity, AM 1.5G spectrum, and 25°C using a class AAA solar simulator (Abet Technologies Sun 3000). Further, the series resistance (Rs) values were estimated from J-V measurements for two different illuminations of 1 sun and 0.1 sun following the Bowden method [193]. The two-diode model recombination current density components were extracted from pseudo J-V characteristics measured using Suns-Voc illumination voltage tester from Sinton Instruments [194, 195]. EQE maps were generated using an LBIC tool (Semilab WT-2000PVN) at four available wavelengths of 407 nm, 658 nm, 877 nm, and 984 nm. In the following discussion, mono and multi correspond to monocrystalline and multicrystalline Al-BSF solar cells, respectively, with batch average efficiencies of 20% and 18.28%. The batch size was four from each group.

8.2 Experimental results and discussion

8.2.1 Variation in performance parameters

The absolute variation in efficiency of mono and multi solar cells as a function of light soaking duration is shown in Figure 8.2. The open square and horizontal lines in Figure 8.2 correspond to the mean and median, respectively, of the data points. The mean and median values are almost the same for all light-soaking conditions. Hence, the mean value is used as representative of the data points in the subsequent discussions to highlight the functional dependency. Variations in normalized (with respect to values before light soaking) performance parameters



Figure 8.2: Variation of efficiency of mono and multi solar cells as a function of light soaking time.

are given in Figure 8.3. As a guide to the eye, a line is drawn between the data point corresponding to the initial condition and degraded condition after light soaking of 24 h. During the regeneration process, normalized performance parameters follow an exponential fit [43, 44] as depicted by continuous lines in Figure 8.3. Both mono and multi solar cells showed significant initial degradation within 24 h, followed by regeneration. The change in batch average efficiency after 24 h of light soaking was from 20% to 19.48% and from 18.28% to 17.90% for mono and multi solar cells, respectively. This corresponds to a relative reduction in efficiency of 2.66% and 2.06%, respectively for mono and multi solar cells, as shown in Figure 8.3 (a). This efficiency loss was attributed to an average reduction of 5.92 mV and 3.75 mV in V_{OC} , $0.55~mA/cm^2$ and $0.43~mA/cm^2$ in J_{SC} and 0.45% and 0.38% in FF for mono and multi solar cells, respectively. Light soaking up to 125 h has resulted in regaining of efficiency with batch average value improving to 19.89% and 17.96% for mono and multi solar cells, respectively. Interestingly, the performance parameters V_{OC} and FF were regenerated to 99.5% of the initial condition for both mono and multi solar cells after 67 h of light soaking as shown in Figure 8.3 (b) and (d). Figure 8.3 (c) indicates that J_{SC} has maximum degradation among the performance parameters and shows a near-saturation behavior beyond 67 h of light soaking for both mono and multi solar cells.

LeTID is reported to be a carrier-induced degradation mechanism where the degradation kinet-



Figure 8.3: Variation in normalized performance parameters of mono and multi solar cells as a function of light soaking time.

ics is directly correlated with the density of excess carriers generated in the device. The higher the carrier concentration, the higher the rate of transformation of defect precursors to recombination active defects [42, 174]. For a fixed illumination, the excess minority carrier density will be lower in multicrystalline samples as compared to monocrystalline wafers due to the presence of crystallographic defects such as grain boundaries and metallic defects [226, 227]. Hence, mono cells are expected to exhibit a higher rate of degradation and regeneration than multi cells. Sio et al. have observed a lower LeTID in multi than in Cz and mono-like samples [20]. Figure 8.3 indicates that mono cells show more degradation and better regeneration compared to multi cells. Different degradation and regeneration trends for monocrystalline and multicrystalline solar cells affirm that LeTID behavior depends on the type, concentration, and distribution of defects within the wafer. Since all the performance parameters show significantly different degradation and regeneration characteristics for both the groups of solar cells, the two-diode model analysis was employed to study the factors contributing to the variation in performance parameters [49, 228–231]. In the two-diode model, four sets of parameters J_{01} , J_{02} , R_s , and R_{sh} are used to represent the recombination and resistive components of single junction silicon solar cell. The ideality factors; n_1 and n_2 are fixed respectively to 1 and 2 while fitting the 2-diode model parameters. The recombination current density J_{02} corresponds to the recombination loss within the space charge region. In contrast, J_{01} corresponds to the recombination loss in the rest of the solar cell, such as silicon-SiN_x : H interface, diffused emitter, bulk, and rear sides of the cell. R_s and R_{sh} represent the effective series and shunt resistance values across the terminals of the solar cell. J_{01} and J_{02} are estimated from Suns-V_{OC} measurements while R_s and R_{sh} are estimated from lighted J-V measurement.

8.2.2 Variation in two model parameters

Figure 8.3 (a-d) shows J₀₁ and J₀₂, R_s and R_{sh} variation with light soaking for both mono and multi solar cells. The trend followed by J_{01} and J_{02} in Figure 8.4 (marginal increase followed by gradual decrease) is in agreement with that of the performance parameter in Figure 8.2. No significant variation in Rs and Rsh values were noticed for both the groups of solar cells, confirming that light soaking has not introduced any additional resistive losses in the solar cells. Consistent variations in J₀₂ suggest that the space charge region is also affected significantly during both degradation and regeneration. The variation in J_{01} and J_{02} was severe for mono solar cells with an increase in J_{01} and J_{02} of 101 fA/cm² and 12 nA/cm², respectively for a light soaking duration of 24 h. Further, the elevation in J_{01} and J_{02} (with respect to values before light soaking) reduced to 53 fA/cm² and 7 nA/cm² respectively beyond 67 h of light soaking. For multi solar cells, the increase in J_{01} and J_{02} after 24 h of light soaking were about 68 fA/cm² and 6 nA/cm² respectively. For 67 h and 88 h of light soaking, J_{01} was reduced further only by a value of 10 fA/cm² and 28 fA/cm² respectively, indicating that the recovery in J_{02} was much slower in multi solar cells. In addition, no appreciable improvement in J_{02} was observed during the regeneration phase. This indicates that, unlike mono samples, there was no regeneration within the space charge region for multi cells. The defects formed within the space charge region of the multi cells during LeTID were retained there itself during the regeneration phase. The comparatively smaller variation in J_{01} and J_{02} among the multi solar cells during the regeneration phase is consistent with the lower regeneration trends depicted in Figure 8.2.



Figure 8.4: J_{01} and J_{02} , R_s and R_{sh} variation with light soaking for both mono and multi solar cells.

8.2.3 Fill Factor loss analysis

For single junction silicon solar cells, the FF value is influenced by all four parameters of two diode model: $(J_{01} \text{ and } J_{02}, R_s \text{ and } R_{sh})$ [193, 229–231]. A detailed FF loss analysis was employed for all the light-soaked mono and multi solar cells following the method proposed by Khanna et al. [196]. Figure 8.4 (a-d) shows the variation in FF loss due to J_{01} , J_{02} , R_s and R_{sh} of both mono and multi solar cells after light soaking.

Both mono and multi solar cells exhibited only marginal variation in R_s for the entire 125 h of light soaking (see Figure 8.4 (c)). Hence, no change in FF loss due to Rs, Δ FF(R_s), was noticed after light soaking. The average of Δ FF(R_s) during the entire light soaking duration was 1.05 % and 0.3 % respectively, for mono and multi solar cells as shown in Figure 8.5 (c). Δ FF(R_s) was lower for multi due to lower R_s (see Figure 8.4 (c)). The values of R_{sh} were always greater than 150 k Ω cm² during the entire light soaking period for both the group of cells (Figure 8.4 (d)).

Such high R_{sh} values assured zero FF loss due to R_{sh} for both mono and multi solar cells (see Figure 8.5 (d)). Hence, the loss and regeneration in FF during the light soaking can be mainly attributed to the variation in J_{01} and J_{02} .

The FF loss due to J_{01} and J_{02} after light soaking are shown in Figure 8.5 (a) and (b). $\Delta FF(J_{01})$, and $\Delta FF(J_{02})$, represent the absolute loss in FF due to J_{01} and J_{02} respectively. The major component of FF loss was due to J_{01} for both mono and multi cells. Both $\Delta FF(J_{01})$ and $\Delta FF(J_{02})$ were higher for multi solar cells due to the higher recombination in multicrystalline wafers compared to monocrystalline wafers. The FF loss due to recombination current components



Figure 8.5: Variation in FF loss due to J_{01} and J_{02} , R_s , R_{sh} of both mono and multi solar cells after light soaking.

 J_{01} and J_{02} (Δ FF(J_{01}), and Δ FF(J_{02})) shown in Figure 8.5 (a) and (b) follows the same trend as that of J_{01} and J_{02} shown in Figure 8.4 (a) and (b). For both mono and multi solar cells, the absolute change in Δ FF(J_{01}) was only 0.11% and 0.08%, respectively after 24 h of light soaking. However, major degradation in FF with respect to light soaking was due to J_{02} . The absolute

change in $\Delta FF(J_{02})$ was 0.38% and 0.28%, respectively for mono and multi solar cells after 24 h of light soaking. Regain in FF was relatively lower for multi solar cells as $\Delta FF(J_{01})$, and $\Delta FF(J_{02})$ did not improve significantly beyond 24 h of light soaking. In contrast, for mono solar cells, the average value of $\Delta FF(J_{01})$ and $\Delta FF(J_{02})$ reduced by 0.07% and 0.30% respectively which resulted in improvement in FF of 0.37% after 67 h of light soaking. FF loss analysis suggests that recombination at the space charge region was significantly large in deciding the overall degradation and regeneration of FF values in both mono and multi solar cells.

8.2.4 LBIC for short circuit current analysis

Figure 8.6 and Figure 8.7 represent the LBIC EQE maps for representative solar cells from mono and multi at four available wavelengths of 407 nm, 658 nm, 877 nm, and 984 nm for three different conditions. t = 00 h, t = 24 h, and t = 67 h, respectively, correspond to the initial (before light soaking), degraded and regenerated conditions. The average EQE value over the entire scanned area of a 6-inch solar cell is listed at the top right corner of each EQE map. Except at 407 nm, the EQE maps follow LeTID trends with an initial degradation followed by recovery. For mono, the average EQE value reduced from 80.54% to 79.24% at 984 nm, from 90.51% to 89.33% at 877 nm and from 94.92% to 93.27% at 658 nm. For multi solar cells, the average EQE value reduced from 72.88% to 71.46% at 984 nm, from 86.05% to 84.86% at 877 nm, and from 93.42% to 92.13% at 658 nm after 24 h of light soaking. The reduction in EQE values observed at 877 nm and 984 nm for mono and multi are in agreement with previous reports [40, 46, 48], where the degradation was mainly attributed to an increase in recombination loss at the deep bulk region. In addition, significant degradation in EQE at 658 nm was observed for both groups, indicating that LeTID can be present throughout the bulk of the solar cells. It has been previously reported that hydrogen diffused from the PECVD-deposited dielectric films such as SiN_X : H or AlO_X: H layer leads to complex defect formation, which is responsible for LeTID [25, 26]. Hence, from the degradation observed in EQE maps at 658 nm, 877 nm, and 984 nm it can be inferred that the hydrogen-related defect species responsible for LeTID can be present throughout the bulk. After subjecting the cells to 24 hours of light soaking, the most substantial variation in average EQE is observed at 658 nm for monocrystalline cells. This variation in EQE at 658 nm, closely corresponding to the wavelength range of maximum photon flux, can be attributed to the more significant degradation of J_{SC} in mono cells when compared with the observed trend in multicrystalline cells, as illustrated in Figure 8.3(c).



Figure 8.6: EQE map of representative solar cells from mono at 984 nm, 877 nm, 658 nm and 407 nm for t = 00 h, t = 24 h and t = 67 h.



Figure 8.7: EQE map of representative solar cells from multi at 984 nm, 877 nm, 658 nm and 407 nm for t = 00 h, t = 24 h and t = 67 h.

The regeneration in EQE at wavelengths 658 nm, 877 nm and 958 nm was observed only for mono cells. The difference in absolute average EQE during the regeneration was in the range of

0.75-1% (with respect to t = 24 h), for all three wavelengths. The regain in EQE at 658 nm, 877 nm and 984 nm is attributed to the regeneration of the bulk quality due to the transformation of defect species during prolonged exposure to light and heat [13, 14]. Nearly similar EQE values observed after prolonged exposure to light and heat suggest that transformation of defect and gettering was minimal for multi solar cells. LeTID-related defects and the defect precursor behave differently in the grain and at the grain boundaries [223, 224]. The presence of relatively very high concentrations of impurities and crystallographic defects in multicrystalline wafers hinders the diffusion of defect species to the gettering site [13, 14]. Hence, the transformation of recombination active defect into an inactive state and their gettering is relatively slower in multicrystalline wafers. As a consequence, J_{01} variations are relatively less, resulting in near saturation behaviour of J_{SC} for multi solar cells beyond 48 h of light soaking.

