

Pulsed-DC Reactive Sputtered Aluminum Oxide For The Surface Passivation Of Crystalline Silicon Solar Cell

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By

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2019

*Dedicated to my Mother, Father
and my beloved son Divyaan.*

Thesis Approval

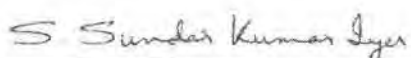
The Thesis entitled

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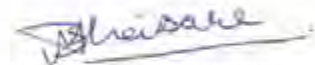
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Abstract

Advancements in renewable energy technologies for the electricity generation have led to less dependency on fossil fuels like petrol and coal. In particular, the solar photovoltaic (SPV) technology has become a fast-growing field today, among different renewable energy technologies with an impressive research and development in this field and cost reductions. The basic energy conversion device in SPV is the “solar cell” that uses photons from the sunlight as input source to generate charge carriers followed by transportation of these charge carriers into the external circuit. More efficient solar cell means more electricity generated per unit area of the conversion device. The particular focus on manufacturing of most efficient and low-cost solar cells brings in many challenges in the field of research and development.

The crystalline silicon (c-Si) solar cells have shown highest conversion efficiency of $\eta = 26.7\%$ among different cell technologies, and also dominates most of the PV market due to high compatibility with the existing very large scale integration (VLSI) silicon technology and manufacturing. In a conventional c-Si solar cell, various factors need to be addressed to achieve high efficiency. Among these factors, the loss of light generated carrier due to recombination at the surface of silicon may be realized by the surface passivation layer.

The aluminum oxide (AlO_x) film was widely investigated as passivation layer of p-type c-Si surface, because of its inherent property of high density of negative fixed oxide charges (Q_f) in the film which are used to repel electrons from the p-type surface and hence could minimize the surface recombination losses, this mechanism is known as field-effect passivation. In this report, we present the reactive sputter (RS) deposited AlO_x film for passivation layer of p-type c-Si surface. To achieve the low-cost factor of surface passivated solar cell manufacturing, the high-quality film is obtained using RS technique with pulsed-DC power supply. Integration of RS technique in cell-line manufacturing for film deposition is a big challenge to the solar industries.

The work comprises of process development and optimization for deposition of high quality AlO_x film by RS technique, to be applied as surface passivation layer of p-type c-Si. The process development involves, characterization of the film using electrical, material and opto-electronic measurement techniques to assess the film quality and applicability as passivation

layer. The quality of the AlO_x film deposited by RS technique was not studied very well in terms of its interfacial properties. Also the biggest challenge using this technique was repeatability and uniformity of the film quality. In this work, we have used an industry standard RS system from Applied Material Inc. called Endura, which is already in use in semiconductor industries for metal deposition. We have used this system for AlO_x dielectric film deposition on c-Si substrate using O₂ as reactive gas and Ar as sputter gas ambient. To achieve uniform and repeatable results using RS system for high quality film deposition, have led us to develop new recipes and further optimize them as per the requirement. A rigorous study on the material and interfacial property was carried out using sophisticated instruments. These studies are benchmarked to the AlO_x film deposited using different techniques like chemical vapor deposition (CVD) and atomic layer deposition (ALD), reported in the literature.

The optimized process condition for pulsed-DC RS AlO_x film deposition, with the application of optimized post-deposition annealing (PDA) condition on the film, results in reasonably good surface passivation with effective surface recombination velocity (S_{eff}) of 40 cm.s⁻¹ on p-type (FZ) c-Si wafer with 7.8 Ω.cm resistivity. The electrical measurements shows, this film carries high negative fixed oxide charges (Q_f) of 6×10^{12} cm⁻² that supports field-effect passivation and low density of interface states (D_{it}) of 2.3×10^{11} eV⁻¹.cm⁻² that supports chemical passivation. The technique has also shown high deposition rate of 5 nm.min⁻¹ with optimized process condition, which is significantly higher as compared to typical thermal ALD processes investigated for solar cells applications. The film has shown thick interfacial layer (IL) of 8.2 nm at AlO_x/c-Si interface, for 26 nm film deposition, using high-resolution transmission electron microscope (TEM). The composition of the film and IL were assessed using elemental depth-profile through X-ray photoelectron spectroscopy (XPS). Which shows the IL was found to be aluminum silicate. Using fourier transform infra-red spectrometer (FTIR) measurement, the presence of absorbance peak at 1090 cm⁻¹ also confirms the formation of interfacial oxide in the film after annealing.

The electron energy loss spectroscopy (EELS) measurement was used to study the origin of Q_f in the RS AlO_x film and IL, which shows the presence of both tetrahedral (*T*) and octahedral (*O*) coordinated Al in as-deposited condition. However the concentration of *T* coordinated Al increases after annealing at optimized condition, hence supports the finding of

increase in negative Q_f after annealing. The T/O peak intensity ratio was studied for distribution of Q_f , which shows presence of high negative Q_f at IL/ c-Si interface and gradual decrease of these charges near IL/ AlO_x interface. The presence of different intermediate oxidation states of Si $2p$ at the IL of the film annealed in different conditions, was obtained using depth-resolved XPS measurements. This study of different intermediate oxidation states in the IL, was used to understand reason behind an improvement in D_{it} values after annealing of film.

The thermal stability of pulsed-DC RS AlO_x film against firing temperature as required by industrial screen-printed solar cell fabrication process was also studied in this work. The films were deposited using optimized process condition and subjected to optimized PDA condition for this study. The film was exposed to elevated temperature of 400-700 °C for 2 s using rapid thermal processing (RTP) in N_2 ambient, which shows the surface passivation degrades for the firing temperature at 700 °C. This temperature is lower than the typical firing temperatures (~ 850 °C) used for manufacturing of industrial screen-printed solar cells. The film, however, may be used as passivation layer on advance passivated emitter and rear cell (PERC) structure with Ni/Cu contact where the firing temperature is in the range of 500 °C or less. The thermal stability of stack structure for AlO_x film capped with inductively coupled plasma (ICP)-CVD $SiN_x:H$ was also studied, as many reports suggests an improvement in thermal stability for the stack structure against firing temperature. Through electrical characterization, we have observed net decrease in negative Q_f with marginal improvement in D_{it} for the stack structure. Also the surface passivation has shown relatively poor quality as compared to single layer AlO_x film. Hence additional film did not make any improvement in high temperature thermal stability for surface passivation of p-type c-Si, unlike the ALD and PECVD AlO_x films reported elsewhere.

In conclusion, the pulsed-DC RS deposited AlO_x film may be applied as the surface passivation layer in silicon solar cell structures for advanced structures such as PERC.

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List of Symbols

Symbol	Description	Unit
α	Absorption coefficient	cm^{-1}
α_c	Critical angle	degree
$\Delta\sigma$	Excess photoconductance	S
Δn	Excess minority carrier density	cm^{-3}
Δn_s	Excess electron concentration at the semiconductor surface	cm^{-3}
ΔV_{FB}	Difference in flat-band voltage	V
ΔV_{MG}	Difference in mid-gap voltage	V
ϵ	Permittivity of the material	F. cm^{-1}
ϵ_r	Relative permittivity of dielectric material	
ϵ_0	Permittivity of free space, 8.854×10^{-14}	F. cm^{-1}
ϵ_{ox}	Dielectric constant of the oxide film	
$\epsilon_{\text{r-AlOx}}$	Dielectric constant of aluminum oxide	
$\epsilon_{\text{r-SiO}_2}$	Dielectric constant of silicon dioxide	
ϵ_s	Relative permittivity of silicon	
η	Efficiency	%
λ	Wavelength	m
μ_n	Electron mobility	$\text{cm}^2.(\text{V.s})^{-1}$
μ_p	Hole mobility	$\text{cm}^2.(\text{V.s})^{-1}$
ν	Frequency of vibration	Hz
σ_n	Electron capture cross-section area	cm^2
σ_p	Hole capture cross-section area	cm^2
τ	Minority carrier life-time	s
τ_{Auger}	Life-time due to Auger recombination	s
τ_{bulk}	Life-time due to bulk recombination	s
τ_{eff}	Effective minority carrier life-time	s
τ_n	Electron life-time in p-type	s
τ_p	Hole life-time in n-type	s
τ_{ON}	Reactive sputter time	s
τ_{OFF}	Pulse-reverse time to neutralize the target surface charges	s

τ_{BtB}	Life-time due to band-to-band recombination	s
τ_s	Life-time due to surface recombination	s
τ_{SRH}	Life-time due to Shockley-Read-Hall recombination	s
ϕ_B	Bulk potential	eV
ϕ_M	Metal work-function	eV
ϕ_{MS}	Work function difference between the metal gate and semiconductor	eV
ϕ_s	Semiconductor work-function	eV
φ	Work function depends on spectrometer and material	eV
χ	Electron affinity for Semiconductor	V
ω	Angular frequency	rad.s ⁻¹
$a(\lambda)$	Wavelength dependent molar absorption coefficient	L.mol ⁻¹ .cm ⁻¹
A	Absorbance	
A	Cross-sectional area of device	cm ²
b	Path length	cm
B	Band-to-band recombination coefficient	cm ³ .s ⁻¹
c	Concentration of chemical bonds	mol.L ⁻¹
C_{acc}	Accumulation capacitance	F.cm ⁻²
C_{MG}	Capacitance at mid-gap voltage	F.cm ⁻²
C_{FB}	Flat band capacitance	F.cm ⁻²
C_p	Auger recombination coefficient for holes	cm ⁶ .s ⁻¹
C_{min}	Minimum value of capacitance	F.cm ⁻²
C_{max}	Capacitance at voltage corresponding to G_{max}	F.cm ⁻²
$C_{\text{S,min}}^{\text{HF}}$	Minimum value of semiconductor capacitance	F.cm ⁻²
$C_{\text{S,FB}}$	Semiconductor flat band capacitance	F.cm ⁻²
$C_{\text{S,MG}}$	Semiconductor capacitance at mid-gap voltage	F.cm ⁻²
D_{it}	Energy density of interface state	cm ⁻² .eV ⁻¹
D_n	Diffusion coefficient for electrons	cm ² .s ⁻¹
D_p	Diffusion coefficient for holes	cm ² .s ⁻¹
E	Photon energy	eV
E_{BD}	Effective breakdown field	V.cm ⁻¹
E_{BG}	Band-gap energy	eV

E_C	Conduction band energy	eV
E_f	Fermi level energy	eV
E_V	Valance band energy	eV
E_T	Trap-energy level	eV
f	Frequency	Hz
G	Generation rate	$\text{cm}^{-3}.\text{s}^{-1}$
G_{max}	Peak conductance	$\text{S}.\text{cm}^{-2}$
h	Planck's constant, 6.62×10^{-34}	J.s
I_0	Reverse saturation current	A
I_L	Light-generated current	A
I_m	Current at maximum power point	A
I_{total}	Total diode current	A
I_{sc}	Short-circuit current	A
I	Intensity of light	$\text{W}.\text{m}^{-2}$
I_0	Intensity of light from the reference sample	$\text{W}.\text{m}^{-2}$
J	Current density	$\text{A}.\text{cm}^{-2}$
J_0	Reverse saturation current density	$\text{A}.\text{cm}^{-2}$
J_{0b}	Base saturation current density	$\text{A}.\text{cm}^{-2}$
J_{0e}	Emitter saturation current density	$\text{A}.\text{cm}^{-2}$
J_G	Gate leakage current density	$\text{A}.\text{cm}^{-2}$
k	Boltzmann constant, 1.38×10^{-23}	$\text{J}.\text{K}^{-1}$
L_{bulk}	Bulk diffusion length	cm
L_D	Debye length	cm
L_{eff}	Effective diffusion length	cm
L_n	Diffusion length of electrons	cm
L_p	Diffusion length of holes	cm
n	Ideality factor	
n^+	Highly doped phosphorous concentration	cm^{-3}
n_0	Electron density at thermal equilibrium	cm^{-3}
N_A	Acceptor impurity concentration	cm^{-3}
N_C	Effective density of states for electrons in conduction band	cm^{-3}
N_D	Donor impurity concentration	cm^{-3}

n_i	Intrinsic concentration	cm^{-3}
N_{it}	Interface state density	cm^{-2}
n_s	Electron densities at the surface	cm^{-3}
N_v	Effective density of states for holes in valance band	cm^{-2}
p^+	Highly doped boron concentration	cm^{-3}
p_0	Hole density at thermal equilibrium	cm^{-3}
P_{in}	Input to p-n junction solar cell	W
p_s	Hole densities at the surface	cm^{-3}
q	Charge on electron, 1.6×10^{-19}	C
Q_f	Fixed oxide charges	cm^{-2}
R_{Auger}	Auger recombination rate	$\text{cm}^{-3} \cdot \text{s}^{-1}$
r_e	Classical electron radius, 2.81×10^{-18}	M
R_{BtB}	Band-to-band recombination rate	$\text{cm}^{-3} \cdot \text{s}^{-1}$
R_s	Shockley-Read-Hall recombination rate at surface	$\text{cm}^{-2} \cdot \text{s}^{-1}$
S_{eff}	Effective surface recombination velocity	$\text{cm} \cdot \text{s}^{-1}$
$S_{eff,max}$	Maximum value of effective surface recombination velocity	$\text{cm} \cdot \text{s}^{-1}$
S_{front}	Surface recombination velocity at front surface of p-n junction	$\text{cm} \cdot \text{s}^{-1}$
S_r	Surface recombination velocity	$\text{cm} \cdot \text{s}^{-1}$
S_{rear}	Surface recombination velocity at rear surface of p-n junction	$\text{cm} \cdot \text{s}^{-1}$
T	Absolute temperature	K
T_{ox}	Film thickness	nm
v_{th}	Thermal velocity of electrons	$\text{cm} \cdot \text{s}^{-1}$
V	Applied voltage	V
V_{BD}	Breakdown voltage	V
V_{FB}	Flat-band voltage	V
V_G	Gate Voltage	V
V_m	Voltage at maximum power point	V
V_{MG}	Mid-gap voltage	V
$V_{MG,ideal}$	Ideal value of mid-gap voltage	V
V_p	Pulsed voltage	V

V_{oc}	Open-circuit voltage	V
W	Wafer thickness	cm
W_{dep}	Depletion width	cm
$X_{d,max}$	Maximum depletion length	cm
X_{MG}	Depletion width at mid-gap	cm

List of Acronyms

Acronym	Description
AC	Alternate current
AFM	Atomic force microscope
ALD	Atomic layer deposition
ARA	Aluminum-oxygen rich aluminosilicate
ARC	Anti-reflection coating
As-dep	As-deposited
b-Si	Black silicon
BE	Binding energy
BSF	Back surface field
c-Si	Crystalline silicon
CPV	Concentrating photovoltaic
C-V	Capacitance versus voltage
CVD	Chemical vapor deposition
CZ	Czochralski
DC	Direct current
DI	De-ionized
DSC	Dye-sensitized solar cells
ECR	Electron cyclotron resonance
EELS	Electron energy loss spectroscopy
ELNES	Energy loss near edge spectra
EOT	Equivalent oxide thickness
FF	Fill factor
FGA	Forming gas ambient
FWHM	Full width at half maximum
FTIR	Fourier transform infra-red spectroscope
FZ	Float zone
G-L	Gaussian-Lorentzian
G-V	Conductance versus voltage
HF	Hydrofluoric

ICP-CVD	Inductive coupled plasma chemical vapour deposition
IL	Interfacial layer
IM	Iodine-Methanol
IPD	Inter-poly dielectrics
IR	Infra-red
I-V	Current versus voltage
J-V	Current density versus voltage
KE	Kinetic energy
LFC	Local-fired contact
LPCVD	Low pressure chemical vapour deposition
Multi-Si	Multicrystalline silicon
Mono-Si	Monocrystalline silicon
MPP	Maximum power point
MOS	Metal oxide semiconductor
MOCVD	Metal-organic chemical vapor deposition
<i>O</i>	Octahedral coordination
PA-ALD	Plasma-assisted atomic layer deposition
PC1D	One-dimensional numerical semiconductor simulation tool for personal computer
PD	Power density
PDA	Post-deposition annealing
PECVD	Plasma enhanced chemical vapour deposition
PERC	Passivated emitter and rear cell
PERL	Passivated emitter with rear locally diffused
PMA	Post-metallization annealing
PSG	Phosphor silicate glass
PV	Photovoltaic
PVD	Physical vapor deposition
pulsed-DC	Pulsed-direct current power supply
QSSPC	Quasi-steady-state photoconductance
RCA	Radio Corporation of America
RF	Radio frequency power supply

RI	Refractive index
RMS	Root mean square
RT	Room temperature
RTA	Rapid thermal annealing
RTP	Rapid thermal processing
RS	Reactive sputter
SCS	Semiconductor characterization system
SE	Spectroscopic ellipsometer
SPV	Solar photovoltaic
SRA	Silicon-oxygen rich aluminosilicate
SRH	Shockley-Read-Hall theory
<i>T</i>	Tetrahedral coordination
TEM	Transmission electron microscope
TMA	Tri-methylaluminum
UV	Ultra-violet
UV-Vis-NIR	Ultra violet-visible-near infrared spectroscopy
VLSI	Very large scale integration
XRR	X-ray reflectometer
XPS	X-ray photoelectron spectroscopy

Chapter 1. Introduction

Advancements in renewable energy technologies for the electricity generation have led to less dependency on fossil fuels like petrol and coal. Fossil fuels could extinguish with time, whereas the renewable source of energy like wind, solar and hydro are abundantly available on earth. In particular the solar photovoltaic (SPV) technology has become a fast-growing field today among the renewable energy technologies with an impressive research and development in this field and cost reductions. The SPV technologies were easily scalable and have applications in small-scale to large-scale electricity generation. The basic energy conversion device in SPV is known as “solar cell,” which uses photons from the sunlight as the input source to generate charge carriers, followed by transportation of these charge carriers into external circuit. More efficient solar cell means more electricity generated per unit area of the conversion device. However this should be available at a reasonable cost for affordable electricity. This particular area of manufacturing high efficient solar cells brings in many challenges in the field of research and development.