Interestingly, opposite trends were observed for EQE for the two groups of cells at 407 nm. The initial average EQE of 88.11% and 65.98% increased to 88.83% and 67.05% for mono and multi, respectively, after 24 h of light soaking. It then decreased to 88.13% for mono and 66.55% for multi cells after 67 h of light soaking. This suggests that the impact of LeTID-related defects is not similar in emitter and bulk for both types of solar cells. The initial increment in average EQE observed after 24 h of light soaking can be attributed to the diffusion of hydrogen towards the interface, resulting in better passivation of dangling bonds at the Si-SiN_X : H interface. Further reduction in EQE at 407 nm during subsequent light and heat treatment indicates the reduction in passivation quality either due to the effusion of hydrogen from the interface or the formation of LeTID-related defects.

8.2.5 PL imaging for uniformity analysis

Figure 8.8 represents the open circuit PL images of representative solar cells from mono and multi after light soaking. Histograms (t = 00 h, t = 24 h and t = 67 h) are shown below PL images. PL images confirm that both degradation and regeneration in V_{OC} were more for mono than for multi cells. For mono cells, average PL count reduced from 2.12×10^4 to 1.60×10^4 after 24 h and then increased to 1.95×10^4 after light soaking of 67 h, whereas for multi solar cells the reduction in average PL count was from 1.02×10^4 to 0.75×10^4 after 24 h and then it increased to 0.82×10^4 after 67 h of light soaking. The PL intensity distribution trend is directly related to the variation in J_{01} and J_{02} . Higher change in J_{01} and J_{02} for mono cells resulted in larger variation in V_{OC} and PL intensity count during both degradation and



Figure 8.8: PL images of representative solar cells from mono and multi before and after light soaking. Histograms of PL intensity for initial (t = 00 h), degraded (t = 24 h) and regenerated (t = 67 h) are shown beneath PL images.

regeneration phase.

For multi solar cells, a notable reduction in V_{OC} of 3.75 mV and PL count of 0.25×10^4 during the degradation phase was due to the variation in both J_{01} and J_{02} . However, unlike mono solar cells, no significant reduction in J_{02} was observed for multi solar cells during the regeneration phase. This has resulted in lower regeneration of V_{OC} and PL intensity as seen in Figure 8.8. The histogram of the PL intensity distribution clearly indicates that PL intensity variations were uniform and proportional throughout for both groups of solar cells during LeTID and the subsequent regeneration phase. Also, the shift in the PL peak of mono and multi solar cells validates the carrier injection dependency of LeTID and regeneration. This is evident from the histogram of mono solar cells where two PL peaks corresponding to two carrier injection levels are visible. Further, these two peaks shifted toward the left during the degradation phase and then toward the right during the regeneration phase.

8.2.6 Comparison of Results in This Work with Existing Literature

In agreement with previous studies, this work observed an initial degradation followed by regeneration in performance parameters in solar cells [17, 39, 46, 167, 232, 233]. Since the extent of degradation and regeneration due to light and heat are determined by various factors such as processing conditions (passivation, emitter diffusion, firing), bulk quality, bulk doping, and the conditions of light soaking and annealing, different research groups reported different values for variations in performance parameters. Table 8.1 provides a summary of the research findings related to the decrease in efficiency resulting from LeTID in cells for a wide range of operational conditions [157].

Source	Year	Solar cell	Degradation	Conditions	Ref
		type			
Ramspeck et al.	2012	PERC	5-6%	75°C, 0.4 suns, 400h	[167]
Petter et al.	2015	PERC	$\approx 16\%$	75°C, 1 sun, 200h	[17]
Luka et al.	2015	PERC	10%	75°C, 1 sun, 48h	[232]
Krauß et al.	2016	PERC	11.2%	80°C, 0.8 suns, 325h	[39]
Padmanabhan et	2016	PERC	4.3%	90°C, 1sun, 21h	[46]
al.					
Chan et al.	2017	PERC,	12.7%	70°C, 0.46 suns, 480h	[233]
Sio et al.	2018	PERC,	9.6%	65°C, 1 suns,5 h	[20]
Sen et al.	2020	PERC,	6%	75°C, 1 suns, 250h	[37]
Padmanabhan et	2016	AlBSF (mc	1.8%	90°C, 1 sun, 24h	[46]
al.		Si)			
Resmi et al.	2023	AlBSF	2.6%	75°C, 1 sun, 24h	This
		(c-Si)			work
Resmi et al.	2023	AlBSF (mc-	2.0%	75°C, 1 sun, 24h	This
		Si)			work

Table 8.1: Relative reduction in efficiency of solar cells associated with LeTID under a wide range of operational conditions [157].

In this study, we observed a maximum relative reduction in batch average efficiency of 2.6% for monocrystalline Si solar cells and 2.0% for multicrystalline Si solar cells. The ob-

served maximum extent of degradation in multicrystalline Si solar cells aligns with the studies of Padmanabhan et al.[46], who reported a 1.8% efficiency degradation after light soaking at 1 sun illumination at 90°C for 24 hours. Consistent with previous reports, the efficiency regained in this work exceeded 99.5%. Additionally, we investigated various factors influencing performance parameters during LeTID using two-diode models, which were not previously reported. Furthermore, the EQE variations at different depths within the solar cells were in agreement with previous studies [40, 43, 46]. The findings reported in this study have practical implications for the design of solar cells and the development of measures for LeTID mitigation, offering valuable insights into the degradation process.

8.3 Summary

This work demonstrates that the recombination at the space charge region plays a significant role in performance parameter variations due to light and heat. Significant changes in both recombination current densities, J_{01} and J_{02} together contribute to higher degradation and faster recovery in monocrystalline solar cells. Lower LeTID and slower regeneration in multicrystalline cells are due to relatively high concentrations of metallic impurities and grain boundaries. FF loss analysis suggests that degradation and recovery in FF is limited by recombination in space charge region in both monocrystalline and multicrystalline cells. LBIC EQE maps at 658 nm, 877 nm and 984 nm reveal the formation of defects throughout the bulk. However, the LBIC EQE maps at 407 nm show an increasing trend initially, followed by degradation. We speculate that the diffusion of hydrogen to the interface and the resulting better emitter surface passivation is responsible for the initial improvement, and the subsequent degradation could be due to the effusion of hydrogen away from the interface or due to the formation of LeTID-related defects at the surface.

Chapter 9

Conclusion and Future Work

9.1 Conclusion

In this research, we investigated the chemical species involved in the light-induced degradation of p-type and n-type samples that have been passivated using plasma-enhanced chemical vapor deposited (PECVD) hydrogenated silicon nitride under typical outdoor ambient conditions. To unravel the mechanisms at play in this degradation process, we employed a comprehensive approach, which includes electrical characterization, Fourier Transform Infrared spectroscopy, and photoluminescence spectroscopy. The findings of this study unveiled noteworthy reductions in the electrical characteristics of both n-type and p-type samples, accompanied by an increase in defect density. This decrease in electrical performance was particularly evident in the effective minority carrier lifetime values and the band-to-band photoluminescence (PL) intensities for both types of samples on exposure to outdoor light soaking. The apparent defect density exhibited an increase, transitioning from $3.39 \times 10^{-3} \,\mu s^{-1}$ to $1.68 \times 10^{-2} \,\mu s^{-1}$ for p-type samples and $3.42 \times 10^{-4} \,\mu s^{-1}$ to $3.46 \times 10^{-3} \,\mu s^{-1}$, for n-type samples following cumulative solar insolation of 95.7 kWh/m². To further explore the performance degradation, we conducted an in-depth analysis of the chemical species involved in the degradation mechanism using various physical characterization techniques. Our investigation focused on changes in the Fourier Transform Infrared (FTIR) absorbance intensities of key chemical species, including SiN_vH_a, SiN_zH_b, SiH_m, SiO_n, and SiO_{2i} after exposure to light soaking. These analyses provided confirmation that both oxygen and hydrogen contribute to the degradation process in both p-type and n-type samples. In addition to FTIR analysis, our study employed spectroscopic photoluminescence analysis to reinforce these findings. The spectroscopic PL analysis affirmed the decrease in the concentration of silicon-oxygen species. It further supported our understanding of the degradation mechanisms in these solar cell samples by corroborating the reduction in effective lifetime in the n-type samples.

Subsequently, the thesis delved deeply into examining recombination characteristics in industrial monocrystalline (c-Si) and multicrystalline (mc-Si) silicon wafers when subjected to illuminated annealing at 75°C. This comprehensive analysis encompassed the assessment of both surface and bulk properties. The degradation behavior was thoroughly examined through the utilization of opto-electrical characterization techniques. Photoluminescence intensity variations indicate an expansion of defective regions with prolonged light soaking in both c-Si and mc-Si samples. However, the regeneration observed in PL intensity and effective minority carrier lifetime is less pronounced in mc-Si samples compared to c-Si samples. This disparity can be attributed to the higher density of crystallographic defects and metallic impurities present in mc-Si samples. The analysis of recombination characteristics for both surface and bulk regions reveals distinct responses during illuminated annealing. Bulk recombination plays a dominant role and initially deteriorates within the first 24 hours but subsequently regenerates as the duration of light soaking increases. In contrast, the emitter surface exhibits improved performance for both c-Si and mc-Si compared to its initial state, primarily due to hydrogen diffusion. Notably, when the light soaking extends beyond 24 hours, c-Si samples show increased surface recombination, hinting at the potential formation of LeTID-related defects. However, this phenomenon is not observed in the emitter surface of mc-Si, even after 125 hours of light soaking, suggesting the absence of LeTID-related defect formation at the emitter surface. This study underscores that the emitter not only contributes to bulk regeneration but also significantly influences surface behavior.

Indeed, this study thoroughly investigated how the performance parameters of both monocrystalline and multicrystalline silicon solar cells change when subjected to elevated temperatures during illumination. Interestingly, monocrystalline solar cells exhibit more significant degradation but also demonstrate more effective regeneration in key performance parameters: open circuit voltage (V_{OC}), short circuit current density (J_{SC}) and fill factor (FF) are observed for monocrystalline solar cells. The Suns-V_{OC} measurements have provided compelling evidence that the recombination current densities within both the space charge region (J_{02}) and the remaining areas of the solar cell (J_{01}) play pivotal roles in the phenomenon of light and elevated temperature-induced degradation (LeTID) and subsequent regeneration characteristics. Throughout the degradation phase, substantial changes are evident in both J_{01} and J_{02} for both monocrystalline and multicrystalline solar cells. It's important to highlight that during the regeneration phase, a significant decrease in J_{02} is observed exclusively in monocrystalline solar cells, while J_{01} exhibits improvements in both types of cells. An analysis of FF loss indicates that recombination in the space charge region is primarily responsible for both degradation and regeneration in FF.

In contrast to many prior studies, our research reports a similar reduction in external quantum efficiency (EQE) at wavelengths of 984 nm, 877 nm, and 658 nm. This suggests that defects associated with LeTID are not limited solely to the deep bulk but are distributed throughout the bulk of the material. The absence of any EQE improvement after prolonged exposure to light and heat implies that defect transformation and gettering processes are not adequate to fully restore J_{SC} in multicrystalline solar cells. Furthermore, EQE mapping at 407 nm suggests that the LeTID behavior of the emitter differs from that of the bulk.

Many of the suggested high-efficiency solar cell designs, such as SHJ, TOPCon solar cells etc., employ an n-type base material and hydrogen-rich passivation layers, which means their performance may be compromised in real-world conditions due to defects associated with hydrogen and oxygen. The investigation of recombination characteristics and the application of spectroscopic analysis presented in this study hold promise for gaining insights into defect physics, understanding the underlying degradation mechanisms, and creating models for the degradation processes in high-efficiency solar cell architectures.

9.2 Future scope of the thesis

As per the ITRPV 2023 report, p-type passivated emitter rear cells (PERC) currently dominate other cell types in terms of market share. Projecting into 2033, the forecast anticipates tunnel oxide passivated contact (TOPCon) solar cells will constitute 60% of the market share, with silicon heterojunction (SHJ) solar cells closely following at 19%. TOPCon solar cells are attracting increased attention due to their various advantages, such as the ready availability of raw materials, a straightforward process sequence, and the potential for achieving high efficiency. However, these high-efficiency solar cell designs use hydrogen-rich layers as a surface passivation layer and an anti-reflection coating. Recognizing the significance of understanding

the impact of hydrogen-induced defects on the performance degradation of these cell structures during normal operating conditions, conducting a thorough study in this domain becomes imperative. This research plays a critical role in further enhancing the efficiency of these solar cells.

From a reliability perspective, it is worthwhile to investigate the recombination characteristics of solar cell structures over extended light soaking durations, potentially reaching up to 1000 hours. Recent reports suggest that surface-related defects primarily influence the longterm stability of solar cells. Given that SiO₂ film acts as a barrier against hydrogen diffusion and SiO₂/SiN_X : H stack serves as a passivation layer for solar cells, it is valuable to explore the impact of LeTID in such solar cells while varying the SiO₂ thickness.

In today's silicon photovoltaic industry, Ga-doped Si wafers are commonly utilized due to their high bulk lifetime. However, limited literature is available regarding the effects of light and heat on the performance stability of Ga-doped solar cells. Consequently, a more comprehensive analysis of the recombination characteristics in Ga-doped solar cells is necessary. Furthermore, it is essential to investigate the LeTID behavior of Cu/Ni contact solar cells and compare them with solar cells featuring Ag contacts.

Appendix A

Variation in solar irradiance, temperature, humidity and wind speed

Light soaking of the samples described in Chapter 6 was done outdoors at the NCPRE PV module monitoring station in Mumbai, India, in January, February, and March of 2020. The variation in solar irradiance and temperature from 10.00 am to 4.00 pm of each day of light soaking is provided in Figure A.1. The maximum, average, and minimum values of humidity in



Figure A.1: Variation in solar irradiance from 10.00 am to 4.00 pm for the days on which light soaking is carried out. Both these sets of data are reordered at the site of the experiment using a PV module monitoring station.

Mumbai, India, are also provided in Figure A.2. The humidity data provided was not recorded at the experiment site but at a location 7.55 km away from the experiment site.



Figure A.2: Variation in the maximum, average, and minimum value of ambient humidity and windspeed for the days on which light soaking is carried out. The humidity and wind data are recorded at a site 7.55 km away from the experiment site.

Appendix B

Quantification of defects in Si wafers

B.1 Estimation of oxygen concentration in Si wafers

The infrared absorption measurements at the characteristics peak of oxygen at the 9 μ m band (wave number is 1107 cm⁻¹) are used for quantitative analysis of oxygen in silicon. This peak is due to the silicon-oxygen bond stretching vibration. The absorption coefficient can be obtained from the characteristic peaks of oxygen (1107 cm⁻¹). The absorption is related to the silicon-oxygen bond stretching vibration and hence the oxygen concentration in the sample. The absorption coefficient due to oxygen is calculated based on ASTM standard 1188, as described below.

- 1. The transmittance (T_p) of the sample wafers at 1107.08 cm⁻¹ is determined by fitting the five data points (data point at 1107.08 cm⁻¹, two data points on the right and two data points on the left) using the least square method.
- 2. The baseline transmittance (T_b) is calculated by fitting six data points (the data point at 1299.9 cm⁻¹ and the two neighboring data points as well as the data point at 940cm⁻¹ and the two neighboring data points) using the least squares method.
- 3. The absorption coefficient due to interstitial oxygen $\alpha_0 = = \alpha_p \alpha_b$. α_p and α_b are calculated using the Eq.B.1 and B.2.

4. The concentration of interstitial oxygen is estimated by multiplying the absorbance by a conversion coefficient 3.14×10^{17} .

$$\alpha_{\rm p} = -\frac{1}{\rm W} \ln \left(\frac{0.09 - e^{1.7\rm W} + \sqrt{(0.09 - e^{1.7\rm W})^2 + 0.36\rm T_p^2 e^{1.7\rm W}}}{0.18\rm T_p} \right) \tag{B.1}$$

$$\alpha_{\rm b} = -\frac{1}{\rm W} \ln \left(\frac{0.09 - e^{1.7\rm W} + \sqrt{(0.09 - e^{1.7\rm W})^2 + 0.36\rm T_b^2 e^{1.7\rm W}}}{0.18\rm T_b} \right) \tag{B.2}$$

where α_p is peak absorption coefficient (cm⁻¹), α_b is baseline absorption coefficient (cm⁻¹), W is thickness (cm), T_p is peak transmittance and T_b baseline transmittance.

B.2 Estimation of hydrogen concentration in Si wafers

The total hydrogen concentration is estimated from the area under the absorbance spectra of the S–H bond measured using FTIR spectra. The equation Eq.B.3 relate the concentration of Si–H bonds per cm⁻³.

$$[Si-H] = \frac{Si-H_{Area}}{7.4 \times 10^{18} \times W}$$
(B.3)

where $Si-H_{Area}$ is the area under the S-H vibrational peak centered at 2160 cm⁻¹. It is obtained by multiplying peak absorbance and full width at half maximum (FWHM), and W is the thickness (cm).

B.3 Estimation of electrically active iron concentration in multicrystalline Si wafers

Electrically active Fe concentration and its spatial distribution in multicrystalline Si samples were estimated based on lifetime characterization before and after light soaking as given in Eq.B.4 [234].

$$Fe_i = C * \left(\frac{1}{\tau_{Fe}} - \frac{1}{\tau_{FeB}}\right)$$
(B.4)

where τ_{FeB} and τ_{Fe} represent the measured effective lifetime before and after dissociation of the FeB pair by flash lighting. Factor C depends on the doping density, excess carrier concentration,

and proportion of Fe present as Fe and FeB pair. The value of C can be evaluated as given in Eq.B.5 [68].

$$C(\Delta n) = \frac{1}{X_{Fe} - X_{FeB}}$$
(B.5)

$$X_{Fe} = \frac{(p_0 + \Delta n)v_{th}}{\frac{1}{\sigma_{n,Fe}}(\Delta_n + n_{1FeB}) + \frac{1}{\sigma_{p,Fe}}(p_0 + \Delta n + p_{1FeB})},$$
(B.6)

$$X_{\text{FeB}} = \frac{(p_0 + \Delta n)v_{\text{th}}}{\frac{1}{\sigma_{n,\text{FeB}}}(\Delta_n + n_{1\text{Fe}}) + \frac{1}{\sigma_{p,\text{FeB}}}(p_0 + \Delta n + p_{1\text{Fe}})}$$
(B.7)

where $\sigma_{p,Fe}$ and $\sigma_{p,FeB}$ are capture cross section of the defects Fe and FeB respectively (cm²). n_{1FeB} and p_{1FeB} are the SRH defect density terms for the defect FeB (cm⁻³). n_{1Fe} and p_{1Fe} are the SRH defect density terms for the defect Fe (cm⁻³). The defect density terms are calculated using the defect parameters specified in Table 3.1 in subsection 3.1.1 [234].

For measuring the electrically active concentration of Fe, 6-inch diamond wire-sawn multicrystalline Si wafers of 280 μ m thick and 1-3 Ω cm were used. They were then textured using the acid texturing method to enhance the light rapping. Nine samples of size 2 inch \times 2 inch were cut from each wafer using laser cutting. These samples were RCA cleaned and then passivated by using a QHM solution. The passivation solution was prepared by dissolving 1.5g of quinhydrone in 100 ml of methanol. The samples were kept in the passivation solution for about 60 min to allow sufficient time for the sample surface to get passivated. Lifetime characterization was then done by keeping the sample in a polythene zip lock bag containing QHM solution using the Sinton Lifetime Tester and PL imaging imaging tool from Great Eyes.

Since most of the Fe in p-type Si exist in the form of FeB complex, the measured lifetime is mainly determined by the SRH recombination centers due to FeB defect. The FeB pair can be dissociated by subjecting the samples to highly intense illumination. The dissociation of the FeB pair was accomplished using 50 flashes (maximum intensity of about 33 suns) emitted from the flash head of the Sinton Instrument [234]. The samples were characterized before and after light soaking using lifetime measurement and PL imaging. According to Macdonald et al., the presence of Fe in Si samples can be confirmed by a crossover point [234]. It is defined as the excess carrier density at which the carrier lifetime in crystalline silicon remains unchanged after dissociating FeB pairs. The crossover point occurs at $\Delta n = 10^{14}$ cm⁻³ when the doping concentration of the sample is less than 10^{17} cm⁻³ [234].



Figure B.1: Effective lifetime variations in a p-type multicrystalline Si sample as a function of excess carrier density before and after light dissociation of FeB.



Figure B.2: Estimated electrically active average Fe concentration in multicrystalline Si samples.

The presence of Fe in p-type multicrystalline Si samples used in this study was confirmed using inductively coupled plasma mass spectroscopy. It was further confirmed by the presence of crossover in the lifetime characteristics as shown in Figure B.1. From lifetime measurement before and after dissociation, the average Fe concentration present in the sample is estimated using Eq.B.5. The concentration of electrically active Fe was found to be in the range of 3.3×10^{10} cm⁻³ to 2.8×10^{11} cm⁻³ for the multicrystalline Si samples as shown in Figure B.2. The open square and horizontal lines in Figure B.2 correspond to the mean and median, respectively, of the data points. PL imaging before and after dissociation gives spatial distribution of the Fe



Figure B.3: PL image showing the distribution of electrically active Fe concentration across the multicrystalline Si sample.

across the sample [235]. The distribution of Fe concentration across the samples was also estimated from the lifetime map of samples obtained using PL imaging as shown in Figure B.3.

Bibliography

- M. A. Green, E. D. Dunlop, G. Siefer, M. Yoshita, N. Kopidakis, K. Bothe, and X. Hao, "Solar cell efficiency tables (version 61)," *Progress in Photovoltaics: Research and Applications*, vol. 31, no. 1, pp. 3–16, 2023.
- [2] "Canadian solar sets a 23.81% conversion efficiency world record for n-type large area multi-crystalline silicon solar cell." https://www.prnewswire.com/newsreleases/canadian-solar-sets-a-23-81-conversion-efficiency-world-record-for-n-typelarge-area-multi-crystalline-silicon-solar-cell-301018856.html, 2023. Accessed on Dec 2023.
- [3] C. Claeys and E. Simoen, *Characterization and Detection of Metals in Silicon and Germanium: Origin, Characterization, Control, and Device Impact*, pp. 75–123. 2018.
- [4] K. Graff, *Metal impurities in silicon-device fabrication*, vol. 24. Springer Science & Business Media, 2013.
- [5] A. A. Istratov and E. R. Weber, "Physics of copper in silicon," *Journal of The Electrochemical Society*, vol. 149, no. 1, p. G21, 2001.
- [6] G. Gaspar, C. Modanese, H. Schøn, M. Di Sabatino, L. Arnberg, and E. J. Øvrelid, "Influence of copper diffusion on lifetime degradation in n-type czochralski silicon for solar cells," *Energy Procedia*, vol. 77, pp. 586–591, 2015. 5th International Conference on Silicon Photovoltaics, SiliconPV 2015.
- [7] W. Wang, Z. Xi, D. Yang, and D. Que, "Recombination activity of nickel in czochralski silicon during rapid thermal process," *Materials Science in Semiconductor Processing*, vol. 9, no. 1, pp. 296–299, 2006. 11th International Conference on Defects - Recognition Imaging and Physics in Semiconductors (DRIP-XI)Sept. 13-19 in Beijing.

- [8] T. Buonassisi, M. A. Marcus, A. A. Istratov, M. Heuer, T. F. Ciszek, B. Lai, Z. Cai, and E. R. Weber, "Analysis of copper-rich precipitates in silicon: Chemical state, gettering, and impact on multicrystalline silicon solar cell material," *Journal of Applied Physics*, vol. 97, no. 6, p. 063503, 2005.
- [9] C. Rudolf, P. Saring, L. Stolze, and M. Seibt, "Co-precipitation of copper and nickel in crystalline silicon," *Materials Science and Engineering: B*, vol. 159-160, pp. 365– 368, 2009. EMRS 2008 Spring Conference Symposium K: Advanced Silicon Materials Research for Electronic and Photovoltaic Applications.
- [10] A. Mondon, J. Bartsch, M. Kamp, A. Brand, B. Steinhauser, N. Bay, J. Horzel, M. Glatthaar, and S. Glunz, "Plated nickel-copper contacts on c-si: from microelectronic processing to cost effective silicon solar cell production," 2014.
- [11] S. Kluska, J. Bartsch, A. Büchler, G. Cimiotti, A. A. Brand, S. Hopman, and M. Glatthaar, "Electrical and mechanical properties of plated ni/cu contacts for si solar cells," *Energy Procedia*, vol. 77, pp. 733–743, 2015. 5th International Conference on Silicon Photovoltaics, SiliconPV 2015.
- [12] "International technology roadmap for photovoltaic." https://www.vdma.org/ international-technology-roadmap-photovoltaic. Accessed: Jul 20, 2024.
- [13] D. Bredemeier, D. C. Walter, and J. Schmidt, "Possible candidates for impurities in mc-si wafers responsible for light-induced lifetime degradation and regeneration," *Solar RRL*, vol. 2, no. 1, p. 1700159, 2018.
- [14] J. Schmidt, D. Bredemeier, and D. C. Walter, "On the defect physics behind light and elevated temperature-induced degradation (letid) of multicrystalline silicon solar cells," *IEEE Journal of Photovoltaics*, vol. 9, no. 6, pp. 1497–1503, 2019.
- [15] F. Kersten, P. Engelhart, H.-C. Ploigt, A. Stekolnikov, T. Lindner, F. Stenzel, M. Bartzsch, A. Szpeth, K. Petter, J. Heitmann, and J. W. Müller, "Degradation of multicrystalline silicon solar cells and modules after illumination at elevated temperature," *Solar Energy Materials and Solar Cells*, vol. 142, pp. 83–86, 2015. Proceedings of the 5th International Conference on Crystalline Silicon Photovoltaics (SiliconPV 2015).