The solar cells can be classified into different categories, based on their manufacturing technology. Figure 1.1 shows different solar cell technologies with the market share percentage contributed by these technologies namely: thin-films, crystalline silicon (c-Si) and other compound semiconductor technologies [1,2]. Organic PV technologies are negligible fraction of manufacturing today. Table 1.1 lists the best conversion efficiency (η) for these technologies on the laboratory scale [3].

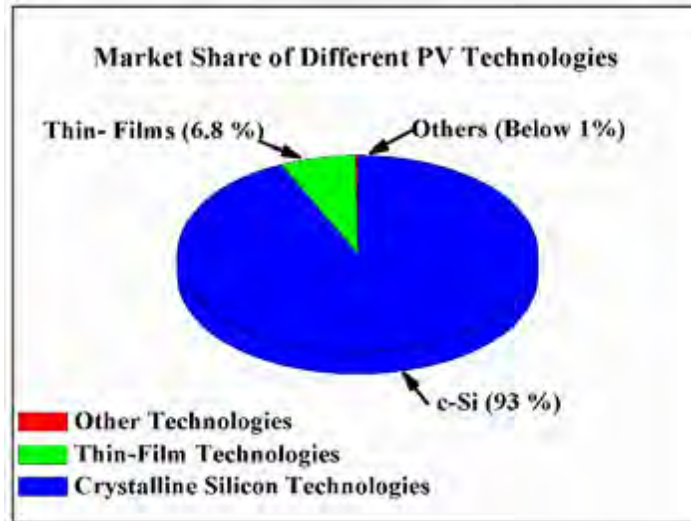


Figure 1.1 Market shares of different photovoltaic technologies [1,2].

The solar cell technologies can be classified into wafer based and thin-film technologies. The thin-film solar cells can be further classified into organic and inorganic type solar cells. The organic solar cells are made by using polymers or organic molecules, for electricity generation, and are also classified under the “emerging technology”. These are relatively low-cost technologies due to simple fabrication process steps and are lighter in weight due to the use of flexible substrates like plastic. The dye-sensitized solar cell (DSC) under this technology has shown best cell efficiency, η of $11.9 \pm 0.4 \%$, whereas organic solar cells has shown η of $11.2 \pm 0.3 \%$ [2]. With this technology, the stability and proper encapsulation are the major concerns [4].

On the other hand thin-film (inorganic) and c-Si wafer based solar cell technologies have shown relatively good light conversion efficiency as compared to organic solar cells. For the CdTe and CIGS thin-films solar cells, η of $21.0 \pm 0.4 \%$ and η of $21.7 \pm 0.4 \%$, respectively have been reported [3]. These types of cells are relatively economical because of less expensive and less amount of materials used for the fabrication. The fabrication of inorganic thin-films cells involves the chemical deposition technique which makes it relatively simple to manufacture. The disadvantage of the above mentioned thin film cells are: the toxicity of Cd and scarcity of Te materials which leads to lack of interest by the manufacturers for CdTe cells. Whereas for CIGS cells, the deposition process becomes more complicated due to difficulty in control over deposition process [5]. Having these issues with the technology, another type of thin-film solar cells have emerged with an advantage of

low-temperature for processing, known as amorphous silicon (a-Si) thin-film cells that has shown η of 10.2 ± 0.3 % [3,6].

Table 1.1 Best conversion efficiency reported for different PV technologies solar cells on laboratory scale [3].

Technology	Cells	Area	Cell efficiency, η (%)
Thin-films	CIGS	1.044 cm ² (dp)	21.7 \pm 0.5
	CdTe	1.0623cm ² (ap)	21.0 \pm 0.4
	a-Si	1.001 cm ² (da)	10.2 \pm 0.3
Organic cell	Dye-sensitised cell	1.005 cm ² (da)	11.9 \pm 0.4
	Organic cell	0.992 cm ² (da)	11.2 \pm 0.3
Crystalline silicon	Multi-Si	3.923 cm ² (ap)	22.3 \pm 0.4
	Mono-Si (rear junction cells)	79.0 cm ² (da)	26.7 \pm 0.5

Abbreviations: (ap) - aperture area, (da) - designated illuminated area.

As listed in Table 1.1, the c-Si solar cells have shown highest η of 26.7 % among different technologies. Figure 1.1 shows, this technology also dominates most of the PV market, since it's highly compatible with the existing VLSI silicon technology and manufacturing. The record energy conversion efficiency, η of 26.7 % was reported for laboratory make c-Si solar cell, whereas industrial c-Si solar cells have shown η of 22.5 % [1]. The silicon based concentrating photovoltaic (CPV), which works on the concept of an optical concentrator system, i.e., used to focus the solar radiation into small solar cell, leads to further improvement in η even beyond 25 % [3]. Similarly multi-junction solar cells also give very high efficiency. But due to their high costs for design and manufacturing, they are invariable restricted to niche applications such as in space.

In conventional c-Si solar cell, various factors leads to losses, viz.: reflection from the front surface, coverage area from metal contacts, parasitic resistance and various areas of

recombination for minority charge carriers, needs to be addressed to achieve higher efficiency. In the subsequent section we will discuss and present different ways to reduce the losses due to recombination of charge carriers, hence to improve the efficiency of the c-Si solar cell.

1.1 Recombination mechanisms in crystalline silicon

In a semiconductor, as light falls on the Si surface a photon with enough energy will get absorbed and results in an electron to get excited from the valance band and moves to the conduction band after gaining sufficient energy. During this process a ‘hole’ is created in the valance band and thus an electron-hole pair is generated. The process is called “generation” of carriers. The exact opposite process is called “recombination” of carriers. To make high efficiency solar cell, the basic requirements are the generation of large number of free charge carriers and to minimize the recombination of these photon generated free charge carriers.

Three types of recombination mechanisms are dominant in a semiconductor material: (a) band-to-band, (b) Auger and (c) trap-assisted recombination, as shown in Figure 1.2 [7].

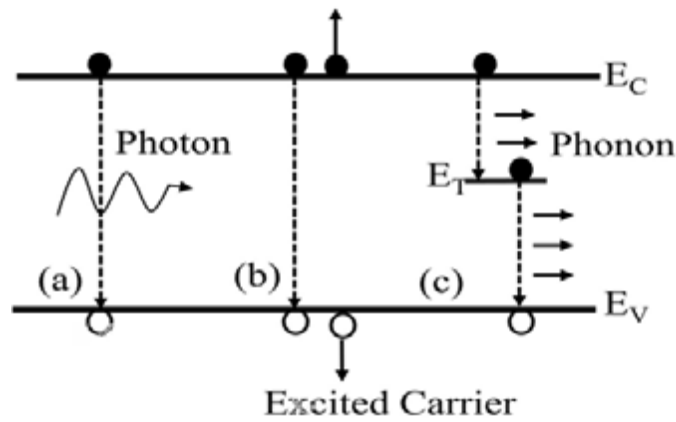


Figure 1.2 Recombination mechanisms in a semiconductor material: (a) band-to-band, (b) Auger and (c) trap-assisted recombination [7].

(a) In band-to-band recombination mechanism, an electron from the conduction band recombines with a hole in the valance band with an emission of a photon. The band-to-band recombination rate (R_{BtB}) is expressed by eq. (1.1), considering for p-type semiconductor material,

$$R_{BtB} = Bp_0\Delta n \quad (\text{cm}^{-3}.\text{s}^{-1}) \quad (1.1)$$

where, B represents the band-to-band recombination coefficient ($\text{cm}^3 \cdot \text{s}^{-1}$), p_0 represents the equilibrium charge carrier density (cm^{-3}) and Δn represents the excess minority charge carrier density (cm^{-3}). In direct band-gap materials the conduction band minima and the valance band maxima are directly align, hence during the recombination process an excess energy is released in the form of photon with energy equal to the band-gap energy of the material. Such kind of recombination are mostly dominating in direct band-gap semiconductor materials. Whereas in indirect band-gap material where the conduction band minima and valance band maxima are not align, the recombination process takes place in the form of phonon assisted transition. Where a phonon is lattice vibration and carries low energy and large momentum. In indirect semiconductor like Si, such kind of recombination is negligible, since the transition must be assisted with the phonon and photon.

(b) In Auger recombination, an electron from the conduction band recombines with the hole in the valance band. During this process excess energy is transferred as kinetic energy to another free electron in the conduction band, which makes it move to a higher energy state in the conduction band or similarly a hole makes a movement deeper into the valance band after gaining kinetic energy. For p-type semiconductor, Auger recombination rate (R_{Auger}) may be expressed as eq. (1.2)

$$R_{\text{Auger}} = C_p p_0^2 \Delta n \quad (\text{cm}^{-3} \cdot \text{s}^{-1}) \quad (1.2)$$

where, C_p represents the Auger recombination coefficient for holes ($\text{cm}^6 \cdot \text{s}^{-1}$). This type of recombination mechanism dominates mostly for the materials with higher doping concentration.

(c) In trap-assisted recombination, a free electron from the conduction band is captured in a defect level in the energy band-gap known as trap-energy (E_T) level. This trap would then captures a hole leading to recombination. During this process the excess energy is dissipated as phonon. This recombination mechanism is described by the Shockley-Read-Hall (SRH) theory. Hence it is also known as SRH recombination [7]. The SRH recombination rate can be expressed as a function of trap densities (interface defect densities in case of recombination at the interface between materials), capture cross-section area for hole, σ_p and electrons, σ_n (cm^2) and charge carrier density in the silicon bulk or at the surface.

The defects in the silicon bulk may be created during material processing. For example with the Czochralski (CZ) crystal growth technique, the Si wafers have more defect

density as compared to float zone (FZ) technique [8,9]. On the other hand, the surface of Si wafer is more prone to defects due to abrupt discontinuity of a crystal lattice structure, which gives rise to unsaturated bond known as dangling bond. These are actually the recombination centres at the surface which can be reduced by using different passivation technique that will be discussed later in this chapter. The SRH recombination rate (R_s) at the surface is given by eq. (1.3).

$$R_s = \frac{s_n s_p (p_s n_s - n_i^2)}{s_n (n_s + n_{1s}) + s_p (p_s + p_{1s})} \quad (\text{cm}^{-2} \cdot \text{s}^{-1}) \quad (1.3)$$

where s_n and s_p are defined as $s_n = \sigma_{ns} v_{th} N_{it}$; $s_p = \sigma_{ps} v_{th} N_{it}$, here v_{th} represents thermal velocity of electrons ($\text{cm} \cdot \text{s}^{-1}$), σ_n and σ_p represent capture cross-section area of electron and hole (cm^2), respectively, here subscript 's' refers to the surface quantities, N_{it} is interface state density (cm^{-2}), n_s & p_s are electron and hole carrier densities at the surface, n_1 & p_1 are the statistical factors, given as follows

$$n_1 \equiv N_C \exp\left(\frac{E_T - E_C}{kT}\right); p_1 \equiv N_V \exp\left(\frac{E_C - E - E_T}{kT}\right) \quad (\text{cm}^{-3}) \quad (1.4)$$

where, N_C and N_V are effective density of states for electrons in the conduction band and holes in valence band (cm^{-3}), respectively. E_C represents the conduction band energy (eV) and E_T represents trap-energy level (eV), k represents the Boltzmann constant which is $1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ and T represents absolute temperature (K).

The surface recombination velocity, S_r ($\text{cm} \cdot \text{s}^{-1}$) which is a measure of how fast the light-generated or excess charge carriers recombine at the surface of the semiconductor, is given by eq. (1.5)

$$S_r = \frac{R_s}{\Delta n_s} \quad (\text{cm} \cdot \text{s}^{-1}) \quad (1.5)$$

where R_s represents surface SRH recombination rate ($\text{cm}^{-2} \cdot \text{s}^{-1}$), Δn_s represents excess electron concentration (cm^{-3}) at the semiconductor surface. From eq. (1.3) and (1.5), it is deduced that S_r can be reduced with reduction in number of N_{it} and/or by reduction in either type of charge carriers at the surface. The value of S_r can be calculated from the minority charge carrier life-time, τ (s) as well, i.e., the average time a charge carrier spends in an excited state before recombining.

In the semiconductor the effective minority charge carrier life-time, τ_{eff} (s), comprises the effects of all the recombination including bulk as well as surface, which is given by eq. (1.6),

$$\frac{1}{\tau_{eff}} = \left(\frac{1}{\tau_{SRH}} + \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{BtB}} \right) + \frac{1}{\tau_S} \quad (s^{-1}) \quad (1.6)$$

where, τ_{Auger} is due to Auger recombination based on impurities and defects in the material, such kind of recombination is most dominating in heavily doped materials. The τ_{BtB} appears due to band-to-band recombination. While τ_{SRH} appears due to SRH recombination that depends on the defects at various levels in the semiconductor material. The minority carrier life-time in bulk of semiconductor, τ_{bulk} (s) includes the effect of all the three above mentioned recombination mechanisms. The minority carrier life-time due to recombination of charge carriers at the surface is given as τ_s (s). In case of symmetrical structure where both the front and rear surfaces of semiconductor are passivated symmetrically, the effective surface recombination velocity (S_{eff}) is defined using eq. (1.7) and (1.8),

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S_{eff}}{W} \quad (s^{-1}) \quad (1.7)$$

$$S_{eff} = \frac{W}{2} \left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}} \right) \quad (cm.s^{-1}) \quad (1.8)$$

where, W represents the wafer thickness in cm. From the quasi-steady-state photo-conductance (QSSPC) technique, one can obtain the value of τ_{eff} on the passivated semiconductor surface [10]. The value of τ_{bulk} (s) can be measured using QSSPC technique with the application of a chemical passivation on semiconductor surface [11]. The above equation is valid for the properly passivated samples with low value of S_{eff} . Whereas for poorly passivated sample with $S_{eff} \rightarrow \infty$, surface recombination is limited by the diffusion of charge carriers, and the relationship is given by eq. (1.9) and (1.10) [12].

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \left(\frac{W}{2S_{eff}} + \frac{1}{D_n} \left(\frac{W}{\pi} \right)^2 \right)^{-1} \quad (s^{-1}) \quad (1.9)$$

$$S_{eff} = \frac{\pi^2 D_n W (\tau_{bulk} - \tau_{eff})}{2\pi^2 D_n \tau_{bulk} \tau_{eff} - 2W^2 (\tau_{bulk} - \tau_{eff})} \quad (cm.s^{-1}) \quad (1.10)$$

where D_n represents diffusion coefficient of electrons ($\text{cm}^2.\text{s}^{-1}$). On the other hand, for asymmetrical structure like p-n junction, where emitter region is relatively doped higher as compared to the base region, the calculation of S_{eff} changes again, as defined by eq. (1.11) [13].

$$S_{\text{eff}} = \frac{J_{0e}(N_A + \Delta n)}{qn_i^2} \quad (\text{cm}.\text{s}^{-1}) \quad (1.11)$$

where J_{0e} represents the emitter saturation current density ($\text{A}.\text{cm}^{-2}$). N_A represents the acceptor impurity concentration (cm^{-3}) and n_i represents intrinsic concentration (cm^{-3}) of the semiconductor material, q represents the electronic charge which is 1.6×10^{-19} C. The eq. (1.11) is the simplified equation assuming that the minority carrier life-time in emitter region is much less than life-time in base region and the life-time is independent of Δn [13].

1.2 Solar cell performance parameters

The typical structure of p-n junction solar cell and current versus voltage (I-V) characteristics are shown in Figure 1.3 (a) and (b), respectively.

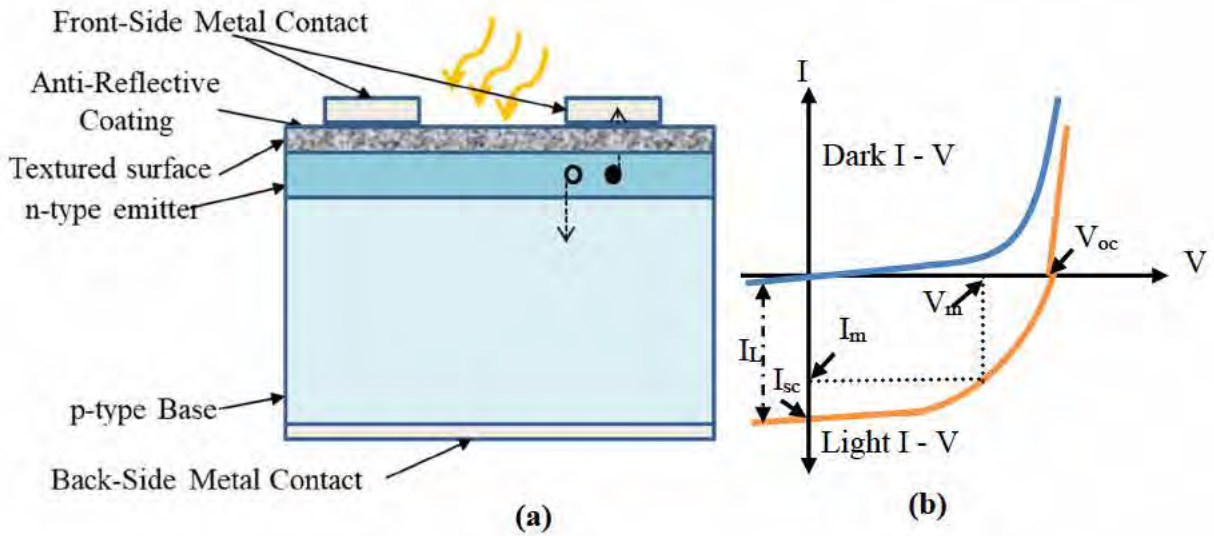


Figure 1.3 (a) Typical p-n junction solar cell structure, (b) I-V characteristics of p-n junction solar cell.