- [16] F. Kersten, F. Fertig, K. Petter, B. Klöter, E. Herzog, M. B. Strobel, J. Heitmann, and J. W. Müller, "System performance loss due to letid," *Energy Procedia*, vol. 124, pp. 540–546, 2017. 7th International Conference on Silicon Photovoltaics, SiliconPV 2017, 3-5 April 2017, Freiburg, Germany.
- [17] K. Petter, K. Hubener, F. Kersten, M. Bartzsch, F. Fertig, B. Kloter, and J. Muller, "Dependence of letid on brick height for different wafer suppliers with several resistivities and dopants," *9th Int. Work. Cryst. Silicon Sol. Cells*, vol. 6, no. 4, pp. 1–17, 2016.
- [18] D. Sperber, A. Heilemann, A. Herguth, and G. Hahn, "Temperature and light-induced changes in bulk and passivation quality of boron-doped float-zone silicon coated with sinx:h," *IEEE Journal of Photovoltaics*, vol. 7, no. 2, pp. 463–470, 2017.
- [19] D. Chen, M. Kim, B. V. Stefani, B. J. Hallam, M. D. Abbott, C. E. Chan, R. Chen, D. N. Payne, N. Nampalli, A. Ciesla, T. H. Fung, K. Kim, and S. R. Wenham, "Evidence of an identical firing-activated carrier-induced defect in monocrystalline and multicrystalline silicon," *Solar Energy Materials and Solar Cells*, vol. 172, pp. 293–300, 2017.
- [20] H. C. Sio, H. Wang, Q. Wang, C. Sun, W. Chen, H. Jin, and D. Macdonald, "Light and elevated temperature induced degradation in p-type and n-type cast-grown multicrystalline and mono-like silicon," *Solar Energy Materials and Solar Cells*, vol. 182, pp. 98–104, 2018.
- [21] D. Chen, P. G. Hamer, M. Kim, T. H. Fung, G. Bourret-Sicotte, S. Liu, C. E. Chan, A. Ciesla, R. Chen, M. D. Abbott, B. J. Hallam, and S. R. Wenham, "Hydrogen induced degradation: A possible mechanism for light- and elevated temperature- induced degradation in n-type silicon," *Solar Energy Materials and Solar Cells*, vol. 185, pp. 174–182, 2018.
- [22] D. Chen, P. Hamer, M. Kim, C. Chan, A. Ciesla nee Wenham, F. Rougieux, Y. Zhang, M. Abbott, and B. Hallam, "Hydrogen-induced degradation: Explaining the mechanism behind light- and elevated temperature-induced degradation in n- and p-type silicon," *Solar Energy Materials and Solar Cells*, vol. 207, p. 110353, 2020.
- [23] D. Kang, H. C. Sio, X. Zhang, J. Yang, J. Jin, and D. Macdonald, "Light and elevated temperature induced degradation in mono-like and float-zone silicon: Correlations to ma-

terial types, silicon nitride films, and dopant diffusion," *IEEE Journal of Photovoltaics*, vol. 11, no. 5, pp. 1167–1175, 2021.

- [24] G. Krugel, W. Wolke, J. Geilker, S. Rein, and R. Preu, "Impact of hydrogen concentration on the regeneration of light induced degradation," *Energy Procedia*, vol. 8, pp. 47–51, 2011. Proceedings of the SiliconPV 2011 Conference (1st International Conference on Crystalline Silicon Photovoltaics).
- [25] A. C. n. Wenham, S. Wenham, R. Chen, C. Chan, D. Chen, B. Hallam, D. Payne, T. Fung, M. Kim, S. Liu, S. Wang, K. Kim, A. Samadi, C. Sen, C. Vargas, U. Varshney, B. V. Stefani, P. Hamer, G. Bourret-Sicotte, N. Nampalli, Z. Hameiri, C. Chong, and M. Abbott, "Hydrogen-induced degradation," in 2018 IEEE 7th World Conference on Photovoltaic Energy Conversion (WCPEC) (A Joint Conference of 45th IEEE PVSC, 28th PVSEC 34th EU PVSEC), pp. 0001–0008, 2018.
- [26] M. A. Jensen, A. Zuschlag, S. Wieghold, D. Skorka, A. E. Morishige, G. Hahn, and T. Buonassisi, "Evaluating root cause: The distinct roles of hydrogen and firing in activating light- and elevated temperature-induced degradation," *Journal of Applied Physics*, vol. 124, no. 8, p. 085701, 2018.
- [27] R. Eberle, W. Kwapil, F. Schindler, M. C. Schubert, and S. W. Glunz, "Impact of the firing temperature profile on light induced degradation of multicrystalline silicon," *physica status solidi (RRL) – Rapid Research Letters*, vol. 10, no. 12, pp. 861–865, 2016.
- [28] A. Zuschlag, D. Skorka, and G. Hahn, "Degradation and regeneration in mc-si after different gettering steps," *Progress in Photovoltaics : Research and Applications*, vol. 25, no. 7, pp. 545–552, 2017.
- [29] D. Bredemeier, D. C. Walter, R. Heller, and J. Schmidt, "Impact of hydrogen-rich silicon nitride material properties on light-induced lifetime degradation in multicrystalline silicon," *physica status solidi (RRL) – Rapid Research Letters*, vol. 13, no. 8, p. 1900201, 2019.
- [30] C. Sen, P. Hamer, A. Soeriyadi, B. Wright, M. Wright, A. Samadi, D. Chen, B. V. Stefani,D. Zhang, J. Wu, F. Jiang, B. Hallam, and M. Abbott, "Impact of surface doping profile

and passivation layers on surface-related degradation in silicon perc solar cells," *Solar Energy Materials and Solar Cells*, vol. 235, p. 111497, 2022.

- [31] D. Bredemeier, D. Walter, S. Herlufsen, and J. Schmidt, "Lifetime degradation and regeneration in multicrystalline silicon under illumination at elevated temperature," *AIP Advances*, vol. 6, no. 3, p. 035119, 2016.
- [32] C. E. Chan, D. N. R. Payne, B. J. Hallam, M. D. Abbott, T. H. Fung, A. M. Wenham, B. S. Tjahjono, and S. R. Wenham, "Rapid stabilization of high-performance multicrystalline p-type silicon perc cells," *IEEE Journal of Photovoltaics*, vol. 6, no. 6, pp. 1473–1479, 2016.
- [33] C. Vargas, K. Kim, G. Coletti, D. Payne, C. Chan, S. Wenham, and Z. Hameiri, "Carrierinduced degradation in multicrystalline silicon: Dependence on the silicon nitride passivation layer and hydrogen released during firing," *IEEE Journal of Photovoltaics*, vol. 8, no. 2, pp. 413–420, 2018.
- [34] U. Varshney, M. Abbott, A. Ciesla, D. Chen, S. Liu, C. Sen, M. Kim, S. Wenham, B. Hoex, and C. Chan, "Evaluating the impact of sinx thickness on lifetime degradation in silicon," *IEEE Journal of Photovoltaics*, vol. 9, no. 3, pp. 601–607, 2019.
- [35] J. Lindroos, A. Zuschlag, D. Skorka, and G. Hahn, "Silicon nitride deposition: Impact on lifetime and light-induced degradation at elevated temperature in multicrystalline silicon," *IEEE Journal of Photovoltaics*, vol. 10, no. 1, pp. 8–18, 2020.
- [36] F. Kersten, J. Heitmann, and J. W. Müller, "Influence of al2o3 and sinx passivation layers on letid," *Energy Procedia*, vol. 92, pp. 828–832, 2016. Proceedings of the 6th International Conference on Crystalline Silicon Photovoltaics (SiliconPV 2016).
- [37] C. Sen, C. Chan, P. Hamer, M. Wright, C. Chong, B. Hallam, and M. Abbott, "Eliminating light- and elevated temperature-induced degradation in p-type perc solar cells by a two-step thermal process," *Solar Energy Materials and Solar Cells*, vol. 209, p. 110470, 2020.
- [38] C. Winter, A. Zuschlag, D. Skorka, and G. Hahn, "Influence of dielectric layers and thermal load on LeTID," *AIP Conference Proceedings*, vol. 1999, no. 1, p. 130020, 2018.

- [39] K. Krauß, A. A. Brand, F. Fertig, S. Rein, and J. Nekarda, "Fast regeneration processes to avoid light-induced degradation in multicrystalline silicon solar cells," *IEEE Journal* of Photovoltaics, vol. 6, no. 6, pp. 1427–1431, 2016.
- [40] F. Maischner, S. Maus, J. Greulich, S. Lohmüller, E. Lohmüller, P. Saint-Cast, D. Ourinson, H. Vahlman, K. Hergert, S. Riepe, S. Glunz, and S. Rein, "Letid mitigation via an adapted firing process in p-type perc cells from smart cast-monocrystalline, czochralski and high-performance multicrystalline silicon," *Progress in Photovoltaics: Research and Applications*, vol. 30, no. 2, pp. 123–131, 2022.
- [41] K. Kim, R. Chen, D. Chen, P. Hamer, A. Ciesla nee Wenham, S. Wenham, and Z. Hameiri, "Degradation of surface passivation and bulk in p-type monocrystalline silicon wafers at elevated temperature," *IEEE Journal of Photovoltaics*, vol. 9, no. 1, pp. 97– 105, 2019.
- [42] W. Kwapil, T. Niewelt, and M. C. Schubert, "Kinetics of carrier-induced degradation at elevated temperature in multicrystalline silicon solar cells," *Solar Energy Materials and Solar Cells*, vol. 173, pp. 80–84, 2017. Proceedings of the 7th international conference on Crystalline Silicon Photovoltaics.
- [43] Z. Hu, Q. He, S. Yuan, D. Lin, L. Song, X. Yu, and D. Yang, "Kinetics study on carrier injection-induced degradation and regeneration at elevated temperature in p-type cast-monosilicon passivated emitter rear contact solar cells," *Solar RRL*, vol. 5, no. 7, p. 2100035, 2021.
- [44] N. Wehmeier, G. Fischer, S. Herlufsen, F. Wolny, M. Wagner, K. Bothe, and M. Müller, "Kinetics of the light and elevated temperature induced degradation and regeneration of quasi-monocrystalline silicon solar cells," *IEEE Journal of Photovoltaics*, vol. 11, no. 4, pp. 890–896, 2021.
- [45] J.-R. Huang, Y.-F. Lin, K. Liang, S. Su, S. H. Chen, and L.-W. Cheng, "Investigation of light-induced regeneration phenomena on p-type cz perc cells," in 2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC), pp. 1–3, 2015.
- [46] M. Padmanabhan, K. Jhaveri, R. Sharma, P. K. Basu, S. Raj, J. Wong, and J. Li, "Lightinduced degradation and regeneration of multicrystalline silicon al-bsf and perc solar

cells," *physica status solidi (RRL) – Rapid Research Letters*, vol. 10, no. 12, pp. 874–881, 2016.

- [47] E. Cho, A. Rohatgi, and Y.-W. Ok, "Comparison of light-induced degradation and regeneration in p-type monocrystalline full aluminum back surface field and passivated emitter rear cells," *Current Applied Physics*, vol. 18, no. 12, pp. 1600–1604, 2018.
- [48] Z. Hu, L. Song, D. Lin, T. Zhao, Q. He, S. Yuan, X. Yu, and D. Yang, "The effect and mechanism of current injection to suppress light and elevated temperature induced degradation in p-type cast-mono and multicrystalline silicon passivated emitter and rear cells," *Solar Energy*, vol. 235, pp. 12–18, 2022.
- [49] C. Xiao, S. Johnston, C.-S. Jiang, V. LaSalvia, D. B. Sulas-Kern, M. D. Kempe, D. L. Young, D. C. Jordan, M. M. Al-Jassim, and I. Repins, "Long-term degradation of passivated emitter and rear contact silicon solar cell under light and heat," *Solar RRL*, vol. 6, no. 1, p. 2100727, 2022.
- [50] J. Nelson, *The Physics of Solar Cells*. Imperial College Press and Distributed by World Scientific Publishing Co., 2003.
- [51] M. Wolf, G. Noel, and R. Stirn, "Investigation of the double exponential in the current—voltage characteristics of silicon solar cells," *IEEE Transactions on Electron Devices*, vol. 24, no. 4, pp. 419–428, 1977.
- [52] J. P. Charles, G. Bordure, A. Khoury, and P. Mialhe, "Consistency of the double exponential model with physical mechanisms of conduction for a solar cell under illumination," *Journal of Physics D: Applied Physics*, vol. 18, no. 11, p. 2261, 1985.
- [53] U. Stutenbaeumer and B. Mesfin, "Equivalent model of monocrystalline, polycrystalline and amorphous silicon solar cells," *Renewable Energy*, vol. 18, no. 4, pp. 501–512, 1999.
- [54] T. Markvart and L. Castañer, "Chapter i-1-a principles of solar cell operation," in *McEvoy's Handbook of Photovoltaics (Third Edition)* (S. A. Kalogirou, ed.), pp. 3–28, Academic Press, third edition ed., 2018.
- [55] K. K. N. S.M. Sze, Physics of semiconductor devices. John Wiley Sons, 2006.

- [56] R. F. Pierret, Advanced semiconductor fundamentals. USA: Addison-Wesley Longman Publishing Co., Inc., 1987.
- [57] R. Braunstein, "Radiative transitions in semiconductors," *Physical Review*, vol. 99, pp. 1892–1893, 1955.
- [58] J. Haynes, M. Lax, and W. Flood, "Analysis of intrinsic recombination radiation from silicon and germanium," *Journal of Physics and Chemistry of Solids*, vol. 8, pp. 392– 396, 1959.
- [59] W. Michaelis and M. H. Pilkuhn, "Radiative recombination in silicon p-n junctions," *physica status solidi* (b), vol. 36, no. 1, pp. 311–319, 1969.
- [60] T. Trupke, M. A. Green, P. Würfel, P. P. Altermatt, A. Wang, J. Zhao, and R. Corkish, "Temperature dependence of the radiative recombination coefficient of intrinsic crystalline silicon," *Journal of Applied Physics*, vol. 94, no. 8, pp. 4930–4937, 2003.
- [61] G. W. Hooft, "The radiative recombination coefficient of GaAs from laser delay measurements and effective nonradiative carrier lifetimes," *Applied Physics Letters*, vol. 39, no. 5, pp. 389–390, 1981.
- [62] A. Richter, S. W. Glunz, F. Werner, J. Schmidt, and A. Cuevas, "Improved quantitative description of auger recombination in crystalline silicon," *Physical Review B*, vol. 86, p. 165202, 2012.
- [63] J. Dziewior and W. Schmid, "Auger coefficients for highly doped and highly excited silicon," *Applied Physics Letters*, vol. 31, no. 5, pp. 346–348, 1977.
- [64] A. Hangleiter and R. Häcker, "Enhancement of band-to-band auger recombination by electron-hole correlations," *Physical Review Lett.*, vol. 65, pp. 215–218, 1990.
- [65] P. P. Altermatt, J. Schmidt, G. Heiser, and A. G. Aberle, "Assessment and parameterisation of Coulomb-enhanced Auger recombination coefficients in lowly injected crystalline silicon," *Journal of Applied Physics*, vol. 82, no. 10, pp. 4938–4944, 1997.
- [66] M. J. Kerr and A. Cuevas, "General parameterization of Auger recombination in crystalline silicon," *Journal of Applied Physics*, vol. 91, no. 4, pp. 2473–2480, 2002.

- [67] H. H. W. E. Istratov, A., "Iron and its complexes in silicon," *Applies Physics A*, vol. 69, pp. 13–44, 1999.
- [68] D. Macdonald and L. J. Geerligs, "Recombination activity of interstitial iron and other transition metal point defects in p- and n-type crystalline silicon," *Applied Physics Letters*, vol. 85, pp. 4061–4063, 11 2004.
- [69] A. Carvalho, P. Santos, J. Coutinho, R. Jones, M. J. Rayson, and P. R. Briddon, "Light induced degradation in b doped cz-si solar cells," *physica status solidi (a)*, vol. 209, no. 10, pp. 1894–1897, 2012.
- [70] T. Niewelt, J. Schön, J. Broisch, W. Warta, and M. Schubert, "Electrical characterization of the slow boron oxygen defect component in czochralski silicon," *physica status solidi* (*RRL*) – *Rapid Research Letters*, vol. 9, no. 12, pp. 692–696, 2015.
- [71] T. Niewelt, J. Schön, W. Warta, S. W. Glunz, and M. C. Schubert, "Degradation of crystalline silicon due to boron–oxygen defects," *IEEE Journal of Photovoltaics*, vol. 7, no. 1, pp. 383–398, 2017.
- [72] J. Vanhellemont, A. Kaniava, M. Libezny, E. Simoen, and C. Claeys, "On the recombination activity of oxygen precipitation related lattice defects in silicon," *MRS Online Proceedings Library*, vol. 378, p. 35–40, 2011.
- [73] J. Murphy, R. McGuire, K. Bothe, V. Voronkov, and R. Falster, "Minority carrier lifetime in silicon photovoltaics: The effect of oxygen precipitation," *Solar Energy Materials and Solar Cells*, vol. 120, pp. 402–411, 2014.
- [74] W. Shockley and W. T. Read, "Statistics of the recombinations of holes and electrons," *Physical Review*, vol. 87, pp. 835–842, 1952.
- [75] R. Hezel and K. Jaeger, "Low-temperature surface passivation of silicon for solar cells," *Journal of The Electrochemical Society*, vol. 136, no. 2, p. 518, 1989.
- [76] C. Leguijt, P. Lölgen, J. Eikelboom, A. Weeber, F. Schuurmans, W. Sinke, P. Alkemade,
 P. Sarro, C. Marée, and L. Verhoef, "Low temperature surface passivation for silicon solar cells," *Solar Energy Materials and Solar Cells*, vol. 40, no. 4, pp. 297–345, 1996.

- [77] P. Gruenbaum, J. Gan, R. King, and R. Swanson, "Stable passivations for high-efficiency silicon solar cells," in *IEEE Conference on Photovoltaic Specialists*, pp. 317–322 vol.1, 1990.
- [78] A. W. Stephens, A. G. Aberle, and M. A. Green, "Surface recombination velocity measurements at the silicon–silicon dioxide interface by microwave-detected photoconductance decay," *Journal of Applied Physics*, vol. 76, no. 1, pp. 363–370, 1994.
- [79] K. Jaeger and R. Hezel, "A novel thin silicon solar cell with al2o3 as surface passivation," in 18th IEEE Photovoltaic Specialists Conference, p. 1752–1753, 1985.
- [80] B. Hoex, S. B. S. Heil, E. Langereis, M. C. M. van de Sanden, and W. M. M. Kessels, "Ultralow surface recombination of c-Si substrates passivated by plasma-assisted atomic layer deposited Al2O3," *Applied Physics Letters*, vol. 89, no. 4, p. 042112, 2006.
- [81] H. Takato, I. Sakata, and R. Shimokawa, "Surface passivation of silicon substrates using quinhydrone/methanol treatment," in *Proceedings of 3rd World Conference on Photovoltaic Energy Conversion*, 2003., vol. 2, pp. 1108–1111 Vol.2, 2003.
- [82] B. Chhabra, S. Bowden, R. L. Opila, and C. B. Honsberg, "High effective minority carrier lifetime on silicon substrates using quinhydrone-methanol passivation," *Applied Physics Letters*, vol. 96, no. 6, p. 063502, 2010.
- [83] R. Har-Lavan, R. Schreiber, O. Yaffe, and D. Cahen, "Molecular field effect passivation: Quinhydrone/methanol treatment of n-Si(100)," *Journal of Applied Physics*, vol. 113, no. 8, p. 084909, 2013.
- [84] N. Grant, K. McIntosh, J. Tan, F. Rougieux, J. Bullock, Y. Wan, and C. Barugkin, "Light enhanced hydrofluoric acid passivation for evaluating silicon bulk lifetimes," in *Proceedings of 28th European Photovoltaic Solar Energy Conference and Exhibition Paris, France*, p. 883–887, 2013.
- [85] J. Bullock, D. Kiriya, N. Grant, A. Azcatl, M. Hettick, T. Kho, P. Phang, H. C. Sio, D. Yan, D. Macdonald, M. A. Quevedo-Lopez, R. M. Wallace, A. Cuevas, and A. Javey, "Superacid passivation of crystalline silicon surfaces," *ACS Applied Materials & Interfaces*, vol. 8, no. 36, pp. 24205–24211, 2016. PMID: 27553365.

- [86] R. S. Bonilla and P. R. Wilshaw, "A technique for field effect surface passivation for silicon solar cells," *Applied Physics Letters*, vol. 104, no. 23, p. 232903, 2014.
- [87] R. S. Bonilla, C. Reichel, M. Hermle, and P. R. Wilshaw, "Corona field effect surface passivation of n-type ibc cells," *Energy Procedia*, vol. 92, pp. 336–340, 2016. Proceedings of the 6th International Conference on Crystalline Silicon Photovoltaics (SiliconPV 2016).
- [88] M. J. Kerr and A. Cuevas, "Very low bulk and surface recombination in oxidized silicon wafers," *Semiconductor Science and Technology*, vol. 17, no. 1, p. 35, 2001.
- [89] R. S. Bonilla, C. Reichel, M. Hermle, P. Hamer, and P. R. Wilshaw, "Long term stability of c-si surface passivation using corona charged sio2," *Applied Surface Science*, vol. 412, pp. 657–667, 2017.
- [90] G. Bourret-Sicotte, P. Hamer, R. S. Bonilla, K. Collett, A. Ciesla, J. Colwell, and P. R. Wilshaw, "Shielded hydrogen passivation a potential in-line passivation process," *physica status solidi (a)*, vol. 214, no. 7, p. 1700383, 2017.
- [91] T. Mueller, S. Schwertheim, M. Scherff, and W. R. Fahrner, "High quality passivation for heterojunction solar cells by hydrogenated amorphous silicon suboxide films," *Applied Physics Letters*, vol. 92, no. 3, p. 033504, 2008.
- [92] T. Mueller, S. Schwertheim, and W. R. Fahrner, "Crystalline silicon surface passivation by high-frequency plasma-enhanced chemical-vapor-deposited nanocomposite silicon suboxides for solar cell applications," *Journal of Applied Physics*, vol. 107, no. 1, p. 014504, 2010.
- [93] N. E. Grant and K. R. McIntosh, "Low surface recombination velocities achieved by silicon dioxide grown electrochemically in nitric acid," in 2011 37th IEEE Photovoltaic Specialists Conference, pp. 003573–003576, 2011.
- [94] N. E. Grant and K. R. McIntosh, "Silicon surface passivation by anodic oxidation annealed at 400°c," *ECS Journal of Solid State Science and Technology*, vol. 3, no. 2, p. P13, 2013.
- [95] Y. Wan, K. R. McIntosh, and A. F. Thomson, "Characterisation and optimisation of PECVD SiNx as an antireflection coating and passivation layer for silicon solar cells," *AIP Advances*, vol. 3, no. 3, p. 032113, 2013.
- [96] A. Belghachi, "Detailed analysis of surface recombination in crystalline silicon solar cells," in 2013 International Renewable and Sustainable Energy Conference (IRSEC), pp. 161–166, 2013.
- [97] F. W. Chen, T.-t. A. Li, and J. E. Cotter, "Pecvd silicon nitride surface passivation for high-efficiency n-type silicon solar cells," in 2006 IEEE 4th World Conference on Photovoltaic Energy Conference, vol. 1, pp. 1020–1023, 2006.
- [98] Y. Wan, K. R. McIntosh, A. F. Thomson, and A. Cuevas, "Low surface recombination velocity by low-absorption silicon nitride on c-si," *IEEE Journal of Photovoltaics*, vol. 3, no. 1, pp. 554–559, 2013.
- [99] S. Duttagupta, Z. Hameiri, T. Grosse, D. Landgraf, B. Hoex, and A. G. Aberle, "Dielectric charge tailoring in pecvd sio_x/sin x stacks and application at the rear of al local back surface field si wafer solar cells," *IEEE Journal of Photovoltaics*, vol. 5, no. 4, pp. 1014–1019, 2015.
- [100] J. Schmidt and M. Kerr, "Highest-quality surface passivation of low-resistivity p-type silicon using stoichiometric pecvd silicon nitride," *Solar Energy Materials and Solar Cells*, vol. 65, no. 1, pp. 585–591, 2001. PVSEC 11 Part I.
- [101] Y. Larionova, V. Mertens, N.-P. Harder, and R. Brendel, "Surface passivation of n-type Czochralski silicon substrates by thermal-SiO2/plasma-enhanced chemical vapor deposition SiN stacks," *Applied Physics Letters*, vol. 96, no. 3, p. 032105, 2010.
- [102] R. S. Bonilla, F. Woodcock, and P. R. Wilshaw, "Very low surface recombination velocity in n-type c-Si using extrinsic field effect passivation," *Journal of Applied Physics*, vol. 116, no. 5, p. 054102, 2014.
- [103] Z. Chen, S. K. Pang, K. Yasutake, and A. Rohatgi, "Plasma-enhanced chemical-vapordeposited oxide for low surface recombination velocity and high effective lifetime in silicon," *Journal of Applied Physics*, vol. 74, no. 4, pp. 2856–2859, 1993.