When light incident on the solar cell, the photons get absorbed in the semiconductor and generates free electron-hole pairs. At the p-n junction these carriers get separated and transported through the solar cell towards external load for the electricity generation. The I-V

characteristics of the solar cell generally appears in the IVth quadrant in the graph, as shown in Figure 1.3 (b). The total current (I_{total}) of the p-n junction diode after illumination is given by eq. (1.12) [14].

$$I_{total} = I_0 \left(e^{qV/nkT} - 1 \right) - I_L \quad (\text{A}) \quad (1.12)$$

where V represents applied voltage (V), n represents the ideality factor which is a deviation from the ideal I-V characteristics (n = 1 for low level injection and n = 2 for high level injection). I_0 represents the reverse saturation current (A), which is defined from the basic properties of the semiconductor material and the p-n junction, and is given by eq. (1.13) [14],

$$I_0 = qA \left(\frac{D_n}{L_n} n_{p0} + \frac{D_p}{L_p} p_{n0} \right) \quad (\text{A}) \quad (1.13)$$

where A represents the cross-sectional area of device (cm²), $D_{(n, p)}$ represents the diffusion coefficients of electrons and holes (cm².s⁻¹), $L_{(n, p)}$ represents the diffusion lengths of electrons and holes (cm). Here diffusion length is defined as the average length a charge carrier diffuses into semiconductor before it recombines and is given by $L_n = \sqrt{D_n \tau_n}$ where τ_n (s) is the minority carrier life-time of electron and therefore it is related to the S_r . The terms n_{p0} represents the minority carrier electrons in the p-side under the equilibrium condition and similarly p_{n0} represents the minority carrier holes in the n-side under the equilibrium condition. To further simplify the eq. (1.13), the term reverse saturation current density (J_0) is defined as $I_0.A^{-1}$, as given in eq. (1.14),

$$J_0 = J_{0e} + J_{0b} \quad (\text{A.cm}^{-2}) \quad (1.14)$$

where, J_{0e} represents emitter saturation current density (A.cm⁻²), which is measured using QSSPC technique on symmetrical structure [10,13] and is given by eq. (1.15),

$$J_{0e} = \frac{qn_i^2 S_{eff}}{(N_A + \Delta n)} \quad (\text{A.cm}^{-2}) \quad (1.15)$$

Hence, the reverse saturation current density is dependent on the S_{eff} value as well. In eq. (1.14), the J_{0b} represents the base saturation current density (A.cm⁻²), is given by eq. (1.16) [15],

$$J_{0b} = \frac{qn_i^2 D}{L_{eff} N_A} \quad (\text{A.cm}^{-2}) \quad (1.16)$$

where, D represents minority carrier diffusion coefficient ($\text{cm}^2.\text{s}^{-1}$) and L_{eff} represents the effective diffusion length (cm), which depends on rear surface recombination velocity S_{rear} ($\text{cm}.\text{s}^{-1}$), bulk diffusion length L_{bulk} (cm) and W (cm), is given by eq. (1.17) [15],

$$L_{\text{eff}} = L_{\text{bulk}} \frac{1 + \frac{S_{\text{rear}}L_{\text{bulk}}}{D} \tanh\left(\frac{W}{L_{\text{bulk}}}\right)}{\frac{S_{\text{rear}}}{D} + \tanh\left(\frac{W}{L_{\text{bulk}}}\right)} \quad (\text{cm}) \quad (1.17)$$

The I_L term in eq. (1.12) is known as light-generated current (A), which is defined by eq. (1.18) [14],

$$I_L = qAG(L_n + W_{\text{dep}} + L_p) \quad (\text{A}) \quad (1.18)$$

where G represents the generation rate ($\text{cm}^{-3}.\text{s}^{-1}$) and W_{dep} represents the depletion width (cm). Hence the I_L represents the light current due to carriers generated within the $(L_n + W_{\text{dep}} + L_p)$ length.

The other important terms obtained from I-V characteristics is the short-circuit current I_{sc} (A) and open-circuit voltage V_{oc} (V), these terms are used to determine the efficiency, η of the solar cell, which is defined by eq. (1.19) [14],

$$\eta = \frac{I_{\text{sc}}V_{\text{oc}}FF}{P_{\text{in}}} \quad (\%) \quad (1.19)$$

where P_{in} represent the input incident radiation flux ($\text{W}.\text{cm}^{-2}$) multiplied with area of incidence (cm^2). I_{sc} represents the maximum current when load is shorted, $I_{\text{sc}} = -I_L$ when $V = 0$, in eq. (1.12). V_{oc} represents the maximum voltage when load is open, i.e., with $I = 0$, is given by eq. (1.20) [14],

$$V_{\text{oc}} = \frac{nkT}{q} \ln\left(\frac{I_L}{I_0} + 1\right) \quad (\text{V}) \quad (1.20)$$

The value of V_{oc} can be affected by both the I_L and I_0 , where I_0 depends on the properties of material like diffusion coefficient, diffusion length and S_{eff} as given in eq. (1.14), (1.15) and (1.16). Hence the value of S_{eff} eventually have impact on η of the solar cell, from the value of I_0 in V_{oc} as defined in eq. (1.20).

The fill factor (FF) is generally expressed in percentage and is defined as the ratio of maximum power ($I_m \times V_m$) to product of ($I_{\text{sc}} \times V_{\text{oc}}$). Where the I_m (A) and V_m (V) from maximum power are the value of current and voltage, respectively when the cell produces

maximum power, at maximum power point (MPP). The position of MPP is normally close to the bend in I-V curve characteristics of the cell. The FF is also a measure of the squareness of the I-V curve of solar cell, which is given by eq. (1.21) [14],

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (1.21)$$

As discussed in the previous sections, the surface of the semiconductor has most recombination centres due to abrupt ending of crystal structure and defects, hence the impact of surface recombination velocity of the individual surfaces viz. front (S_{front}) [i.e., at emitter] and rear (S_{rear}) [i.e., at base] on the overall η of solar cell were simulated using PC1D simulator [16]. The p-type c-Si solar cell with the cell parameters as given in Table 1.2, was simulated using PC1D simulator. The effect of front surface recombination velocity (S_{front}) and rear surface recombination velocity (S_{rear}) on solar cell efficiency are shown in Figure 1.4 (a) and (b), respectively.

Table 1.2 The p-n junction c-Si solar cell parameters input to PC1D simulator to study the impact of surface recombination velocity at the front and rear surface on solar cell η [16].

Solar cell parameters	Input values
Cell area	1 cm ²
Wafer thickness	200 μ m
Wafer resistivity	1 Ω .cm
Front surface texture	5 μ m
n ⁺ emitter doping	5.5×10^{19} cm ⁻³
p-type base doping	1.5×10^{16} cm ⁻³
Wafer bulk lifetime	5 ms
Anti-reflection coating	Thickness = 75 nm, Refractive index (RI) =2
Front surface recombination velocity (S_{front})	Varied between 1 to 10^6 cm.s ⁻¹
Rear surface recombination velocity (S_{rear})	Varied between 1 to 10^6 cm.s ⁻¹

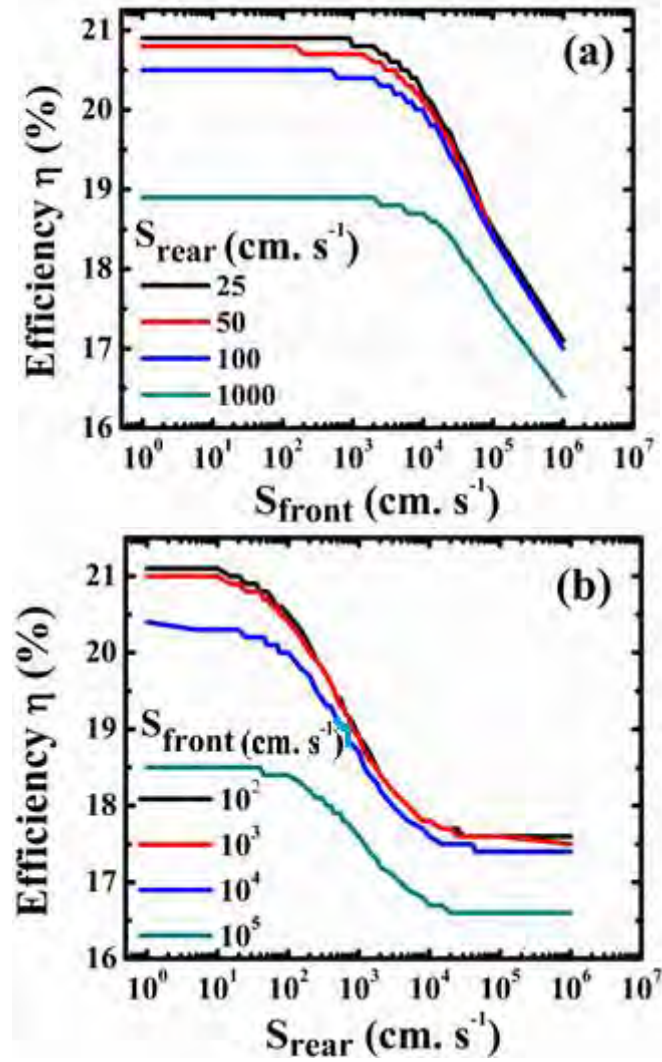


Figure 1.4 Impact of surface recombination on p-n junction solar cell efficiency η simulated using PC1D simulator, by (a) varying the S_{front} , while keeping S_{rear} constant (b) varying the S_{rear} , while keeping S_{front} constant.

Figure 1.4 (a) shows the effect of S_{front} on solar cell η (%) for different values of S_{rear} set as 25, 50, 100 and 1000 cm.s⁻¹. The high η of 20.5 % is observed for cells with the values of $S_{\text{rear}} < 100$ cm.s⁻¹ and $S_{\text{front}} < 10^3$ cm.s⁻¹. Figure 1.4 (b) shows the effect of S_{rear} on solar cell η (%) for different values of S_{front} set as 10², 10³, 10⁴ and 10⁵ cm.s⁻¹. An improvement in η from 18.5 % upto 21 % is possible for solar cell with $S_{\text{front}} < 10^3$ cm.s⁻¹ and $S_{\text{rear}} < 100$ cm.s⁻¹. Since the emitter region is heavily doped in p-n junction solar cell, which results in the value of $S_{\text{front}} \sim 10^4$ cm.s⁻¹. Hence with the passivated rear surface ($S_{\text{rear}} < 100$ cm.s⁻¹), high efficiency can be achieved for this particular solar cell architecture.

1.3 Surface passivation of crystalline silicon

The surface passivation is a process through which the process of recombination of light generated hole-electron pair get reduced via reduction of number of recombination centres at the semiconductor surface and/or by creating electrostatic charge at surface. The two common mechanisms for surface passivation are chemical passivation and field-effect passivation as described below.

1.3.1 Chemical passivation

The method by which recombination centres at the surface can be reduced by decreasing the number of dangling bonds is known as chemical passivation. This can be achieved by deposition or growth of an appropriate film on the silicon surface. This will saturate the dangling bonds and hence reduce N_{it} , as shown in Figure 1.5 (a). For example, thermally grown SiO_2 and hydrogenated amorphous silicon (a-Si:H) can be used as chemical passivation layers. The O or H atoms from these films make bonds with unsaturated dangling bonds and hence reduces N_{it} . Another method to improve the surface passivation is by post-deposition annealing (PDA) process in forming gas ambient (FGA). The FGA is a mixture of hydrogen and nitrogen gases, at high temperature in the range of 350-400 °C. The hydrogen from FGA diffuse through the dielectric material to make Si:H bonds at the interface to further improve the passivation quality with reduction in N_{it} [17]. The N_{it} is also referred in terms of energy density of interface states, D_{it} ($\text{cm}^{-2} \cdot \text{eV}^{-1}$), i.e., number of N_{it} spread between conduction band (E_c) and valence band (E_v), which is given as eq. (1.22) ,

$$N_{it} = \int_{E_c}^{E_v} D_{it} dE \quad (\text{cm}^{-2}) \quad (1.22)$$

1.3.2 Field-effect passivation

As discussed in the previous section, the surface recombination velocity, can be reduced by preventing the minority charge carriers to reach the surface where the density of recombination centres are high. This can be implemented by creating high-low doping profile near the silicon surface, as shown in Figure 1.5 (b). Another method for reduction of surface recombination velocity by maintaining low concentration of one type of charge carrier than the other at the surface. This can be realised through the electric-field potential at the surface using an electrostatic charges like fixed oxide charges, Q_f (cm^{-2}) of an overlying dielectric

film, as shown in Figure 1.5 (c). The electrostatic charges are usually fixed oxide charges in dielectric film or may be deposited externally through the corona charging method, which results in electrostatic potential barrier at the surface, hence results in reduction of either type of charges at the silicon surface to reduce the surface recombination velocity as explained in section 1.1.

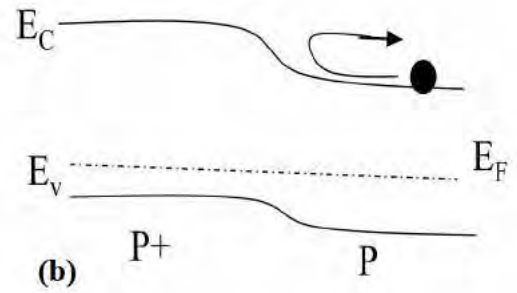
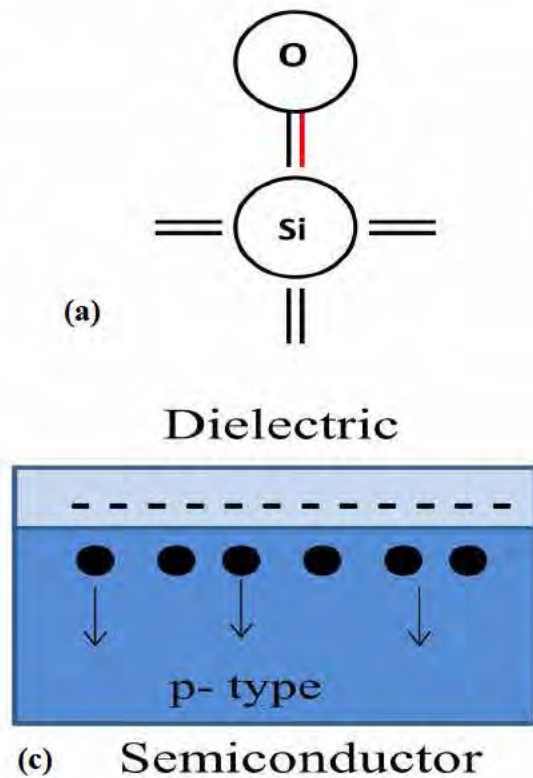


Figure 1. 5 Surface passivation mechanism for crystalline silicon viz. (a) chemical passivation and field-effect passivation further characterized as (b) by high-low doping profile and (c) passivation using dielectric layer with electrostatic charges, i.e., Q_f .

The simulation study reported by Dingemans et al., shows the impact of individual type of passivation via chemical and field-effect passivation on the value of overall S_{eff} by using eq. (1.3) and (1.5), for different values of negative Q_f and N_{it} [12]. Where the PC1D simulation tool was used to obtain the carrier densities at surface (n_s , p_s) under illumination, the result from the publication is shown in Figure 1.6 [12].

The simulated result shows that the value of S_{eff} is relatively high for low value of negative $Q_f \leq 5 \times 10^{10} \text{ cm}^{-2}$, at highly doped emitter surface. Whereas the value of S_{eff} decreases when value of negative Q_f increases beyond $5 \times 10^{11} \text{ cm}^{-2}$, following a $1/Q_f^2$ relation. This effect of change in surface recombination velocity with change in fixed oxide charge density in the dielectric is known as field-effect passivation. While the result also shows, a linear change in S_{eff} values with change in number of N_{it} , the effect is known as

chemical passivation. Hence a high level of surface passivation can be achieved if both chemical as well as field-effect passivation mechanism works together [12].

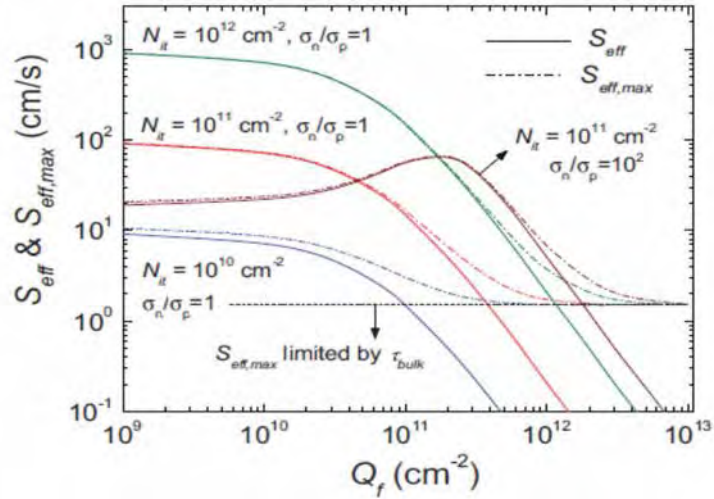


Figure 1.6 The impact of chemical and field-effect passivation on the surface recombination velocity simulated using the equations for S_{eff} and $S_{eff,max}$, as shown in eq. (1.3) and (1.5), for different values of negative Q_f and N_{it} . The n_s and p_s were obtained using PC1D simulator.