- [104] G. Dingemans, M. M. Mandoc, S. Bordihn, M. C. M. van de Sanden, and W. M. M. Kessels, "Effective passivation of Si surfaces by plasma deposited SiOx/a-SiNx:H stacks," *Applied Physics Letters*, vol. 98, no. 22, p. 222102, 2011.
- [105] S. Duttagupta, F.-J. Ma, B. Hoex, and A. G. Aberle, "Extremely low surface recombination velocities on heavily doped planar and textured p+ silicon using low-temperature positively-charged pecvd siox/sinx dielectric stacks with optimised antireflective properties," in 2013 IEEE 39th Photovoltaic Specialists Conference (PVSC), pp. 1776–1780, 2013.
- [106] T. Mishima, M. Taguchi, H. Sakata, and E. Maruyama, "Development status of high-efficiency hit solar cells," *Solar Energy Materials and Solar Cells*, vol. 95, no. 1, pp. 18–21, 2011. 19th International Photovoltaic Science and Engineering Conference and Exhibition (PVSEC-19) Jeju, Korea, 9-13 November 2009.
- [107] Y. Wan, D. Yan, J. Bullock, X. Zhang, and A. Cuevas, "Passivation of c-Si surfaces by sub-nm amorphous silicon capped with silicon nitride," *Applied Physics Letters*, vol. 107, no. 23, p. 231606, 2015.
- [108] S. Y. Herasimenka, C. J. Tracy, V. Sharma, N. Vulic, W. J. Dauksher, and S. G. Bowden, "Surface passivation of n-type c-Si wafers by a-Si/SiO2/SiNx stack with lt;1cm/s effective surface recombination velocity," *Applied Physics Letters*, vol. 103, no. 18, p. 183903, 2013.
- [109] R. S. Bonilla, C. Reichel, M. Hermle, and P. R. Wilshaw, "Extremely low surface recombination in 1 cm n-type monocrystalline silicon," *physica status solidi (RRL) Rapid Research Letters*, vol. 11, no. 1, p. 1600307, 2017.
- [110] A. Descoeudres, Z. C. Holman, L. Barraud, S. Morel, S. De Wolf, and C. Ballif, ">21
- [111] B. Hoex, J. J. H. Gielis, M. C. M. van de Sanden, and W. M. M. Kessels, "On the c-Si surface passivation mechanism by the negative-charge-dielectric Al2O3," *Journal of Applied Physics*, vol. 104, no. 11, p. 113703, 2008.
- [112] S. Duttagupta, F.-J. Ma, S. F. Lin, T. Mueller, A. G. Aberle, and B. Hoex, "Progress in surface passivation of heavily doped n-type and p-type silicon by plasma-deposited alo

x/sin_x dielectric stacks," *IEEE Journal of Photovoltaics*, vol. 3, no. 4, pp. 1163–1169, 2013.

- [113] S. Duttagupta, Advanced Surface Passivation of Crystalline Silicon for Solar Cell Applications. PhD thesis, National University of Singapore, Department of Electrical and Computer Engineering, 2014. Available at https://core.ac.uk/download/pdf/48735964. pdf.
- [114] L. E. Black, T. Allen, A. Cuevas, K. R. McIntosh, B. Veith, and J. Schmidt, "Thermal stability of silicon surface passivation by apcvd al2o3," *Solar Energy Materials and Solar Cells*, vol. 120, pp. 339–345, 2014.
- [115] S. Rein, T. Rehrl, W. Warta, and S. W. Glunz, "Lifetime spectroscopy for defect characterization: Systematic analysis of the possibilities and restrictions," *Journal of Applied Physics*, vol. 91, no. 4, pp. 2059–2070, 2002.
- [116] G. Kissinger, Oxygen Precipitation in Silicon, pp. 273–341. Tokyo: Springer Japan, 2015.
- [117] D. Macdonald, T. Roth, P. N. K. Deenapanray, T. Trupke, and R. A. Bardos, "Doping dependence of the carrier lifetime crossover point upon dissociation of iron-boron pairs in crystalline silicon," *Applied Physics Letters*, vol. 89, no. 14, p. 142107, 2006.
- [118] J. Lindroos and H. Savin, "Formation kinetics of copper-related light-induced degradation in crystalline silicon," *Journal of Applied Physics*, vol. 116, no. 23, p. 234901, 2014.
- [119] S. Choi, B. Jang, J. Kim, H. Song, and M. Han, "Cu-contamination of single crystalline silicon wafers with thickness of 100m during multi-wire sawing process," *Solar Energy*, vol. 125, pp. 198–206, 2016.
- [120] V. Bertagna, F. Rouelle, G. Revel, and M. Chemla, "Electrochemical and radiochemical study of copper contamination mechanism from hf solutions onto silicon substrates," *Journal of The Electrochemical Society*, vol. 144, no. 12, p. 4175, 1997.
- [121] D. A. Ramappa, A. M. Hoff, and W. B. Henley, "Quantitative analysis of copper contamination in silicon by surface photovoltage minority carrier lifetime analysis," *AIP Conference Proceedings*, vol. 550, no. 1, pp. 215–219, 2001.

- [122] H. Savin, M. Yli-Koski, and A. Haarahiltunen, "Role of copper in light induced minority-carrier lifetime degradation of silicon," *Applied Physics Letters*, vol. 95, no. 15, p. 152111, 2009.
- [123] R. Sachdeva, A. A. Istratov, and E. R. Weber, "Recombination activity of copper in silicon," *Applied Physics Letters*, vol. 79, no. 18, pp. 2937–2939, 2001.
- [124] H. Väinölä, M. Yli-Koski, A. Haarahiltunen, and J. Sinkkonen, "Sensitive copper detection in p-type cz silicon using pcd," *Journal of The Electrochemical Society*, vol. 150, no. 12, p. G790, 2003.
- [125] H. Lemke, "Properties of copper donor levels in silicon," *physica status solidi (a)*, vol. 1, no. 2, pp. 283–286, 1970.
- [126] N. Tōyama, "Copper impurity levels in silicon," *Solid-State Electronics*, vol. 26, no. 1, pp. 37–46, 1983.
- [127] M. Seibt, M. Griess, A. A. Istratov, H. Hedemann, A. Sattler, and W. Schröter, "Formation and properties of copper silicide precipitates in silicon," *physica status solidi (a)*, vol. 166, no. 1, pp. 171–182, 1998.
- [128] J. Lindroos, Y. Boulfrad, M. Yli-Koski, and H. Savin, "Preventing light-induced degradation in multicrystalline silicon," *Journal of Applied Physics*, vol. 115, no. 15, p. 154902, 2014.
- [129] K. Chow, W. Ng, and L. Yeung, "Barrier properties of ni, pd and pd-fe for cu diffusion," *Surface and Coatings Technology*, vol. 105, no. 1, pp. 56–64, 1998.
- [130] Q. Huang, K. B. Reuter, Y. Zhu, and V. R. Deline, "A study on the long-term degradation of crystalline silicon solar cells metallized with cu electroplating," *ECS Journal of Solid State Science and Technology*, vol. 5, no. 2, p. Q24, 2015.
- [131] A. N. P. Nash, "The nisi (nickel-silicon) system," *Bulletin of Alloy Phase Diagrams*, vol. 8, p. 6–14, 1987.
- [132] N. Yarykin and J. Weber, "Evidence for room-temperature in-diffusion of nickel into silicon," *Applied Physics Letters*, vol. 109, no. 10, p. 102101, 2016.

- [133] M. Seibt, M. Griess, A. A. Istratov, H. Hedemann, A. Sattler, and W. Schröter, "Formation and properties of copper silicide precipitates in silicon," *physica status solidi (a)*, vol. 166, no. 1, pp. 171–182, 1998.
- [134] M. C. Raval, A. P. Joshi, S. S. Saseendran, S. Suckow, S. Saravanan, C. S. Solanki, and A. Kottantharayil, "Study of nickel silicide formation and associated fill-factor loss analysis for silicon solar cells with plated ni-cu based metallization," *IEEE Journal of Photovoltaics*, vol. 5, no. 6, pp. 1554–1562, 2015.
- [135] S. Rein, Lifetime Spectroscopy: A Method of Defect Characterization in Silicon for Photovoltaic Applications, vol. 31. Springer series in material science, 2005.
- [136] C. S. Fuller and R. A. Logan, "Effect of Heat Treatment upon the Electrical Properties of Silicon Crystals," *Journal of Applied Physics*, vol. 28, no. 12, pp. 1427–1436, 1957.
- [137] W. Kaiser, H. L. Frisch, and H. Reiss, "Mechanism of the formation of donor states in heat-treated silicon," *Physical Review*, vol. 112, pp. 1546–1554, Dec 1958.
- [138] K. Torigoe and T. Ono, "Formation of thermal donor enhanced by oxygen precipitation in silicon crystal," *AIP Advances*, vol. 10, no. 4, p. 045019, 2020.
- [139] M. Tomassini, J. Veirman, R. Varache, E. Letty, S. Dubois, Y. Hu, and Nielsen, "Recombination activity associated with thermal donor generation in monocrystalline silicon and effect on the conversion efficiency of heterojunction solar cells," *Journal of Applied Physics*, vol. 119, no. 8, p. 084508, 2016.
- [140] J. D. Murphy, K. Bothe, R. Krain, V. V. Voronkov, and R. J. Falster, "Parameterisation of injection-dependent lifetime measurements in semiconductors in terms of Shockley-Read-Hall statistics: An application to oxide precipitates in silicon," *Journal of Applied Physics*, vol. 111, no. 11, p. 113709, 2012.
- [141] J. Schmidt and A. Cuevas, "Electronic properties of light-induced recombination centers in boron-doped Czochralski silicon," *Journal of Applied Physics*, vol. 86, no. 6, pp. 3175– 3180, 1999.
- [142] K. Bothe, R. Hezel, and J. Schmidt, "Recombination-enhanced formation of the metastable boron–oxygen complex in crystalline silicon," *Applied Physics Letters*, vol. 83, no. 6, pp. 1125–1127, 2003.

- [143] J. Schmidt and K. Bothe, "Structure and transformation of the metastable boronand oxygen-related defect center in crystalline silicon," *Physical Review B*, vol. 69, p. 024107, 2004.
- [144] K. Bothe, R. Hezel, and J. Schmidt, "Understanding and reducing the boron-oxygenrelated performance degradation in czochralski silicon solar cells," in *Gettering and Defect Engineering in Semiconductor Technology X*, vol. 95 of *Solid State Phenomena*, pp. 223–228, Trans Tech Publications Ltd, 2003.
- [145] K. Bothe and J. Schmidt, "Electronically activated boron-oxygen-related recombination centers in crystalline silicon," *Journal of Applied Physics*, vol. 99, no. 1, p. 013701, 2006.
- [146] V. V. Voronkov and R. Falster, "Latent complexes of interstitial boron and oxygen dimers as a reason for degradation of silicon-based solar cells," *Journal of Applied Physics*, vol. 107, no. 5, p. 053509, 2010.
- [147] V. V. Voronkov, R. Falster, K. Bothe, B. Lim, and J. Schmidt, "Lifetime-degrading boronoxygen centres in p-type and n-type compensated silicon," *Journal of Applied Physics*, vol. 110, no. 6, p. 063515, 2011.
- [148] T. Niewelt, S. Mägdefessel, and M. C. Schubert, "Fast in-situ photoluminescence analysis for a recombination parameterization of the fast BO defect component in silicon," *Journal of Applied Physics*, vol. 120, no. 8, p. 085705, 2016.
- [149] G. Hahn, S. Wilking, and A. Herguth, "Bo-related defects: Overcoming bulk lifetime degradation in crystalline si by regeneration," in *Gettering and Defect Engineering in Semiconductor Technology XVI*, vol. 242 of *Solid State Phenomena*, pp. 80–89, Trans Tech Publications Ltd, 2016.
- [150] V. Voronkov and R. Falster, "Permanent deactivation of boron–oxygen recombination centres in silicon," *physica status solidi* (*b*), vol. 253, no. 9, pp. 1721–1728, 2016.
- [151] S. Wilking, A. Herguth, and G. Hahn, "Influence of hydrogen on the regeneration of boron-oxygen related defects in crystalline silicon," *Journal of Applied Physics*, vol. 113, no. 19, p. 194503, 2013.

- [152] B. Hallam, D. Chen, M. Kim, B. Stefani, B. Hoex, M. Abbott, and S. Wenham, "The role of hydrogenation and gettering in enhancing the efficiency of next-generation si solar cells: An industrial perspective," *physica status solidi* (*a*), vol. 214, no. 7, p. 1700305, 2017.
- [153] B. J. Hallam, P. G. Hamer, A. M. Ciesla née Wenham, C. E. Chan, B. Vicari Stefani, and S. Wenham, "Development of advanced hydrogenation processes for silicon solar cells via an improved understanding of the behaviour of hydrogen in silicon," *Progress in Photovoltaics: Research and Applications*, vol. 28, no. 12, pp. 1217–1238, 2020.
- [154] P. Karzel, A. Frey, S. Fritz, and G. Hahn, "Influence of hydrogen on interstitial iron concentration in multicrystalline silicon during annealing steps," *Journal of Applied Physics*, vol. 113, no. 11, p. 114903, 2013.
- [155] C. Herring, N. M. Johnson, and C. G. Van de Walle, "Energy levels of isolated interstitial hydrogen in silicon," *Physical Review B*, vol. 64, p. 125209, 2001.
- [156] N. H. Nickel, G. B. Anderson, N. M. Johnson, and J. Walker, "Nucleation of hydrogeninduced platelets in silicon," *Physical Review B*, vol. 62, pp. 8012–8015, 2000.
- [157] D. Chen, M. Vaqueiro Contreras, A. Ciesla, P. Hamer, B. Hallam, M. Abbott, and C. Chan, "Progress in the understanding of light- and elevated temperature-induced degradation in silicon solar cells: A review," *Progress in Photovoltaics: Research and Applications*, vol. 29, no. 11, pp. 1180–1201, 2021.
- [158] K. Nakayashiki, J. Hofstetter, A. E. Morishige, T.-T. A. Li, D. B. Needleman, M. A. Jensen, and T. Buonassisi, "Engineering solutions and root-cause analysis for light-induced degradation in p-type multicrystalline silicon perc modules," *IEEE Journal of Photovoltaics*, vol. 6, no. 4, pp. 860–868, 2016.
- [159] A. E. Morishige, M. A. Jensen, D. B. Needleman, K. Nakayashiki, J. Hofstetter, T.-T. A. Li, and T. Buonassisi, "Lifetime spectroscopy investigation of light-induced degradation in p-type multicrystalline silicon perc," *IEEE Journal of Photovoltaics*, vol. 6, no. 6, pp. 1466–1472, 2016.