The values used for the defect carriers cross-sections $\sigma_n = \sigma_p$: 10^{-16} cm^2 [12].

1.4 Application of different materials as surface passivation layers

1.4.1 Silicon dioxide (SiO₂)

The thermally grown silicon dioxide (SiO₂), has shown a good quality of chemical passivation property on silicon solar cells due to its excellent interface property with very low D_{it} of $10^{10} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ [18,19]. The low value of D_{it} was achieved, since the film grows on Si substrate with O₂ gas ambient at high processing temperature (900-1100 °C) known as dry-oxidation process or in H₂O vapour ambient at relatively low temperature range (600-800 °C) known as wet-oxidation process. The thermally grown SiO₂ films have shown an excellent surface passivation with $S_{eff} < 10 \text{ cm} \cdot \text{s}^{-1}$ on both p-type and n-type silicon surfaces after PDA in FGA at 400 °C for 30 min [20].

The thermal stability of these SiO₂ films was tested for different temperature at 400-600 °C (isochronal: by keeping process time constant, i.e., 3 min) and time at 1-6 min (isothermal: by keeping process temperature constant at 550 °C) using rapid thermal

annealing (RTA) in dry N₂ ambient and the S_{eff} was seen to be degrading with time and temperature which may be due to de-passivation at Si-SiO₂ interface [20,21]. Johnson et al. reported a degradation of S_{eff} value by exposure to humidity [22]. Another disadvantage of using thermally grown SiO₂ is the requirement of high temperature and long processing time, which may eventually increase cost of processing. Also high-temperature may degrade the τ_{bulk} . Hence a low-temperature plasma enhanced chemical vapour deposition (PECVD) method used for SiO₂ film deposition, was widely investigated for silicon solar cell applications [23,24]. In another report on chemically grown SiO₂ using nitric acid (HNO₃) was also investigated for surface passivation of solar cells [25].

1.4.2 Amorphous silicon nitride (a-SiN_x)

The amorphous silicon nitride (a-SiN_x) film was found to be most attractive passivation layer for n-type surface, as it was already implemented as an anti-reflection coating (ARC) in silicon solar cells. The film RI can be tuned by varying the film compositions and can be easily deposited at low-temperature using PECVD technique. The PECVD deposition techniques results in hydrogenated SiN_x film. The surface passivation of n-type silicon was mainly because of field-effect passivation mechanism as the film carries large number of positive Q_f in the range of 10¹² cm⁻² and the hydrogen from film will incorporate the chemically passivation mechanism in the surface. The PECVD SiN_x have shown good quality of surface passivation on both diffused and non-diffused Si surfaces [26]. An implied V_{oc} of 723 mV and S_{eff} of 2 cm.s⁻¹ was reported using as-deposited SiN_x film with RI of 2.75 on the planner and non-diffused surface, whereas on textured and boron diffused surface an improvement in surface passivation was realized only after PDA at 500 °C in N₂ ambient for 5 min [26]. The SiN_x film also shows stable surface passivation after exposure to the ultra-violet (UV) radiation [27,28].

On p-type silicon solar cells, this film was applied to passivate n-type highly doped emitter surface. However, when the same was applied on p-type rear surface, the positive charges of SiN_x film is likely leading to the shunting effect due to formation of an inversion layer at rear surface [29,30]. Hence this film is not a suitable choice for passivation of p-type rear-surface.

1.4.3 Hydrogenated amorphous silicon (a-Si:H)

The hydrogenated amorphous silicon (a-Si:H) can be applied as surface passivation layer by using the hydrogen atoms to saturate the dangling bond on the surface and thus minimizes the surface recombination velocity. The PECVD deposited a-Si:H was demonstrated to passivate both n and p-type silicon surfaces, with good quality of passivation achieved only after the PDA process. The quality of passivation was seen to be independent of film thickness for film thickness greater than 10 nm [31]. The disadvantage of a-Si:H film observed was the parasitic absorption in the UV-range and instability of the film after high temperature processing [32].

1.4.4 Aluminum oxide (AlO_x)

As discussed earlier, a $\text{SiN}_x\text{:H}$ film is a suitable choice for passivation of n-type surface due to positive Q_f charges, while application on p-type rear surface degrades the cell quality due to parasitic shunting effect. Hence the AlO_x film which contains negative Q_f , may be a suitable choice for passivation of p-type silicon surface, with the field-effect mechanism. The AlO_x film was successfully implemented as p-type rear-surface passivation layer for p-type silicon solar cells [12,33-35]. Various reports have shown the excellent quality of surface passivation realized using AlO_x film due to combined field-effect passivation mechanism with high number of negative Q_f and chemical passivation mechanism with low number of D_{it} .

1.5 Thesis motivation

As discussed, there is much scope for research work towards an improvement in efficiency of silicon solar cells and at the same time decreasing the cost of the cell, so that one can have economically viable electricity generation through solar cells. In this thesis work, our focus is to minimize losses due to surface recombination on the p-type silicon surface with application of AlO_x film. In this work, we have examined the deposition of AlO_x films using industrial reactive sputter (RS) deposition technique with the use of pulsed-direct current (pulsed-DC) power supply source. This work carries development and optimization of process for film deposition and further the characterization of these films using different techniques to assess the applicability of the film as surface passivation layer. Various in-depth studies of the film and its interface with analysis, has led us to the conclusion that the

pulsed-DC RS AlO_x film is an interesting candidate for application as surface passivation layer on p-type surface.

1.6 Thesis outline

In this chapter we have discussed in brief different kinds of solar cell technologies. The cause of losses in the p-n junction solar cell due to carrier recombination and different surface passivation mechanism used so far for the passivation of c-Si solar cells were described. We have also discussed different materials already playing a role as passivation layer in solar cell industries. At the end, the motivation behind this research work is given in brief. In chapter 2, literature review of various reports on the applicability of the AlO_x film as surface passivation layer with various properties and passivation quality, for film deposited using different techniques will be presented. The chapter will also give the details on experimental techniques used in this work. The details on systems used for various characterization and different methodology used for analysis of results will be discussed in chapter 2. In chapter 3, development and optimization process for AlO_x film deposition using pulsed-DC RS technique will be discussed. The quality of the films formed will be assessed through various material and electrical characterization will be presented. In chapter 4, the impact of different PDA conditions by varying ambient and temperature, on the surface passivation quality of pulsed-DC RS AlO_x film will be discussed towards the optimization of PDA process. In this chapter the detailed study of the material and interface quality using sophisticated characterization tools will also be presented. The origin and distribution of the charges in the film will be discussed in chapter 5. The chapter also gives details on the differences of the passivation result for as-deposited and annealed films. In chapter 6, the impact of different process parameters on the quality of film after application of optimized PDA condition will be presented to develop the economically viable process of the film deposition towards surface passivation application. In chapter 7, the thermal stability of the film will be presented for pulsed-DC RS AlO_x film and the impact of additional $\text{SiN}_x\text{:H}$ capping layer on the thermal stability will be studied. In chapter 8, we present the conclusions of the research work with the future direction.

Chapter 2. Literature Review and Experimental Techniques

2.1 Introduction

As discussed in previous chapter an improvement in performance of silicon solar cells may be realised with an implementation of surface passivation layer. For example on p-type silicon solar cells, the front surface, i.e., emitter, which is normally textured to maximize the absorption of light has a-SiN_x film as ARC deposited on it. The film was also used as passivation layer due to high number of positive Q_f on n⁺ emitter. Whereas rear-surface p-type base, needs a different material for passivation which must contains negative Q_f to avoid parasitic shunting effect [33,36]. Since the AlO_x film contains negative Q_f, this becomes a potential choice for passivation of p-type silicon surface [33,36]. The AlO_x film was successfully implemented as p-type rear-surface passivation layer on p-type silicon solar cells with advance structure like passivated emitter and rear cell (PERC) [95,33-35,37]. Various reports have shown that excellent surface passivation quality by AlO_x film is achieved due to combined effect of field-effect mechanism (high negative Q_f) and chemical passivation mechanism (low D_{it}). Also the application of this material on n-type silicon solar cell for passivation of highly doped p⁺ emitter surface was also explored in many reports [38-40]. Studies have shown that adding negative Q_f on highly doped p-type emitter of n-type solar

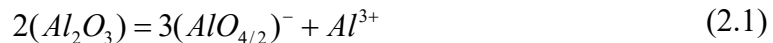
cells improves the cell performance with passivation of the emitter surface. For these reasons AlO_x film has become one major choice as surface passivation layer for p-type silicon [40].

In this chapter we will present a review of the published reports on the applicability of AlO_x film deposited using various techniques for surface passivation layer of silicon solar cells. The review on electrical and material properties of the film, relating the passivation quality will be presented. The impact on cell parameters by using AlO_x surface passivation layer will be presented for various deposition techniques.

A brief description about different systems and experimental set-ups used for the thesis work will be presented in this chapter for reference. The brief description on working principle of the various characterization tools and methodology applied for analysis of the results used in this work will also be presented later in this chapter.

2.2 Theoretical understanding of $\text{AlO}_x/\text{c-Si}$ interface

The origin of field-effect passivation by dielectrics is due to presence of high density of fixed oxide charges, Q_f in the film. In AlO_x film, it is the large density of negative Q_f used for passivation of p-type c-Si surface, with repulsion of the minority carriers (i.e., electron) from the surface. The origin of these negative Q_f in AlO_x film deposited on c-Si was studied and reported by Matsunaga et al., using first-principles plane-wave pseudo-potential method [41]. They proposed that the presence of intrinsic defects like Al-vacancies and O-interstitials, results in origin of negative Q_f charges in the film. On the other hand, Kimoto et al. reported the presence of both tetrahedrally (T) coordinated Al (negatively charged) and octahedrally (O) coordinated Al sites (positively charged) in $\gamma\text{-Al}_2\text{O}_3$ film deposited using atomic layer deposition (ALD) [42], as given below



The study shows that close to the $\gamma\text{-Al}_2\text{O}_3/\text{c-Si}$ interface, T coordinated Al bonded directly with O, seems to be more dominating which results in increase of negative Q_f in the film [35,42,43]. Further increase in the negative Q_f density was observed after annealing of the ALD- Al_2O_3 film, with a concomitant formation of thin SiO_2 interfacial layer at $\text{Al}_2\text{O}_3/\text{c-Si}$ interface [34,44,45]. The increase in negative Q_f values after annealing, was due to increase in T coordinated Al at the interface, which results in improvement of surface passivation quality by plasma-assisted (PA)-ALD Al_2O_3 film [44-46]. The fourier transform infra-red

spectrometer (FTIR) measurement of the film shows, after annealing the presence of the Si-O related absorbance peak intensity increases to the value similar to a good quality thermally grown SiO₂ film [34]. Hence further improvement in surface passivation quality for the AlO_x films was realised by good quality of interface with low value of D_{it} after annealing and hence the combined effect of field-effect and chemical passivation mechanisms may be applied by AlO_x films [34,45-48].

2.3 Various techniques used to deposit AlO_x film as passivation layer of c-Si surface

The AlO_x film deposited using different techniques like ALD, PECVD and RS techniques were extensively studied in c-Si solar cell applications. A report on low cost chemical deposition techniques was also studied for deposition of the AlO_x film in solar cell applications.

2.3.1 Atomic layer deposition

In many reports the ALD Al₂O₃ film, was shown to provide excellent quality surface passivation due to combined effect of both field-effect passivation with high negative Q_f in the range of 10¹³ cm⁻² and chemical passivation with D_{it} in the range of 2 × 10¹¹ eV⁻¹.cm⁻² [12,34,45,48]. The two basic types of ALD techniques were mostly explored for deposition of the Al₂O₃ film, viz.: thermal ALD and PA-ALD. The schematic diagram of typical thermal ALD and PA-ALD systems are shown in Figure. 2.1 (a) and (b), respectively.

In thermal ALD technique the substrate is exposed with Al precursor, i.e., tri-methylaluminum (TMA) with chemical composition of Al(CH₃)₃ and after first half-cycle surface reaction the N₂/Ar gas is used to purge the by-products. After this step, the surface is exposed with the reactant, i.e., water vapour (H₂O) to form mono-layer Al₂O₃ at the substrate, followed by purging step, as shown in eq. (2.2) and (2.3). The cycle of reactions for thermal ALD technique using TMA precursor and H₂O reactant are shown in Figure 2.2 (a), which continues till the required film thickness was achieved. For thermal ALD, the heating system is used to raise the substrate temperature to the typical range of 150-250 °C for film deposition.

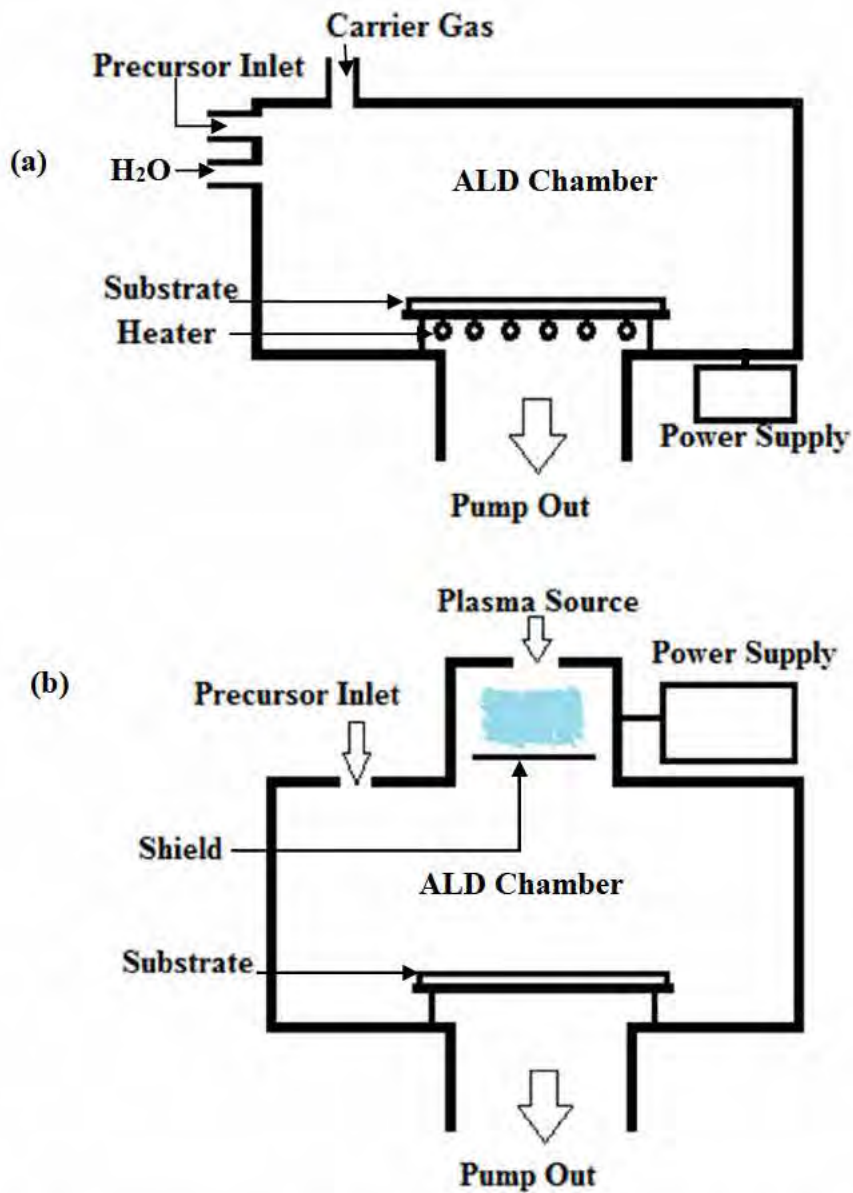
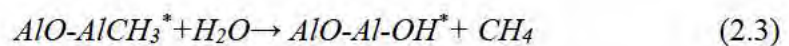


Figure 2.1 Schematic diagram of typical (a) thermal ALD and (b) plasma assisted-ALD systems [49].

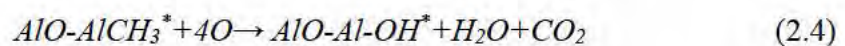
The self-limiting reactions at the surface for ALD system using TMA precursor during the first half-cycle is given as [49]:



For thermal ALD, second half-cycle reaction is



For PA-ALD, second half-cycle reaction is



In case of PA-ALD system the TMA precursor reacts in the presence of plasma from O_2 and deposit at the surface, as shown by self-limiting reactions in eq. (2.2) and (2.4). Due to plasma assisted deposition, the thermal energy requirement is less for PA-ALD systems. Because of high reactivity of plasma, the growth rate per cycle is also higher as compared to thermal ALD technique [50]. The reaction cycle for PA-ALD Al_2O_3 film with TMA precursor and O_2 plasma reactant is shown in Figure 2.2 (b).