- [160] C. Vargas, Y. Zhu, G. Coletti, C. Chan, D. Payne, M. Jensen, and Z. Hameiri, "Recombination parameters of lifetime-limiting carrier-induced defects in multicrystalline silicon for solar cells," *Applied Physics Letters*, vol. 110, no. 9, p. 092106, 2017.
- [161] M. A. Jensen, Y. Zhu, E. E. Looney, A. E. Morishige, C. Vargas, Z. Hameiri, and T. Buonassis, "Assessing the defect responsible for letid: temperature- and injectiondependent lifetime spectroscopy," in 2017 IEEE 44th Photovoltaic Specialist Conference (PVSC), pp. 3290–3294, 2017.
- [162] C. Sen, M. Kim, D. Chen, U. Varshney, S. Liu, A. Samadi, A. Ciesla, S. R. Wenham, C. E. Chan, C. Chong, M. D. Abbott, and B. J. Hallam, "Assessing the impact of thermal profiles on the elimination of light- and elevated-temperature-induced degradation," *IEEE Journal of Photovoltaics*, vol. 9, no. 1, pp. 40–48, 2019.
- [163] M. Kim, D. Chen, M. Abbott, S. Wenham, and B. Hallam, "Role of hydrogen: Formation and passivation of meta-stable defects due to hydrogen in silicon," *AIP Conference Proceedings*, vol. 1999, no. 1, p. 130010, 2018.
- [164] D. Sperber, A. Herguth, and G. Hahn, "A 3-state defect model for light-induced degradation in boron-doped float-zone silicon," *physica status solidi (RRL) – Rapid Research Letters*, vol. 11, no. 3, p. 1600408, 2017.
- [165] T. Niewelt, F. Schindler, W. Kwapil, R. Eberle, J. Schön, and M. C. Schubert, "Understanding the light-induced degradation at elevated temperatures: Similarities between multicrystalline and floatzone p-type silicon," *Progress in Photovoltaics: Research and Applications*, vol. 26, no. 8, pp. 533–542, 2018.
- [166] D. Kang, H. Sio, Z. Xinyu, Q. Wang, H. Jin, and D. Macdonald, "Letid in p-type and n-type mono-like and float-zone silicon and their dependence on sinx film properties," in *Proc. 36th Eur. Photovolt. Solar Energy Conf. Exhib.*, pp. 318–321, 2019.
- [167] K. Ramspeck, S. Zimmermann, H. Nagel, A. Metz, Y. Gassenbauer, B. Birkmann, and A. Seidl, "Light induced degradation of rear passivated mc-si solar cells," in *Proceedings* 27th European Photovoltaic Solar Energy Conference, vol. 861–865, pp. 1–3, 2012.
- [168] U. Varshney, M. Kim, M. U. Khan, P. Hamer, C. Chan, M. Abbott, and B. Hoex, "Impact

of substrate thickness on the degradation in multicrystalline silicon," *IEEE Journal of Photovoltaics*, vol. 11, no. 1, pp. 65–72, 2021.

- [169] T. H. Fung, M. Kim, D. Chen, C. E. Chan, B. J. Hallam, R. Chen, D. N. Payne, A. Ciesla, S. R. Wenham, and M. D. Abbott, "A four-state kinetic model for the carrier-induced degradation in multicrystalline silicon: Introducing the reservoir state," *Solar Energy Materials and Solar Cells*, vol. 184, pp. 48–56, 2018.
- [170] D. Bredemeier, D. Walter, and J. Schmidt, "Light-induced lifetime degradation in highperformance multicrystalline silicon: Detailed kinetics of the defect activation," *Solar Energy Materials and Solar Cells*, vol. 173, pp. 2–5, 2017. Proceedings of the 7th international conference on Crystalline Silicon Photovoltaics.
- [171] W. Kwapil, J. Schön, T. Niewelt, and M. C. Schubert, "Temporary recovery of the defect responsible for light- and elevated temperature-induced degradation: Insights into the physical mechanisms behind letid," *IEEE Journal of Photovoltaics*, vol. 10, no. 6, pp. 1591–1603, 2020.
- [172] C. Vargas, G. Coletti, C. Chan, D. Payne, and Z. Hameiri, "On the impact of dark annealing and room temperature illumination on p-type multicrystalline silicon wafers," *Solar Energy Materials and Solar Cells*, vol. 189, pp. 166–174, 2019.
- [173] A. Graf, A. Herguth, and G. Hahn, "Determination of BO-LID and LeTID related activation energies in Cz-Si and FZ-Si using constant injection conditions," *AIP Conference Proceedings*, vol. 2147, no. 1, p. 140003, 2019.
- [174] G. M. Wyller, M. S. Wiig, I. Due-Sørensen, and R. Søndenå, "The influence of minority carrier density on degradation and regeneration kinetics in multicrystalline silicon wafers," *IEEE Journal of Photovoltaics*, vol. 11, no. 4, pp. 878–889, 2021.
- [175] S. Cheng, F. Ji, C. Zhou, J. Zhu, R. Søndenå, W. Wang, and D. Hu, "Kinetics of light and elevated temperature-induced degradation in cast mono p-type silicon," *Solar Energy*, vol. 224, pp. 1000–1007, 2021.
- [176] S. Glunz, S. Rein, W. Warta, J. Knobloch, and W. Wettling, "Degradation of carrier lifetime in cz silicon solar cells," *Solar Energy Materials and Solar Cells*, vol. 65, no. 1, pp. 219–229, 2001. PVSEC 11 Part I.

- [177] T. Luka, M. Turek, S. Großer, and C. Hagendorf, "Microstructural identification of cu in solar cells sensitive to light-induced degradation," *physica status solidi (RRL) – Rapid Research Letters*, vol. 11, no. 2, p. 1600426, 2017.
- [178] M. Wagner, F. Wolny, M. Hentsche, A. Krause, L. Sylla, F. Kropfgans, M. Ernst, R. Zierer, P. Bönisch, P. Müller, N. Schmidt, V. Osinniy, H.-P. Hartmann, R. Mehnert, and H. Neuhaus, "Correlation of the letid amplitude to the aluminium bulk concentration and oxygen precipitation in perc solar cells," *Solar Energy Materials and Solar Cells*, vol. 187, pp. 176–188, 2018.
- [179] H. Deniz, J. Bauer, and O. Breitenstein, "Nickel precipitation in light and elevated temperature degraded multicrystalline silicon solar cells," *Solar RRL*, vol. 2, no. 9, p. 1800170, 2018.
- [180] M. A. Jensen, A. E. Morishige, S. Chakraborty, R. Sharma, H. S. Laine, B. Lai, V. Rose, A. Youssef, E. E. Looney, S. Wieghold, J. R. Poindexter, J.-P. Correa-Baena, T. Felisca, H. Savin, J. B. Li, and T. Buonassisi, "Solubility and diffusivity: Important metrics in the search for the root cause of light- and elevated temperature-induced degradation," *IEEE Journal of Photovoltaics*, vol. 8, no. 2, pp. 448–455, 2018.
- [181] V. V. Voronkov and R. Falster, "Formation, dissociation, and diffusion of various hydrogen dimers in silicon," *physica status solidi* (*b*), vol. 254, no. 6, p. 1600779, 2017.
- [182] D. Sperber, A. Schwarz, A. Herguth, and G. Hahn, "Bulk and surface-related degradation in lifetime samples made of czochralski silicon passivated by plasma-enhanced chemical vapor deposited layer stacks," *physica status solidi (a)*, vol. 215, no. 24, p. 1800741, 2018.
- [183] C. Chan, P. Hamer, G. Bourret-Sicotte, R. Chen, A. Ciesla, B. Hallam, D. Payne, R. S. Bonilla, and S. Wenham, "Instability of increased contact resistance in silicon solar cells following post-firing thermal processes," *Solar RRL*, vol. 1, no. 11, p. 1700129, 2017.
- [184] P. Hamer, C. Chan, R. S. Bonilla, B. Hallam, G. Bourret-Sicotte, K. A. Collett, S. Wenham, and P. R. Wilshaw, "Hydrogen induced contact resistance in perc solar cells," *Solar Energy Materials and Solar Cells*, vol. 184, pp. 91–97, 2018.

- [185] D. Skorka, A. Zuschlag, and G. Hahn, "Firing and gettering dependence of effective defect density in material exhibiting LeTID," *AIP Conference Proceedings*, vol. 1999, no. 1, p. 130015, 2018.
- [186] S. Chakraborty, Y. Huang, M. Wilson, A. G. Aberle, and J. B. Li, "Mitigating light and elevated temperature induced degradation in multicrystalline silicon wafers and perc solar cells using phosphorus diffusion gettering," *physica status solidi (a)*, vol. 215, no. 13, p. 1800160, 2018.
- [187] D. N. R. Payne, C. E. Chan, B. J. Hallam, B. Hoex, M. D. Abbott, S. R. Wenham, and D. M. Bagnall, "Acceleration and mitigation of carrier-induced degradation in p-type multi-crystalline silicon," *physica status solidi (RRL) – Rapid Research Letters*, vol. 10, no. 3, pp. 237–241, 2016.
- [188] M. Yli-Koski, M. Serué, C. Modanese, H. Vahlman, and H. Savin, "Low-temperature dark anneal as pre-treatment for letid in multicrystalline silicon," *Solar Energy Materials and Solar Cells*, vol. 192, pp. 134–139, 2019.
- [189] M. Tajima, Y. Iwata, F. Okayama, H. Toyota, H. Onodera, and T. Sekiguchi, "Deep-level photoluminescence due to dislocations and oxygen precipitates in multicrystalline Si," *Journal of Applied Physics*, vol. 111, no. 11, p. 113523, 2012.
- [190] S. Pizzini, M. Acciarri, E. Leoni, and A. Le Donne, "About the d1 and d2 dislocation luminescence and its correlation with oxygen segregation," *physica status solidi* (b), vol. 222, no. 1, pp. 141–150, 2000.
- [191] S. Pizzini, M. Guzzi, E. Grilli, and G. Borionetti, "The photoluminescence emission in the 0.7-0.9 ev range from oxygen precipitates, thermal donors and dislocations in silicon," *Journal of Physics: Condensed Matter*, vol. 12, no. 49, p. 10131, 2000.
- [192] M. Tajima, "Spectroscopy and topography of deep-level luminescence in photovoltaic silicon," *IEEE Journal of Photovoltaics*, vol. 4, no. 6, pp. 1452–1458, 2014.
- [193] S. Bowden and A. Rohatgi, "Rapid and accurate determination of series resistance and fill factor losses in industrial silicon solar cells," in *Proceedings of the 17th European Photovoltaic Solar Energy Conference, Munich*, p. 1802–1806, 2001.

- [194] R. A. Sinton and A. Cuevas, "A quasi-steady-state open-circuit voltage method for solar cell characterization," in *Proceedings of the 16th European Photovoltaic Solar Energy Conference, Glasgow, Scotland*, p. 1152–1155, 2002.
- [195] M. J. Kerr, A. Cuevas, and R. A. Sinton, "Generalized analysis of quasi-steady-state and transient decay open circuit voltage measurements," *Journal of Applied Physics*, vol. 91, no. 1, pp. 399–404, 2002.
- [196] A. Khanna, T. Mueller, R. A. Stangl, B. Hoex, P. K. Basu, and A. G. Aberle, "A fill factor loss analysis method for silicon wafer solar cells," *IEEE Journal of Photovoltaics*, vol. 3, no. 4, pp. 1170–1177, 2013.
- [197] M. A. Green, "Self-consistent optical parameters of intrinsic silicon at 300k including temperature coefficients," *Solar Energy Materials and Solar Cells*, vol. 92, no. 11, pp. 1305–1310, 2008.
- [198] B. Hallam, M. Abbott, J. Bilbao, P. Hamer, N. Gorman, M. Kim, D. Chen, K. Hammerton, D. Payne, C. Chan, N. Nampalli, and S. Wenham, "Modelling kinetics of the boronoxygen defect system," *Energy Procedia*, vol. 92, pp. 42–51, 2016. Proceedings of the 6th International Conference on Crystalline Silicon Photovoltaics (SiliconPV 2016).
- [199] M. Kim, M. Abbott, N. Nampalli, S. Wenham, B. Stefani, and B. Hallam, "Modulating the extent of fast and slow boron-oxygen related degradation in Czochralski silicon by thermal annealing: Evidence of a single defect," *Journal of Applied Physics*, vol. 121, no. 5, p. 053106, 2017.
- [200] X. Tan, R. Chen, and F. E. Rougieux, "The mechanism of surface passivation degradation in sio2/sinx stack under light and elevated temperature," *IEEE Journal of Photovoltaics*, vol. 11, no. 6, pp. 1380–1387, 2021.
- [201] A. Herguth, "On the application of lifetime-equivalent defect densities on solar cell level," *IEEE Journal of Photovoltaics*, vol. 11, no. 6, pp. 1410–1418, 2021.
- [202] K. R. McIntosh and L. E. Black, "On effective surface recombination parameters," *Journal of Applied Physics*, vol. 116, no. 1, p. 014503, 2014.