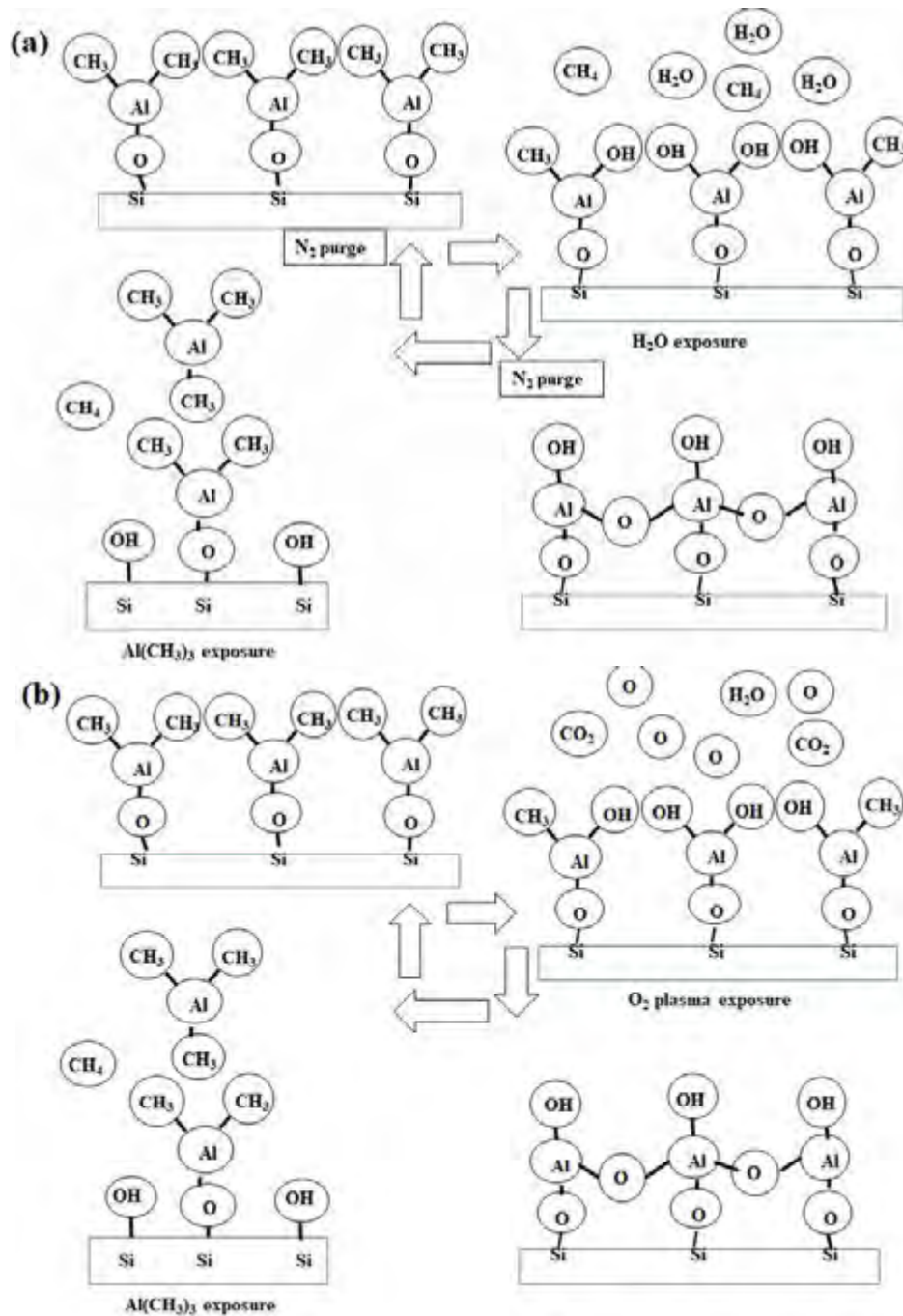


Figure 2.2 Reaction cycles for Al_2O_3 deposition using (a) thermal ALD and (b) plasma assisted-ALD system [50].

The quality of surface passivation was investigated and compared for both thermal ALD and PA-ALD Al₂O₃ films on low doped p-type silicon surface as well as highly doped p⁺ silicon [48,51-52]. For thermal ALD Al₂O₃ film deposition on p-type floatzone (FZ) wafer exhibits good surface passivation quality with S_{eff} of 14.5 cm.s⁻¹ in as-deposited condition itself, since the film deposition was carried out at high temperature (350 °C). However improvement in S_{eff} to 3 cm.s⁻¹ was achieved for films deposited in the substrate temperature range of 150-200 °C and annealed at 400 °C in N₂ ambient for 10 min [52]. The film contained negative Q_f of 2 × 10¹² cm⁻² and D_{it} of 10¹¹ eV⁻¹.cm⁻², after annealing [52]. As compared to thermal ALD Al₂O₃ film PA-ALD Al₂O₃ film, shows even better value of S_{eff} to 2 cm.s⁻¹ for similar process and PDA conditions, due to an improvement in negative Q_f to 5 × 10¹² cm⁻², while the D_{it} values remains same at 10¹¹ eV⁻¹.cm⁻² [52]. The report on impact of annealing on ALD Al₂O₃ film shows, after annealing the D_{it} values are reported to be improved for both thermal and PA-ALD techniques, whereas the negative Q_f value seems to increase more for thermal ALD, since the PA-ALD technique shows high Q_f for as-deposited condition itself [52]. The report also shows the hydrogen content in the film is higher for thermal ALD as compared to PA-ALD technique [52]. Using PA-ALD Al₂O₃ film the best value of S_{eff} = 2 cm.s⁻¹ calculated from τ_{eff} = 6 ms, measured on n-type c-Si surface [51,52]. Whereas on p-type c-Si surface the S_{eff} = 5 cm.s⁻¹ was reported [51,52]. The report also shows high quality surface passivation with value of surface recombination velocity on highly doped p⁺ emitter (S_{n0}) = 109 cm.s⁻¹ for boron doping of 7 × 10¹⁸ cm⁻³, these value was extracted using SENTAURUS device simulation tool by feeding the measured value of J_{0e} versus dopant profile [53].

Using thermal ALD Al₂O₃ film with O₃ as reactant source, the value of J_{0e} = 33 fA.cm⁻² was reported on boron diffused p⁺ silicon (doping of 2 × 10¹⁹ cm⁻³) surface with sheet resistance of 84 Ω.sq⁻¹ on the p⁺/n/p⁺ structure, this was compared with the PA-ALD Al₂O₃ film with O₂ plasma on similar structure which shows J_{0e} = 27 fA.cm⁻² [54]. On phosphorous diffused n⁺ emitter surface with sheet resistance 10-100 Ω.sq⁻¹, the PA-ALD Al₂O₃ film used as passivation layer, results in implied-V_{oc} of 680 mV and on lightly doped n-type surface the implied-V_{oc} improved to 700 mV [55]. These reports suggest that ALD Al₂O₃ film was promising for effectively passivating both p⁺ and n⁺ surfaces.

A conversion efficiency, η of 21.2 % was demonstrated on p-type PERC c-Si solar cell with rear-surface passivated using PA-ALD AlO_x film (20 nm) stacked with PECVD

SiO_x film (70 nm) [36]. A conversion efficiency, η of 23.4 % was reported on n-type c-Si solar cells on passivated emitter with rear locally diffused (PERL) structure [38,39]. The boron doped p⁺ emitter passivated using stack of PA-ALD Al₂O₃ film (30 nm) and PECVD SiN_x (40 nm) [38,39].

The ALD Al₂O₃ films were also tested for passivation of the black-Si (b-Si) wafers with random structures made by dry-etching process using inductively-coupled plasma (ICP) technique, and result gives $S_{\text{eff}} \leq 8 \text{ cm.s}^{-1}$ [56]. The ALD offers conformal deposition of the film on the irregular surface structure in this case.

The typical ALD technique was not being widely accepted by the solar industries for AlO_x film deposition because of very low rate of deposition $< 2 \text{ nm.min}^{-1}$ [52]. To address this issue, new designs for ALD deposition tool were proposed, such as batch ALD and spatial ALD reactor, as shown in Figure 2.3 (a) and (b), respectively [57,58].

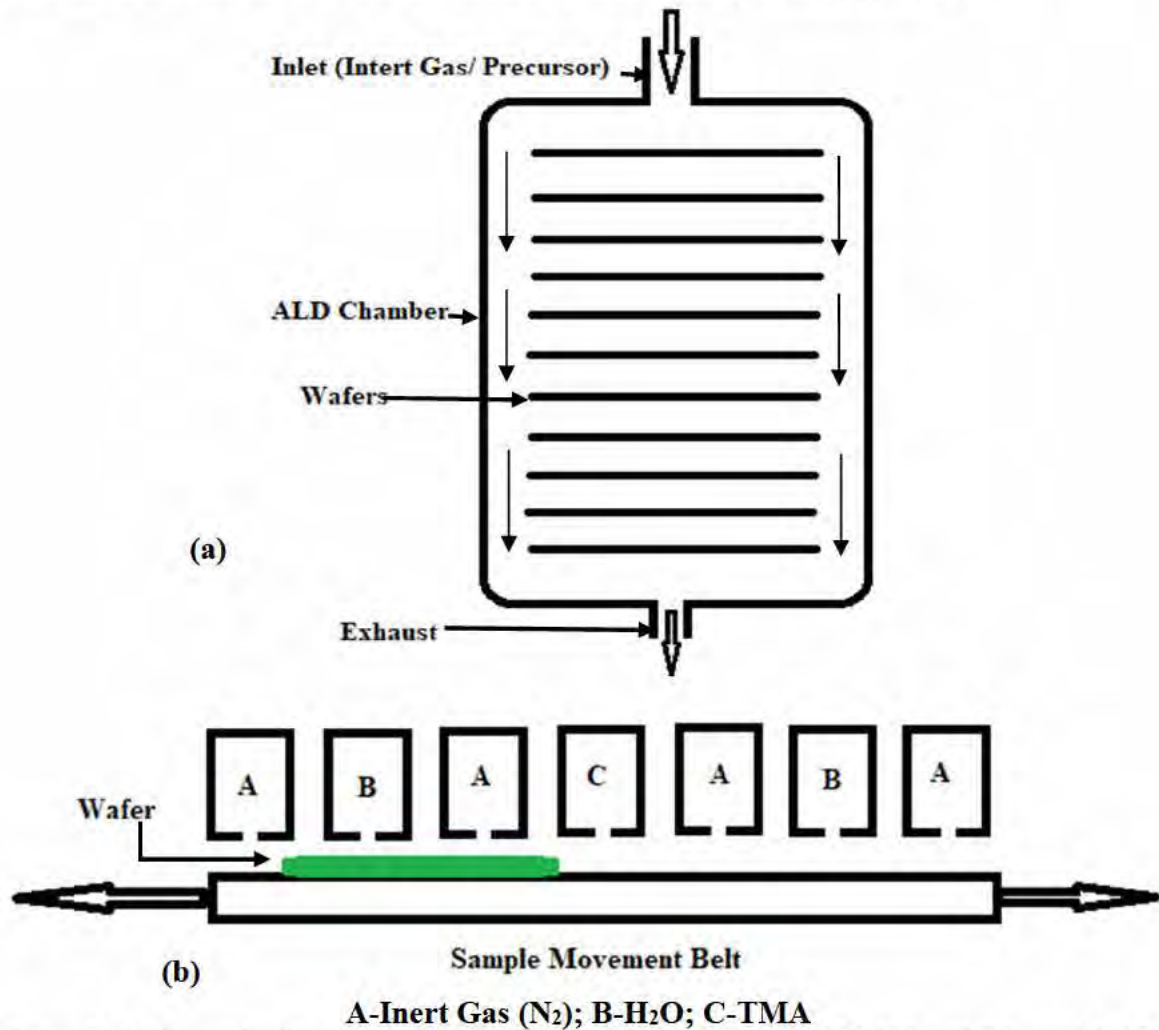


Figure 2.3 Schematic diagrams of typical (a) batch ALD reactor [57,59] and (b) spatial ALD systems [58-60] for solar industry applications.

Figure 2.3 (a) shows, a new arrangement known as batch ALD reactor with the chamber designed to process many number of wafers in one run, hence improving the throughput of the deposition tool [57,59]. The value of $S_{\text{eff}} < 6 \text{ cm.s}^{-1}$ was reported for Al_2O_3 film deposited on p-type c-Si surface using ASM batch ALD reactor with O_3 used as plasma source [61]. The film has shown the negative Q_f of $3.4 \times 10^{12} \text{ cm}^{-2}$ and D_{it} of $1 \times 10^{11} \text{ eV}^{-1}.\text{cm}^{-2}$ on this film after PDA in N_2 ambient at $400 \text{ }^\circ\text{C}$ for 10 min [57,61]. Figure 2.3 (b) shows, a chamber design in which the film deposition occurs in the spatial regime that means wafers are kept on the moving belt while the precursor and oxidation cycles are reacted and exposed on the wafer surface in a sequential manner, known as spatial ALD system [58-60]. This kind of arrangement leads to a very high deposition rate of 70 nm.min^{-1} [58]. The surface passivation quality obtained by spatial ALD and thermal ALD Al_2O_3 film were compared on p-type Czochralski (CZ) c-Si wafer ($1\text{-}3 \text{ } \Omega.\text{cm}$). The result shows for spatial ALD Al_2O_3 film, similar level of surface passivation are achieved for film thickness $> 10 \text{ nm}$ for similar process and PDA conditions [62]. The same report shows high level of surface passivation, S_{eff} of 2.9 cm.s^{-1} using spatial ALD Al_2O_3 film deposited on n-type FZ c-Si wafer ($2.4 \text{ } \Omega.\text{cm}$), i.e., slightly higher as compared to S_{eff} of 1.9 cm.s^{-1} using thermal ALD Al_2O_3 film of same thickness (30 nm). These films were annealed in rapid thermal processing (RTP) at $835 \text{ }^\circ\text{C}$ for 1-2 s [62]. The deposition rate of 72 nm.min^{-1} was reported for this particular spatial ALD system, i.e., very high as compared to conventional ALD system [62].

The value of negative Q_f and D_{it} for spatial ALD Al_2O_3 film, were reported by Werner et al. in two different reports [58,63]. The spatial ALD Al_2O_3 film deposition at the rate of 30 nm.min^{-1} , on n-type CZ c-Si wafer ($4 \text{ } \Omega.\text{cm}$) without any PDA, shows the mid-gap $D_{\text{it}} = 7 \pm 1 \times 10^{10} \text{ eV}^{-1}.\text{cm}^{-2}$, i.e., assessed through quasi-static and high-frequency C-V measurement techniques for film thickness of 10 nm [63]. On another report the negative Q_f of $4 \pm 1 \times 10^{12} \text{ cm}^{-2}$ extracted using corona discharge method for spatial ALD Al_2O_3 film (30 nm) deposited on p-type FZ c-Si ($1.3 \text{ } \Omega.\text{cm}$) wafer was reported [58]. For this sample, the maximum value $S_{\text{eff,max}} = 47 \text{ cm.s}^{-1}$ at $\Delta n = 10^{15} \text{ cm}^{-3}$ was reported after PDA in N_2 ambient at $350 \text{ }^\circ\text{C}$ for 15 min [58]. This implies that the films deposited by spatial ALD technique possess good quality and are suitable for surface passivation application [58,63].

2.3.2 Plasma enhanced or assisted chemical vapor deposition

The PECVD technique was widely used in solar cell manufacturing industries for the deposition of SiN_x film applied as ARC. The schematic diagram of a typical parallel plate

capacitively coupled PECVD system is shown in Figure 2.4. The Al₂O₃ film deposited using TMA precursor and N₂O or O₂ may be used as reactants with Ar plasma in this technique [64].

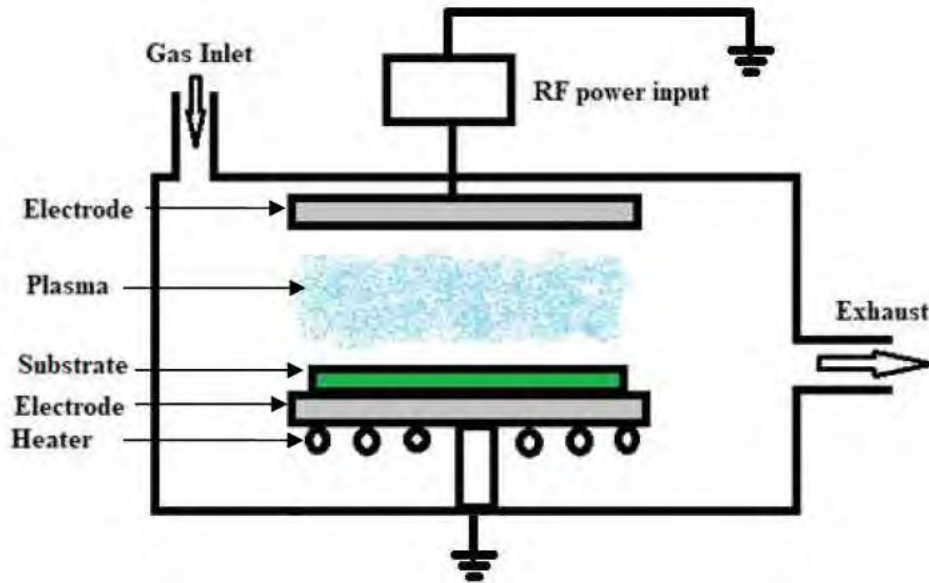


Figure 2.4 Schematic diagram of typical PECVD system [64].

The PECVD Al₂O₃ shows $S_{\text{eff}} < 1 \text{ cm}\cdot\text{s}^{-1}$ on n-type c-Si surface for high deposition rate of $5 \text{ nm}\cdot\text{min}^{-1}$ using this technique. The film was deposited at 200 °C substrate temperature and annealed at 400 °C in N₂ for 10 min, as reported by Dingemans et al. [52]. The PECVD tools with pulsed flow of TMA precursor and O₂ plasma used to deposit Al₂O₃ film with high deposition rate $> 30 \text{ nm}\cdot\text{min}^{-1}$, has shown high quality surface passivation $S_{\text{eff}} < 1 \text{ cm}\cdot\text{s}^{-1}$ [65]. The film was deposited on n-type FZ c-Si wafer, with substrate temperature varied between 50-300 °C during deposition and PDA was carried out in N₂ ambient at 400 °C for 10 min [65].

Saintcast et al. explored very high deposition rate for Al₂O₃ film deposition using PECVD system by Roth & Rau, which is already used in solar industries for SiN_x film deposition. The system uses TMA precursor and N₂O and Ar as reactant gases, for Al₂O₃ film deposition [66]. The deposition was done on large substrate which shows about $100 \text{ nm}\cdot\text{min}^{-1}$ static deposition rate, showing fairly low S_{eff} of $10 \text{ cm}\cdot\text{s}^{-1}$ on low-resistivity p-type c-Si [66]. Film deposited at substrate temperature of 300 °C and annealed at 400 °C in FGA ambient for 25 min [66].

A high conversion efficiency, η of 21.5 % was reported on p-type PERC solar cell structure with rear-surface passivated by using PECVD Al_2O_3 film [36]. An improvement in solar cell efficiency was related to an improved V_{oc} of 684 mV after rear surface passivation using PECVD Al_2O_3 film, i.e., similar to the value of V_{oc} obtained for thermal SiO_2 film passivated silicon solar cells [36,37]. The as-deposited PECVD Al_2O_3 film was shown to contain very high negative Q_f of $2 \times 10^{12} \text{ cm}^{-2}$, since the film deposition was carried out at 300 °C, whereas an improvement in D_{it} to $3 \times 10^{11} \text{ eV}^{-1} \cdot \text{cm}^{-2}$ was realized after PDA in FGA ambient at 425 °C for 15 min [37,67]. This film was applied as rear-surface passivation layer on p-type solar cells, which resulted in reverse saturation current density of the base (J_{0b}) = 52 $\text{fA} \cdot \text{cm}^{-2}$ [36]. In another report by Saintcast et al., the value of reverse saturation current density of the emitter (J_{0e}) = $9.5 \pm 0.7 \text{ fA} \cdot \text{cm}^{-2}$ was shown on boron doped p^+ emitter with sheet resistance $120 \ \Omega \cdot \text{sq}^{-1}$ and PECVD Al_2O_3 passivation film was used to passivate the planner wafer [68].

The PECVD tool, discussed above is capacitively coupled type, while an inductively coupled plasma (ICP) CVD system was also explored for the AlO_x film deposition report by Vieth et al. [69]. The 30 nm thick ICP-CVD AlO_x film was applied as rear surface passivation of p-type PERC silicon solar cell, resulted in S_{eff} of $9 \text{ cm} \cdot \text{s}^{-1}$ after annealing at 425 °C on p-type FZ c-Si wafer ($1.4 \ \Omega \cdot \text{cm}$) [69]. The film contains high value of negative Q_f of $4.5 \times 10^{12} \text{ cm}^{-2}$ and mid-gap D_{it} of $11.0 \pm 4.0 \times 10^{11} \text{ eV}^{-1} \cdot \text{cm}^{-2}$, which is quite high as compared to the typical PECVD and ALD techniques discussed so far [69]. The technique has shown deposition rate of $5 \text{ nm} \cdot \text{s}^{-1}$, as a result of high plasma density during deposition. In this technique, the TMA precursor was used along with O_2 process gas for film deposition. The PERC structure with rear surface passivated using ICP-CVD $\text{AlO}_x/\text{SiN}_x$ layer shows η of 20.1 % [69].

The AlO_x films deposited by ALD and PECVD techniques, shows an improvement in surface passivation quality after PDA in FGA or N_2 ambient at typical annealing temperature between 350-450 °C. The reason for an improvement in passivation quality was mostly related to good quality interface with the reduction in D_{it} value, i.e., activation of chemical passivation mechanism. In all these reports the most commonly used Al precursor was TMA, which results in incorporation of 2-7 % hydrogen in the film during deposition, and this hydrogen transports towards the interface during PDA process and hence results in improvement in $\text{AlO}_x/\text{c-Si}$ interface [70-72].

The disadvantage of above techniques, are use of TMA precursor which is pyrophoric in nature, hence the safety equipment are required to protect from any hazards. In addition to this, the precursor itself is very expensive. Hence adding the costs of safety equipment and chemical made the overall AlO_x films deposition quite expensive. Thus the low cost reactive sputter deposition techniques were explored for AlO_x film deposition for its application as surface passivation layer in c-Si solar cells.

2.3.3 Reactive sputter deposition technique

As discussed in previous sections, for industrial relevance one has to consider a system which gives higher deposition rate and process film with low cost, and a solution lies in the technique called RS deposition. The schematic diagram of typical RS system using radio frequency (RF) power source is shown in Figure 2.5.

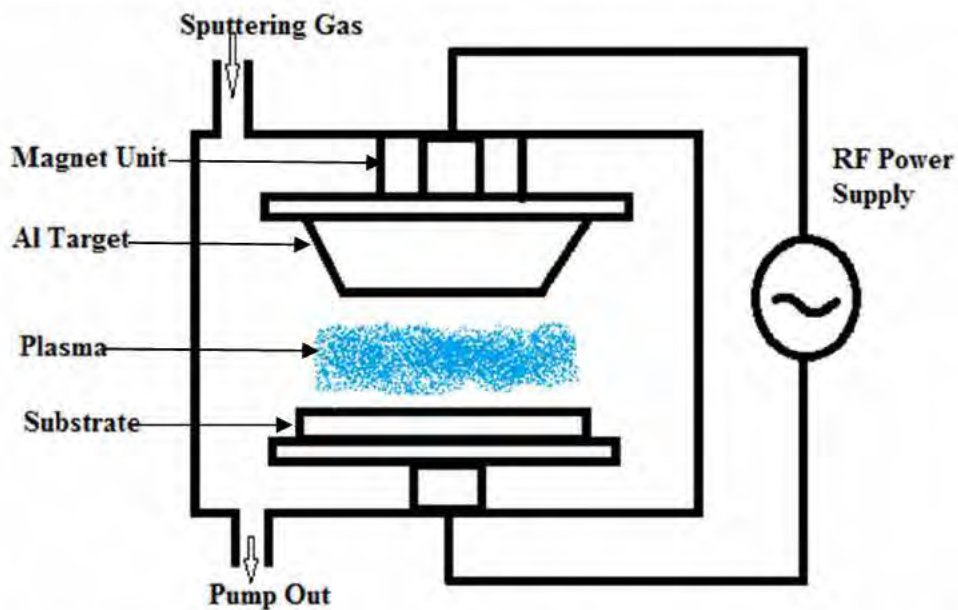


Figure 2.5 Schematic diagram of typical reactive sputter system using RF power supply [73,74].

In a typical RS deposition technique, the AlO_x film deposition is carried out using the RF power supply source, where high purity aluminium target is sputtered in O_2 reactive gas ambient, using Ar as sputter gas [73,74]. The technique has advantage that it does not require expensive chemical precursors for the film deposition.

There are several reports published on the application of RS deposited AlO_x film as surface passivation layer of c-Si [75-79]. The report by Li et al., shows the as-deposited film contains negative Q_f of $8.6 \times 10^{11} \text{ cm}^{-2}$, which is lower compared to the ALD and PECVD techniques [75]. While an improvement in negative Q_f to $3.4 \times 10^{12} \text{ cm}^{-2}$ and D_{it} to $4 \times 10^{12} \text{ eV}^{-1} \cdot \text{cm}^{-2}$ was realized after PDA of the RS AlO_x film at $400 \text{ }^\circ\text{C}$ in N_2 ambient for 30 min [75].

As mentioned in many report, for AlO_x film deposited on c-Si, the PDA process results in improvement of surface passivation quality with an increase in negative Q_f and decrease in D_{it} [34,43,48,67,76]. Agostinelli et al., reported such improvement in passivation quality after PDA was due to formation of thin interfacial oxide (SiO_x), that results in increase of negative Q_f [35]. Li et al., studied an impact of different PDA conditions on RS deposited AlO_x film deposited on low resistivity p-type c-Si wafer. The τ_{eff} of $290 \text{ } \mu\text{s}$ was measured on film after annealing in FGA ambient at $400 \text{ }^\circ\text{C}$ for 60 min, which results in low S_{eff} of $54 \text{ cm} \cdot \text{s}^{-1}$. The same report shows τ_{eff} of $200 \text{ } \mu\text{s}$ was measured on the film annealed in N_2 ambient at $400 \text{ }^\circ\text{C}$ for 60 min, which results in S_{eff} of $74 \text{ cm} \cdot \text{s}^{-1}$ [75]. This indicates an annealing in FGA ambient results in relatively good surface passivation quality as compared to N_2 ambient, the reason stated as the modification of interfacial quality due to presence of hydrogen in FGA ambient [75]. Since hydrogen can be incorporated in this film through PDA ambient only, as the RS AlO_x film deposition was carried out in high purity O_2 and Ar gases by reactively sputtering of high purity Al target [73,74,77].

Very high quality of surface passivation by RS AlO_x film with S_{eff} of $8 \text{ cm} \cdot \text{s}^{-1}$ was reported by Zhang et al. on n-type c-Si surface. The film was deposited at process pressure of 5 mTorr and deposition power of 220 W (i.e., power density of $4.82 \text{ W} \cdot \text{cm}^{-2}$). The film was annealed in N_2 ambient at $425 \text{ }^\circ\text{C}$ for 30 min [78]. Krugel et al. reported the cell performance of p-type local-fired contact (LFC) PERC solar cells, using rear surface passivation of RS AlO_x capped with SiN_x film and shows an improvement in η by $\sim 1 \%$ as compared to Al-back surface field (BSF) solar cells [79]. An efficiency η of 20.1 % was reported on p-type PERC solar cell, using RS AlO_x film applied as rear-surface passivation layer [33]. In this case the solar cell contacts were made using shadow mask with Al evaporation at the back [33]. The RS AlO_x film used in this cells, showed S_{eff} of $35 \text{ cm} \cdot \text{s}^{-1}$ measured on $1 \text{ } \Omega \cdot \text{cm}$ p-type FZ c-Si surface [33,75].

Untila et al. reported AlO_x film deposition using ultrasonic chemical spray pyrolysis method, gives very high deposition rate of $130 \text{ nm}\cdot\text{min}^{-1}$ at a deposition temperature of $500 \text{ }^\circ\text{C}$. The S_{eff} of $70 \text{ cm}\cdot\text{s}^{-1}$ was reported on highly doped p^+ (10^{20} cm^{-3}) c-Si surface using this technique [80].

There are different reports available on high temperature stability of AlO_x film deposited using ALD, PECVD and RS techniques, for the typical firing temperature up to $850 \text{ }^\circ\text{C}$. Since the firing process at such temperature is required to activate the contacts in screen- printed c-Si solar cells. Various reports shows degradation in the passivation quality of these films for PECVD and RS techniques, after firing at such high temperature [33]. However the film deposited using ALD technique, has shown an acceptable surface passivation quality after firing process on screen-printed c-Si solar cells [33,81]. The degradation of passivation quality for ALD and PECVD Al_2O_3 films after firing process was related to the effusion of hydrogen from the film [67,70,71]. To improve the high-temperature stability of AlO_x film, a stack structure of $\text{AlO}_x/\text{SiN}_x$ or $\text{AlO}_x/\text{SiO}_x$ was introduced on the silicon solar cells [82-84].

2.4 Experimental techniques

In this section of the chapter we will discuss about various experimental techniques, systems and methodology used during this work. The sample preparation methods used for different experiments will also be presented in brief in this section.

2.4.1 Electrical characterization

The thin dielectric films deposited on silicon surface were characterized electrically for the assessment of electrical behaviour viz. interfacial properties, electrical charges in the films, breakdown voltage, as well as uniformity using capacitance versus voltage (C-V), conductance versus voltage (G-V) and current versus voltage (I-V) measurements performed on metal oxide semiconductor (MOS) structure, as shown in Figure 2.6. Keithley 4200 semiconductor characterization system (SCS) was used for these measurements.

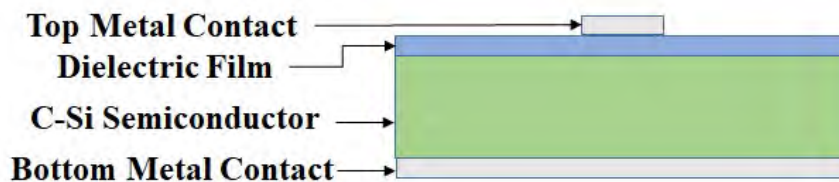


Figure 2.6 MOS capacitor structure for electrical characterization of the dielectric film.

The MOS structure was fabricated by depositing the dielectric film to be characterized on p-type CZ c-Si wafers. The wafers were cleaned before film deposition by standard Radio Corporation of America (RCA) cleaning procedure which involves the standard cleaning SC-I to remove organic contamination and SC-II to remove metal contamination. These were followed by immersing wafer in 2 % hydrofluoric (HF) acid followed by rinsing in de-ionized (DI) water and N₂ drying. The detailed process conditions used for film deposition will be discussed in coming chapters of the thesis, under experimental details. The metal contacts in MOS capacitors were deposited using thermal evaporation of aluminum (Al), the top contact was made using shadow mask of nominal diameter = 200 μm followed by bottom contact with blanket Al deposition. The native oxide on the backside of the wafers were etched using dilute HF before the deposition of Al on the backside.

The electrical measurements were performed on the MOS capacitors, by supplying small alternate current (AC) voltage superimposed on direct current (DC) voltage to the top gate contact while the bottom contact was grounded. The impedance was measured for different values of DC voltages, and the capacitance and conductance were extracted from the impedance. The resultant C-V and G-V plot for a typical MOS device is shown in Figure 2.7.

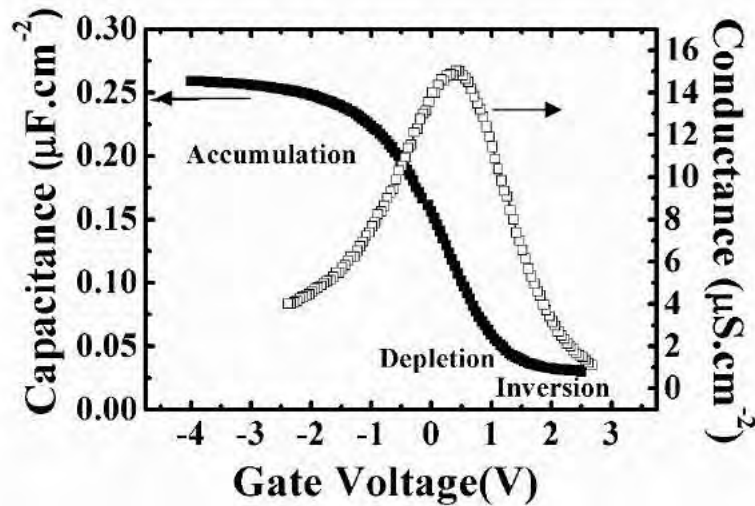


Figure 2.7 The high frequency C-V and G-V plot for the dielectric film measured on MOS capacitor at frequency, $f = 100$ kHz.

The dielectric film thickness, T_{ox} (nm), can be measured from the C-V plot using the eq. (2.5),

$$T_{ox} = \frac{\epsilon_{ox}}{C_{acc}} \quad (\text{nm}) \quad (2.5)$$

where, ϵ_{ox} represents relative permittivity (dielectric constant) of the oxide ($F.cm^{-1}$), and C_{acc} represents value of accumulation capacitance, which is the maximum capacitance value in the C-V plot ($\mu F.cm^{-2}$). The permittivity of the material is given as eq. (2.6),

$$\epsilon = \epsilon_r \epsilon_0 \quad (2.6)$$

where, ϵ_r represent relative permittivity of the dielectric also defined as dielectric constant, and ϵ_0 represents permittivity of free space = $8.854 \times 10^{-14} F.cm^{-1}$.

In this case we will assess the electrical property of Al_2O_3 film which has high dielectric constant, ϵ_{r-AlOx} of 9 [85], hence the equivalent oxide thickness (EOT) in nm, can be extracted from the C-V plot, which is defined as equivalent SiO_2 (with $\epsilon_{r-SiO_2} = 3.9$) thickness required to achieve the similar value of maximum capacitance density for high dielectric constant material, calculated using eq. (2.7) [7,86],

$$EOT = \frac{3.9}{\epsilon_{r-AlO}} T_{ox} \quad (nm) \quad (2.7)$$

where ϵ_{r-AlOx} represents the dielectric constant of AlO_x film, and T_{ox} represents the film thickness (nm) measured using spectroscopic ellipsometer (SE).