- [203] G. Lucovsky, J. Yang, S. S. Chao, J. E. Tyler, and W. Czubatyj, "Nitrogen-bonding environments in glow-discharge—deposited a-Si : H films," *Physical Review B*, vol. 28, pp. 3234–3240, 1983.
- [204] S. Hasegawa, H. Anbutsu, and Y. Kurata, "Connection between si-n and si-h vibrational properties in amorphous sinx: H films," *Philosophical Magazine B*, vol. 59, no. 3, pp. 365–375, 1989.
- [205] S. Hasegawa, M. Matsuda, and Y. Kurata, "Si-H and N-H vibrational properties in glowdischarge amorphous SiNx:H films," *Applied Physics Letters*, vol. 57, no. 21, pp. 2211– 2213, 1990.
- [206] J.-F. Lelièvre, E. Fourmond, A. Kaminski, O. Palais, D. Ballutaud, and M. Lemiti, "Study of the composition of hydrogenated silicon nitride sinx:h for efficient surface and bulk passivation of silicon," *Solar Energy Materials and Solar Cells*, vol. 93, no. 8, pp. 1281– 1289, 2009.
- [207] G. Scardera, T. Puzzer, G. Conibeer, and M. A. Green, "Fourier transform infrared spectroscopy of annealed silicon-rich silicon nitride thin films," *Journal of Applied Physics*, vol. 104, no. 10, p. 104310, 2008.
- [208] G. Stingeder, S. Gara, S. Pahlke, H. Schwenk, E. Guerrero, and M. Grasserbauer, "Quantitative determination of oxygen in silicon by combination of ftir-spectroscopy, inert gas fusion analysis and secondary ion mass spectroscopy," *Fresenius' Zeitschrift für analytische Chemie*, vol. 333, no. 4-5, pp. 576–582, 1989.
- [209] D. B. Mawhinney, J. A. Glass, and J. T. Yates, "Ftir study of the oxidation of porous silicon," *The Journal of Physical Chemistry B*, vol. 101, no. 7, pp. 1202–1206, 1997.
- [210] J. L. Lindström and T. Hallberg, "Vibrational infrared-absorption bands related to the thermal donors in silicon," *Journal of Applied Physics*, vol. 77, no. 6, pp. 2684–2690.
- [211] T. Hallberg and J. L. Lindström, "Infrared vibrational bands related to the thermal donors in silicon," *Journal of Applied Physics*, vol. 79, no. 10, pp. 7570–7581, 1996.
- [212] W. Götz, G. Pensl, W. Zulehner, R. C. Newman, and S. A. McQuaid, "Thermal donor formation and annihilation at temperatures above 500°C in Czochralski-grown Si," *Journal* of Applied Physics, vol. 84, no. 7, pp. 3561–3568, 1998.

- [213] I. Jonak-Auer, R. Meisels, and F. Kuchar, "Determination of the hydrogen concentration of silicon nitride layers by fourier transform infrared spectroscopy," *Infrared Physics Technology*, vol. 38, no. 4, pp. 223–226, 1997.
- [214] G. Morello, "Hydrogen content of amorphous pecvd sinx:h films by infrared spectroscopy and hydrogen forward scattering results," *Journal of Non-Crystalline Solids*, vol. 187, pp. 308–312, 1995. Amorphous Insulating Thin Films II.
- [215] X. Lin, D. Endisch, X. Chen, and A. Kaloyeros, "Silicon nitride films deposited by atmospheric pressure chemical vapor deposition," *Mater. Res. Soc. Symp. Proc.*, vol. 495, no. 107, 1997.
- [216] Y. Tokuda, H. Shimada, and A. Ito, "Light-illumination-induced transformation of electron traps in hydrogen-implanted n-type silicon," *Journal of Applied Physics*, vol. 86, pp. 5630–5635, 11 1999.
- [217] V. P. Markevich and M. Suezawa, "Hydrogen–oxygen interaction in silicon at around 50°c," *Journal of Applied Physics*, vol. 83, pp. 2988–2993, 03 1998.
- [218] N. A. Drozdov, A. A. Patrin, and V. T. Tkachev, "Modification of the dislocation luminescence spectrum by oxygen atmospheres in silicon," *physica status solidi (a)*, vol. 64, no. 1, pp. K63–K65, 1981.
- [219] P. K. Basu, K. Sreejith, T. S. Yadav, A. Kottanthariyil, and A. K. Sharma, "Novel lowcost alkaline texturing process for diamond-wire-sawn industrial monocrystalline silicon wafers," *Solar Energy Materials and Solar Cells*, vol. 185, pp. 406–414, 2018.
- [220] K. Sreejith, A. K. Sharma, S. Kumbhar, A. Kottantharayil, and P. K. Basu, "An additivefree non-metallic energy efficient industrial texturization process for diamond wire sawn multicrystalline silicon wafers," *Solar Energy*, vol. 184, pp. 162–172, 2019.
- [221] K. Sreejith, A. K. Sharma, S. Behera, A. Kottantharayil, and P. K. Basu, "A low cost additive-free acid texturing process for large area commercial diamond-wire-sawn multicrystalline silicon solar cells," *Solar Energy*, vol. 205, pp. 263–274, 2020.
- [222] "Q-lab xenon test chamber." https://www.q-lab.com/documents/public/41b5935b-d41d-4368-a53e-98a3d528baf1.pdf. Accessed: Sep 2023.

- [223] M. A. Jensen, A. E. Morishige, S. Chakraborty, R. Sharma, H. C. Sio, C. Sun, B. Lai, V. Rose, A. Youssef, E. E. Looney, S. Wieghold, J. Poindexter, J.-P. Correa-Baena, D. Macdonald, J. B. Li, and T. Buonassisi, "Do grain boundaries matter? electrical and elemental identification at grain boundaries in letid-affected p-type multicrystalline silicon," in *2017 IEEE 44th Photovoltaic Specialist Conference (PVSC)*, pp. 3300–3303, 2017.
- [224] T. Luka, S. Großer, C. Hagendorf, K. Ramspeck, and M. Turek, "Intra-grain versus grain boundary degradation due to illumination and annealing behavior of multi-crystalline solar cells," *Solar Energy Materials and Solar Cells*, vol. 158, pp. 43–49, 2016. Proceedings of the 6th International Conference on Silicon Photovoltaics.
- [225] D. E. Kane and R. M. Swanson, "Measurement of the emitter saturation current by a contactless photoconductivity decay method," 1985.
- [226] E. R. Weber, "Transition metals in silicon," Applied Physics A, vol. 30, pp. 1–12, 1983.
- [227] A. A. Istratov, T. Buonassisi, R. J. McDonald, A. R. Smith, R. Schindler, J. A. Rand, J. P. Kalejs, and E. R. Weber, "Metal content of multicrystalline silicon for solar cells and its impact on minority carrier diffusion length," *Journal of Applied Physics*, vol. 94, pp. 6552–6559, 11 2003.
- [228] K. Kurobe and H. Matsunami, "New two-diode model for detailed analysis of multicrystalline silicon solar cells," *Japanese Journal of Applied Physics*, vol. 44, no. 12R, p. 8314, 2005.
- [229] J. Greulich, M. Glatthaar, and S. Rein, "Fill factor analysis of solar cells' current–voltage curves," *Progress in Photovoltaics: Research and Applications*, vol. 18, no. 7, pp. 511– 515, 2010.
- [230] A. K. Sharma, S. Mitra, K. P. Sreejith, D. P. Khatri, A. Khan, A. Kottantharayil, and H. Ghosh, "A comprehensive analysis of recombination and resistive losses in silicon solar cells induced by co-firing process," *Surfaces and Interfaces*, vol. 25, p. 101260, 2021.
- [231] K. Sreejith, A. K. Sharma, P. K. Basu, and A. Kottantharayil, "A comprehensive investigation of the potential of metal assisted chemical etched (MACE) nano-textures over

conventional micron-sized iso-textures for industrial silicon solar cell applications," *Solar Energy*, vol. 230, pp. 874–882, 2021.

- [232] T. Luka, S. Eiternick, S. Frigge, C. Hagendorf, H. Mehlich, and M. Turek, "Investigation of light induced degradation of multi-crystalline perc cells," in *Proc. 31st Eur. Photovoltaic Sol. Energy Conf*, pp. 826–828, 2015.
- [233] C. E. Chan, D. N. R. Payne, B. J. Hallam, M. D. Abbott, T. H. Fung, A. M. Wenham, B. S. Tjahjono, and S. R. Wenham, "Rapid stabilization of high-performance multicrystalline p-type silicon perc cells," *IEEE Journal of Photovoltaics*, vol. 6, no. 6, pp. 1473–1479, 2016.
- [234] D. H. Macdonald, L. J. Geerligs, and A. Azzizi, "Iron detection in crystalline silicon by carrier lifetime measurements for arbitrary injection and doping," *Journal of Applied Physics*, vol. 95, pp. 1021–1028, 02 2004.
- [235] D. Macdonald, J. Tan, and T. Trupke, "Imaging interstitial iron concentrations in borondoped crystalline silicon using photoluminescence," *Journal of Applied Physics*, vol. 103, p. 073710, 04 2008.

List of Publications

Journals

- E. Resmi, K. P. Sreejith, A. Kottantharayil, "Analysis of Variation in Recombination Characteristics due to Light and Heat in Industrial Silicon Solar Cells," Solar Energy, vol.252, pp.127-133, 2023, https://doi.org/10.1016/j.solener.2023.01.053.
- E. Resmi, K. P. Sreejith, A. Kottantharayil, "Characterization of Light Induced Degradation in PECVD Silicon Nitride Passivated Cz Silicon Wafers," Journal of Surfaces and Interfaces, vol.38, 2023, https://doi.org/10.1016/j.surfin.2023.102864.
- E. Resmi, K. P. Sreejith, A. Kottantharayil, "Comprehensive Analysis of Recombination Characteristics of due to Illumination under Elevated Temperature in Monocrystalline and Multicrystalline Wafers" under review in Journal silicon

Conferences

- E. Resmi, K. P. Sreejith, A. Kottantharayil, 2D distribution of Fe concentration in mc-Si wafers using optoelectrical characterization, International Conference on Purification and Recycling of Materials 2020, March 8-10, organized by C-MET Hyderabad, MeitY, Govt of India.
- E. Resmi, K. P. Sreejith, A. Kottantharayil, "Characterization of Bulk Degradation due to Light and Elevated Temperature in Industrial Solar Cells" XXIst International Workshop on the Physics of Semiconductor Devices (IWPSD) 2021, Dec. 13-15, IIT Delhi.

Acknowledgments

I extend my heartfelt gratitude to my thesis advisor, Prof. Anil Kottantharayil, whose trust and guidance empowered me to delve into a challenging research domain. His analytical prowess and commitment to innovation elevated the standard of my thesis and nurtured my growth as a researcher. The freedom he granted me in exploring my work fostered my independence.

I am grateful to Prof. Pradeep Nair and Prof. Manoj Neergat for their thorough examination of my progress seminar and for providing valuable feedback that significantly contributed to the advancement of my research. Special thanks to Prof. K. L. Narasimhan and Prof. B. M. Arora for their time, guidance, and feedback. My sincere thanks to Dr. Sreejith K.P. for their unwavering support and mentorship.

I acknowledge the Department of Science and Technology, Government of India, and the Research Council of Norway for funding my doctoral thesis. I acknowledge the Ministry of New and Renewable Energy (MNRE) for providing the facility to do a doctoral thesis through the National Centre for Photovoltaic Research and Education (NCPRE). I also acknowledge the support from the Sophisticated Analytical Instrumentation Facility (SAIF), IIT Bombay, and Hybrid Optoelectronics Laboratory, Department of Physics, IIT Bombay, for resources and assistance in spectroscopic measurements.

I acknowledge all the dedicated staff at NCPRE, including Sandeep K., Nilesh K., Guru B., Almouzzam K., and Siddharth B., for their collaboration on fabricating and characterizing Si wafers and solar cells. I acknowledge the help rendered by Rambabu and Ajeesh A. for the lightsoaking experiments conducted at Module Lab of NCPRE, IIT Bombay. I also acknowledge the scientific staff, Dr. Ashok S., Dr. Hemanta G., and Dr. Suchismita M., for their valuable suggestions. A special thanks goes to NCPRE lab manager Dr. Diksha M. and administrative staff members for their support. I am indebted to my group members, including Kalaivani S., Durgaprasad Khathri, Premsai, Tarun S. Yadhav, and Saima Cherukat.

I am deeply grateful to my family members for their selfless support and constant encouragement throughout my higher studies.