The other parameters such as acceptor doping concentration N_A may be extracted using following set of eq. (2.8) to (2.11), assuming a uniform doping in the semiconductor [86].

$$X_{d,max} = \sqrt{\frac{4\epsilon_s \phi_B}{qN_A}} \quad (cm) \quad (2.8)$$

where, $X_{d,max}$ is maximum depletion length (cm) extracted from the C-V plot using eq. (2.9),

$$C_{Smin}^{HF} = \frac{\epsilon_s}{X_{dmax}} \quad (\mu F.cm^{-2}) \quad (2.9)$$

where C_{Smin}^{HF} is extracted from high- frequency C-V plot using the eq. (2.10),

$$\frac{1}{C_{Smin}^{HF}} = \frac{1}{C_{min}} - \frac{1}{C_{acc}} \quad (2.10)$$

where, C_{min} represents the minimum value of capacitance in $\mu F.cm^{-2}$ in C-V plot. In eq. (2.8), and eq. (2.9) the ϵ_s represents the relative permittivity of silicon = 11.68 and the ϕ_B represents the bulk potential, defined as difference between potential of doped and intrinsic silicon.

$$\phi_B = \frac{kT}{q} \ln \frac{N_A}{n_i} \quad (\text{V}) \quad (2.11)$$

The flat-band voltage (V_{FB}) represents the voltage at which capacitance value equals the flat-band capacitance (C_{FB}), and is extracted using the eq. (2.12) [86],

$$\frac{1}{C_{FB}} = \frac{1}{C_{acc}} + \frac{1}{C_{S,FB}} \quad (2.12)$$

where, $C_{S,FB}$ represents semiconductor flat-band capacitance, extracted using eq. (2.13),

$$C_{S,FB} = \frac{\epsilon_s}{L_D} \quad (2.13)$$

where, L_D represent extrinsic debye length in cm, which is the characteristic screening length, is given by eq. (2.14) [86],

$$L_D = \sqrt{\frac{kT\epsilon_s}{q^2 N_A}} \quad (\text{cm}) \quad (2.14)$$

Another important electrical parameter is the fixed oxide charge density, Q_f which can be extracted from high frequency C-V plot, by determining shift in mid-gap voltage from the ideal value, ΔV_{MG} (V), using eq. (2.15) [86],

$$Q_f = - \left(\frac{\Delta V_{MG} C_{acc}}{q} \right) \quad (\text{cm}^{-2}) \quad (2.15)$$

where $\Delta V_{MG} = V_{MG} - V_{MG,ideal}$, the V_{MG} is the voltage value corresponding to the mid-gap capacitance (C_{MG}) in C-V plot, is given by eq. (2.16),

$$\frac{1}{C_{MG}} = \frac{1}{C_{acc}} + \frac{1}{C_{S,MG}} \quad (2.16)$$

where, $C_{S,MG}$ represents semiconductor mid-gap capacitance, extracted using eq. (2.17),

$$C_{S,MG} = \frac{\epsilon_s}{\sqrt{2}L_D} \frac{1}{\left(\frac{q\phi_B}{kT} - 1 \right)^{1/2}} \quad (2.17)$$

The ideal V_{MG} ($V_{MG,ideal}$) is defined as the V_{MG} when the fixed charge density is zero, which is calculated using eq. (2.18)

$$V_{MG,ideal} = \phi_{MS} + \phi_B + \frac{qN_A X_{MG}}{C_{acc}} \quad (\text{V}) \quad (2.18)$$

where, ϕ_{MS} represents work-function difference, between metal (ϕ_M) and semiconductor (ϕ_S), is extracted using eq. (2.19), from the C-V plot [86],

$$\phi_{MS} = \phi_M - \phi_S = \phi_M - \left(\chi + \frac{E_{BG}}{2q} + \phi_B \right) \quad (V) \quad (2.19)$$

where, χ is known as electron affinity for Si and is given as $q\chi = 4.05$ eV, ϕ_M is the work function of Al metal gate = 4.1 eV and E_{BG} represent band-gap energy of Si = 1.1 eV. The X_{MG} in eq. (2.18), represents depletion width at mid-gap (cm).

The D_{it} is extracted from the high frequency G-V plot, shown in Figure 2.7, using single frequency conductance approximation technique, as given in eq. (2.20) [87].

$$D_{it} = \frac{2}{qA} \frac{G_{max}/\omega}{\left(G_{max}/\omega C_{acc} \right)^2 + \left(1 - C_{max}/C_{acc} \right)} \quad (\text{cm}^2 \cdot \text{eV}^{-1}) \quad (2.20)$$

where, A represents the area of capacitor (cm^2), $\omega = 2\pi f$ represents measurement angular frequency ($\text{rad} \cdot \text{s}^{-1}$), G_{max} represents the value of peak conductance and C_{max} represents the value of capacitance at the voltage corresponding to G_{max} in G-V plot. Through electrical characterization, the two important parameters Q_f and D_{it} of the dielectric film and its interface with silicon are obtained. For these measurements 8 number of devices were measured from each sample.

Another important quality of the dielectric material is the breakdown voltage, which is obtained from the I-V measurement. Figure 2.8, shows the current density versus voltage (J-V) graph for a MOS capacitor measured using Keithley 4200 SCS, by linear voltage sweep.

The voltage at which the gate current increase abruptly is identified as the breakdown voltage, V_{BD} (V). To investigate the uniformity of the film over the wafer, in terms of breakdown voltage, measurements were performed on 20 devices at different locations on the samples.

The breakdown is known to follow the Weibull distribution. Figure 2.9 shows the Weibull plot of the effective breakdown field (E_{BD}) $\text{V} \cdot \text{cm}^{-1}$, is given as eq. (2.21) [7],

$$E_{BD} = \frac{V_{BD}}{EOT} \quad (\text{V} \cdot \text{cm}^{-1}) \quad (2.21)$$

where, V_{BD} is breakdown voltage in V and EOT is equivalent oxide thickness in cm as defined in eq. (2.7). The Weibull distribution plot for E_{BD} of 20 MOS capacitor devices, tested on a wafer is shown in Figure 2.9.

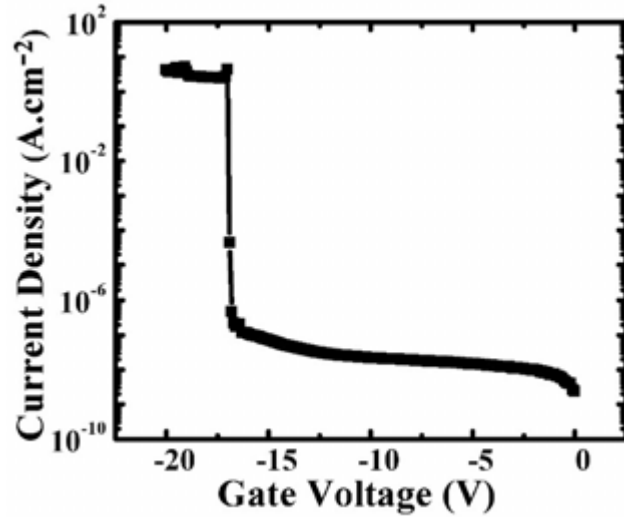


Figure 2.8 The J-V plot for the dielectric film measured on MOS capacitor.

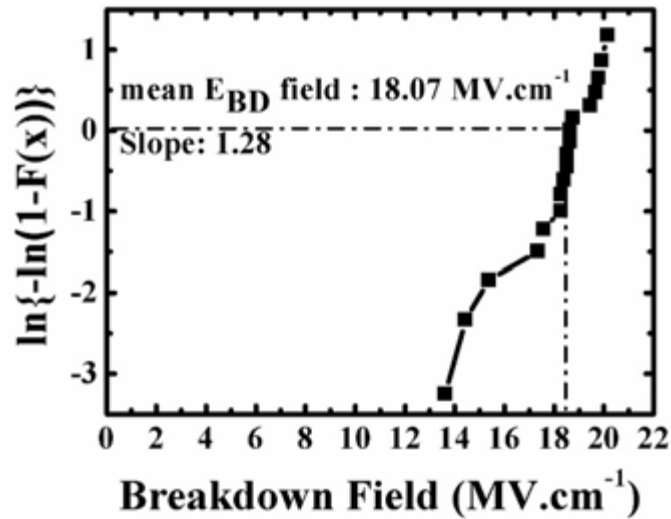


Figure 2.9 The Weibull distribution plot of the E_{BD} for 20 MOS capacitor devices tested on a wafer [7].

The mean E_{BD} for the entire sample is defined as, the effective field below which 63.2 % of the devices are expected to fail. Also the slope of the Weibull distribution estimated by linear fit shows the uniformity in the film. High value of slope means a more uniform film, as most of the devices will breakdown at nearly the same voltage.

The above electrical characteristics are used in this thesis work for assessing the electrical behaviour of the dielectric film for different experimental conditions during process optimization. Material characteristics of the film which may influence the properties of the

dielectric and its interface with Si are investigated using different systems are discussed in the next section.

2.4.2 Material characterization

In this section we will discuss about the material characterization systems used in this work to assess different parameters of the dielectric film, viz. film thickness, film density, topography and uniformity, elemental composition and chemical bonding of the film and most importantly interfacial property.

(a) Spectroscopic ellipsometer

In this work Sentech SE, model number SE800 was used to measure film thickness (T_{ox}) and refractive index (RI), through change in polarization of the incident light on sample [88]. The typical schematic diagram of SE is shown in Figure 2.10.

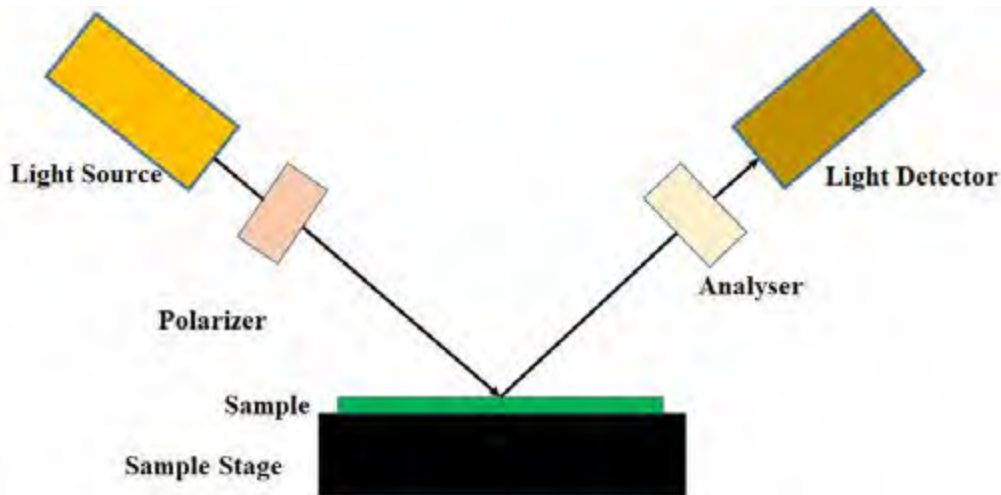


Figure 2.10 Typical schematic diagram and working principle of spectroscopic ellipsometer.

The system has a light source, i.e., xenon (Xe) arc lamp which is used to produce light in the wavelength range of 350-850 nm. The sampling point under the test sample, are focused manually on the sample stage (or chuck). The light from the Xe light source, passes through the polarizer is incident on the sample. The polarizer is used here to linearly polarize the incident light. The linearly polarized incident light, after interacting with the sample, reflects back and becomes elliptically polarized. The change in intensity and orientation of the reflected elliptically polarized light after interaction, are analysed through the analyser and light detector. This optical result generated through SE, is compared to the existing available model defined in the material library and fitted using the software provided with the system.

The system is capable of measuring the film property like T_{ox} and RI of the material. Such measurement was performed at very initial level of the experiment after film deposition to assess the thickness and uniformity. The RI value is noted and reported at wavelength, $\lambda = 635$ nm. The value of RI can give qualitative information about film density and stoichiometry.

(b) X-ray reflectometer

In this work, the Bruker make D8 DISCOVER diffractometer equipped with multilayer mirror used in X-ray reflectometer (XRR) mode for the measurement. This is a non-destructive measurement technique for extraction of film properties like thickness, surface roughness and film density [89]. The typical schematic diagram of XRR system is shown in Figure 2.11.

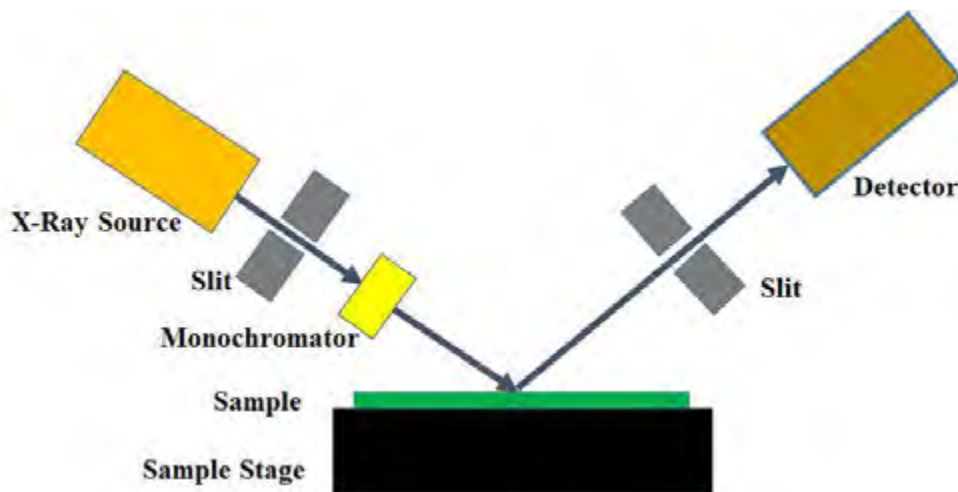


Figure 2.11 Typical schematic diagram and working principle of X-ray reflectometer.

The Cu $K\alpha$ X-ray source produce beam with photon energy $E = 8047$ eV, which travels through the slit and monochromator to focus a narrow and parallel monochromatic beam on sample. In XRR, the beam is incident on sample at very small angles ($< 0.5^\circ$), so as to probe into few nanometres at the surface. The reflected beam from the sample is collected through the slit to the detector. The main principle of XRR exists in total external reflection as a result of beam incident on the sample below the critical angle (α_c). Where the value of α_c depends on material property such as electron density, the classical electron radius ($r_e = 2.81 \times 10^{-18}$ m) and wavelength of X-ray beam. The X-ray beam after reflecting from the surface at grazing angle (i.e., $< \alpha_c$), produces total external reflection. The intensity of the reflected beam is normalized to the surface and plotted against the incident angle in the

logarithmic scale [89]. This reflectivity graph is fitted by using Parratt formalism to obtain the parameters such as film thickness, film density and surface roughness [90]. The intensity of oscillations in reflectivity graph gives information about the film thickness, i.e., more oscillations means thicker the film. While the film density is obtained through the amplitude of the oscillations in reflectivity graph, i.e., high amplitude of the oscillations means higher film density. The surface roughness is assessed through the decay of the reflectivity graph, i.e., fast decay in plot represents rough surface of the film.

(c) Atomic force microscope

The atomic force microscope (AFM), used in this work is Veeco-Digital Instruments make Nanoscope IV. The system is used to assess the surface roughness and topography through the three dimensional image of the film surface [88]. The typical AFM setup, is shown in Figure 2.12.

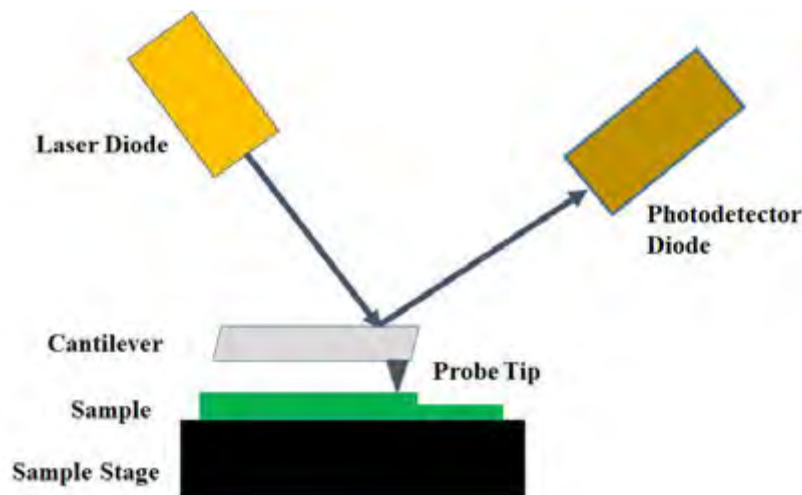


Figure 2.12 Typical schematic diagram of atomic force microscope.

As shown in Figure 2.12, the typical AFM system consists of a light source (laser diode), and probe tip attached to the cantilever and photodetector. The cantilever is typically made of Si or SiN_x , connected with a sharp probe tip. The cantilever is oscillated up and down close to its resonance frequency. When the probe tip with constant oscillation and frequency comes close to different surface, the electro-dynamic force of interaction between the probe tip and the surface starts to act. This interaction results in change in amplitude of cantilever's oscillation, and at the same time, the feedback controller is used to maintain the oscillation amplitude constant [88]. Thus an AFM image is generated using the intermittent contact between the probe tip and surface. The most commonly used AFM measurement technique is

beam-deflection type, as shown in Figure 2.12. The laser diode generated light beam incident on the cantilever, after interaction of probe tip and surface, the cantilever makes an angular displacement as per vertical and lateral movement of probe tip on sample. The light reflected from the cantilever is collected using the photodetector, and is used to detect the surface topography. The AFM works on both contact and contact-less mode. In this work we have used the contact mode to assess the topography of the sample surface.

(d) X-ray photoelectron spectroscopy

In this work the X-ray photoelectron spectroscopy (XPS) characterization system is used to assess the film and interfacial property in terms of film composition and elemental profile [88]. We have used Thermo-VG Scientific make Multilab 2000 XPS system for the measurements to be discussed in chapters 4 and 6, whereas ULVAC-PHI make, PHI 5000 Versa Probe-II for measurements to be discussed in chapter 5. The typical schematic diagram of XPS measurement system is shown in Figure 2.13.

As shown in Figure 2.13, the XPS system comprises of X-ray source, which is Mg K α source with photon energy of $E = 1253.6$ eV, i.e., used in this work. The surface of sample placed in sample stage is irradiated with the X-ray beam using high energy photon, which is transferred to the core-level electrons. After this interaction the electron at core-level gets excited due to high energy photon and ejected with some kinetic energy (KE). These ejected electrons are known as photo emitted electrons. The KE of photo emitted electrons depends on the X-ray and binding energy (BE) of the atoms to the orbit. The electron detector at the receiving end, will analyse the BE of the atoms using the eq. (2.22),

$$BE = h\nu - KE - \phi \quad (\text{eV}) \quad (2.22)$$

where, ϕ represents the work function that depends on the spectrometer and material.

By analysing the KE of the photo-emitted electrons from the atoms, the BE can be determined, which is a unique property of each element. Hence the type of elements in the film can be determined. The analyser in the system will provide the information on the different elements present in the sample surface. The resultant XPS spectrum is the plot between number of photo-emitted electrons and BE.

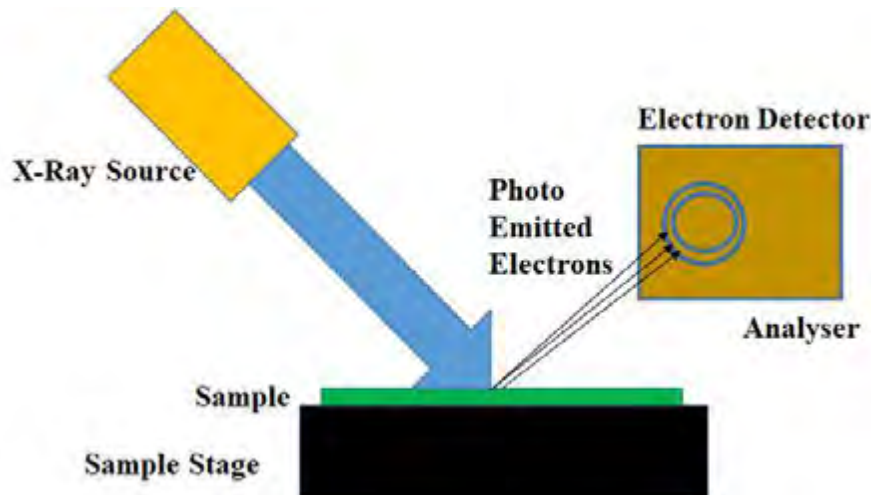


Figure 2.13 Typical schematic diagram and working principle of X-ray photoelectron spectroscope.

The XPS peaks are the characteristic peak of the elements present in film. To assess the chemical composition of the film, the area under these characteristic peak will be obtained with respect to each other to obtain the relative percentage of each element present in the film/volume of the material studied. The elemental depth profile is assessed by bombarding the surface with Ar^+ ions at specific time and power, and obtaining the XPS spectrum after each bombardment steps. The depth profile consist of atomic concentration (%) of each elements plotted against depth (nm).

(e) Transmission electron microscope

In this work the JEOL make JEM 2100F, transmission electron microscope (TEM) was used for high resolution imaging of thin films to assess the crystalline and interfacial property. The typical schematic diagram of TEM system is shown in Figure 2.14 [88].

This system uses very high energy electron beam, which is incident into the ultra-thin sample. The interaction between these electrons and atoms results in some unscattered electron transmission, while some scattered electrons that are both elastic and inelastic in nature.

The unscattered electrons transmitted through the thin sample, were focused into an image plane through electromagnetic lens to create magnified image of the sample. This image shows the film properties such as thickness, interface, crystal orientation and grain boundaries [88].

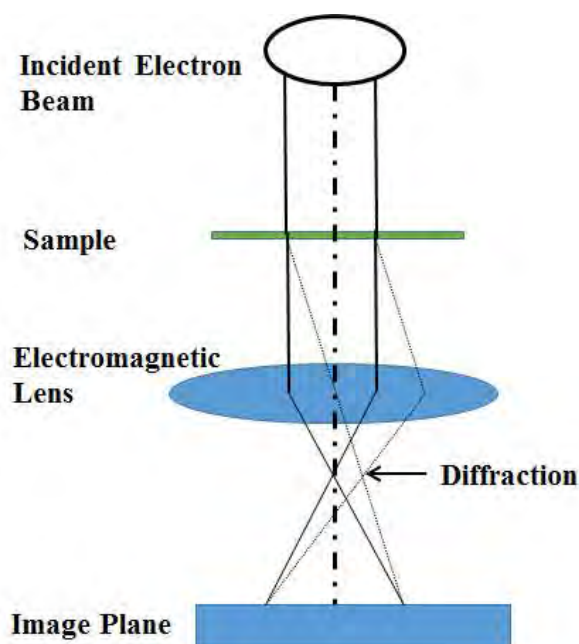


Figure 2.14 Typical schematic diagram and working principle of transmission electron microscope.

Since TEM operates on transmission of high energy electrons through the ultra-thin sample, therefore it requires a sample preparation method to achieve the sample thickness in the range of 100-150 nm for measurement.

The elastically scattered electrons were used to obtain the diffraction pattern of the sample to access information about crystal structure. These scattered electrons deflected in particular angle were focused in back-focal plane of the objective lens to form a diffraction pattern [88].

(f) Electron energy loss spectroscopy

The electron energy loss spectroscopy (EELS) is one of the operation mode in TEM system to obtain information about electronic state and chemical bonding in the film. In this work we have used FEI TITAN 80-300 kV TEM system at International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bengaluru. The system was operated in EELS mode and operated in extraction voltage of 300 kV, to acquire the measurements. As discussed in the previous section, when high energy electron beam incident on ultra-thin sample, some of the electrons gets transmitted (in TEM mode) through the sample while some gets scattered due to interaction with atoms. The inelastically scattered electrons cause loss of energy for an incident electrons on the sample. By collecting the

information on the number of electrons versus energy loss, the EELS spectrum is generated, which is compared with the known samples to determine the chemical bonding between elements [88,91].

In this work the zero-loss peak was removed from the EELS spectrum, by subtracting the reflected tail of the negative part of the zero-loss intensity. While the low-loss region between 1-50 eV in EELS spectrum, consists a series of broad features related to inelastic scattering with valence electron that is used to determine the E_{BG} in film. The EELS spectrum in the range of 50-200 eV, is known as energy loss near edge spectra (ELNES) which are “edges” due to electrons that lost energy in vacancies present in deep core-level of atoms. This corresponds to the binding energy of the respective shell which is used to determine the composition of the film [91].

(g) Fourier transform infra-red spectroscope

In this work the Perkin Elmer make (Spectrum BX II), Fourier transform infra-red spectroscope (FTIR) was used to assess the chemical bonding of the material through infrared spectrum. The typical schematic diagram of FTIR spectroscope system is shown in Figure 2.15.

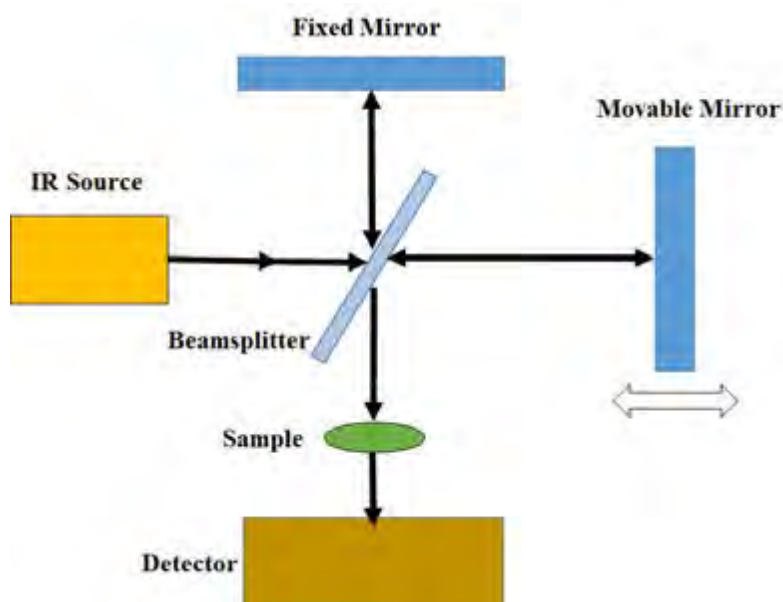


Figure 2.15 The typical schematic diagram of Fourier transform infra-red spectroscope.

Figure 2.15 shows, the FTIR system which comprises of an IR light source, a unit called Michelson interferometer and detector [88]. The Michelson interferometer unit consists

of beamsplitter, fixed mirror and moving mirror. The unit splits the light beam from IR light source into two separate beams, one of which is reflected by a fixed mirror and other by moving mirror. The process of beam splitting and combining after reflection from both the mirrors, create time difference in same optical path, hence the interference signals are generated. The mathematical Fourier transform method is applied on these interference signals to obtain the resultant spectra in terms of wave number. The main advantage of Michelson interferometer is that the resultant spectra were obtained with high accuracy and fast data acquisition. In this system broad-band IR radiation incidents on the sample, where some of the light gets reflected while other gets absorbed. The difference in intensity of light incident after interaction with sample, is plotted as function of wavelength. The absorbance spectrum is plotted against wave number (cm^{-1}) in the range of 400 to 4000 cm^{-1} in this work. The spectra shows different absorbance peaks at specific frequencies which is related to chemical bonding in the sample using Beer-Lambert Law, as given below in eq. (2.23) [88].

$$A = a(\lambda)bc \quad (2.23)$$

where, A represents absorbance, $a(\lambda)$ represents wavelength dependent molar absorption coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and b represents path length (cm), c represents concentration of chemical bonds ($\text{mol}\cdot\text{L}^{-1}$). In absorbance spectrum, each absorbance peak at particular wavelength represents the characteristics of chemical bonding between the specific elements. And the broadness of absorbance peak is related to information about strong bonding between elements.

(h) Ultra violet-visible-near infrared spectroscope

In this work the Perkin Elmer make Lambda 950 model, ultra violet-visible-near infrared spectroscope (UV-Vis-NIR) is used to assess the E_{BG} of the film through the optical absorption spectrum generated by system. The typical block diagram of UV-Vis-NIR spectroscope showing different units in the system is shown in Figure 2.16.

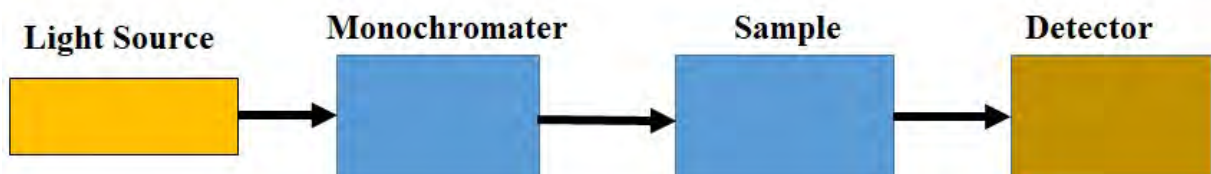


Figure 2.16 The typical block diagram of UV-Vis-NIR spectroscope showing different units in system.

As shown in Figure 2.16, the system comprises of light source to generate the light in the range of UV-Vis and NIR range as the name suggests. The light is then passed through a monochromator, which is used to send single wavelength light at a time to the sample by filtering out the others from light source. In this system, the sample holder is designed to hold one reference sample and one actual sample. The reference sample is normally the undeposited piece of quartz wafer, while the actual sample has film deposited on other piece of same quartz wafer. In the detector, the change in intensity of light (I) after interaction with the film is compared to the intensity of light from the reference sample (I_0). The absorbance (A) is defined by eq. (2.24) [92],

$$A = -\log\left(\frac{I}{I_0}\right) \quad (2.24)$$

The band-gap of the material is known as the difference between the minimum of conduction band and maximum of valance band in material. From the absorbance plot, the value of E_{BG} can be extracted using the Tauc method [93]. Under this method, the $(\alpha E)^2$ is plotted against E and the line crossing the x-axis of the exponential gives the estimated E_{BG} of the film. Here α , is defined as absorption coefficient given by eq. (2.25),

$$\alpha = \frac{A(h\nu - E_{BG})^n}{h\nu} \quad (\text{cm}^{-1}) \quad (2.25)$$

where, A is constant, $E = h\nu$ represents the energy, which is Planck's constant (h) multiplied by the frequency of vibration (ν) from the incident beam and n represents the index which is 1/2 for direct allowed transition material and 2 for indirect allowed transition material like silicon.

2.4.3 Opto-electronic characterization

Under opto-electronic characterization, we measure the minority carrier life-time (τ) of the film under study by optical means. This is carried out using Sinton WCT-120 system, which uses the quasi-steady-state photoconductance (QSSPC) method for measuring the τ of film [11]. The typical schematic diagram of life-time measurement system is shown in Figure 2.17.

As shown in Figure 2.17, the system uses flash light source which causes a short and slow pulse from lamp to be incident on the sample through the IR pass filter. The minority carrier life-time of value $< 100 \mu\text{s}$, is measured using QSSPC mode with high accuracy, while moderate to high values were also measured effectively. The quasi-steady-state condition is

achieved by keeping the pulse time lower than τ . The photo conductance decay w.r.t. time is measured using the inductive-coupled electronics attached inside sample stage, to determine the excess carrier density Δn using the following eq. (2.26) [94],

$$\Delta n = \frac{\Delta\sigma}{qW(\mu_n + \mu_p)} \quad (\text{cm}^{-3}) \quad (2.26)$$

where, $\Delta\sigma$ represents excess photoconductance (S), W represents sample thickness (cm), μ_n and μ_p are electron and hole mobilities $\{\text{cm}^2.(\text{V.s})^{-1}\}$, respectively.

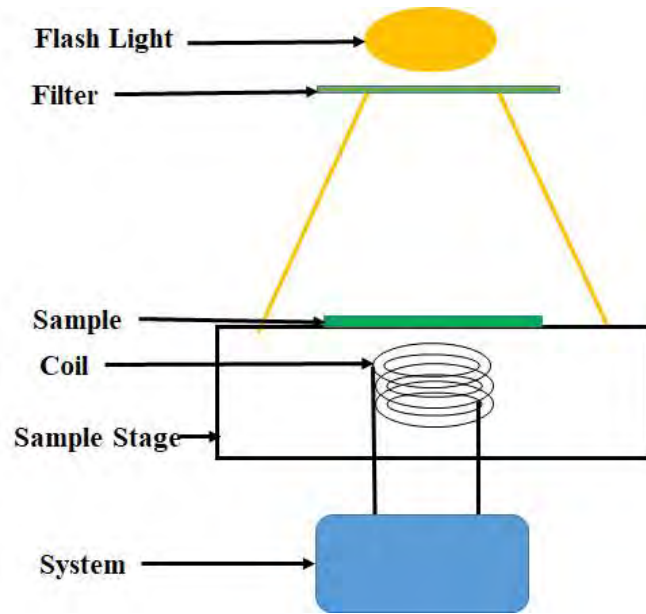


Figure 2.17 The typical schematic diagram of life-time measurement system [11].

The effective minority career lifetime τ_{eff} (s) by QSSPC method, is assessed by using the following eq. (2.27),

$$\tau_{\text{eff}}(\Delta n) = \frac{\Delta n(t)}{G(t) - \frac{\partial \Delta n(t)}{\partial t}} \quad (\text{s}) \quad (2.27)$$

where, $G(t)$ represents the generation rate for electron-hole pairs ($\text{cm}^{-3}.\text{s}^{-1}$), which is determined by using the light intensity on a calibrated detector, $\Delta n(t)$ represents time-dependent average of excess carrier density. Since the τ_{eff} is a measure of recombination at front & rear surfaces and bulk life-time, this is also defined as eq. (2.28),

$$\frac{1}{\tau_{\text{eff}}(\Delta n)} = \frac{1}{\tau_{\text{bulk}}(\Delta n)} + \frac{S_{\text{front}}(\Delta n) + S_{\text{rear}}(\Delta n)}{W} \quad (\text{s}^{-1}) \quad (2.28)$$

In eq. (2.28), $S_{\text{front/rear}}$ are surface recombination velocities for front and rear surface and $\tau_{\text{bulk}}(\Delta n)$ represents the bulk lifetime at Δn . When both the front and rear surfaces are passivated symmetrically with same film, the effective surface recombination velocity, S_{eff} can be determined using eq. (2.29) as given below [11,95],

$$S_{\text{eff}} = \frac{W}{2} \left(\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{bulk}}} \right) \quad (\text{cm.s}^{-1}) \quad (2.29)$$

The same was also discussed in chapter 1, section 1.2. The τ_{bulk} was measured on silicon wafer by immersing the wafer in Iodine-Methanol (IM) solution [95]. The solution was prepared with 1.18 g of Iodine mixing in 50 mL of Methanol. After having obtained the value of τ_{bulk} , the S_{eff} can be determined by using eq. (2.29) at particular value of Δn , which is applicable for symmetrically passivated structure. This procedure for measurement of τ_{eff} and determining S_{eff} is followed for all the experiments stated in this thesis. If there is any change in the procedure, it will be mentioned explicitly in the experiment section of the respective chapters.

2.5 Summary

In this chapter we have reviewed the existing literature on AlO_x film synthesized by different techniques and application of film as the surface passivation of c-Si wafers for solar cell applications. The typical values of S_{eff} and power conversion efficiencies achieved so far by AlO_x film synthesized using ALD, PECVD and RS technique are revised in this chapter. Also the review on film applied as rear or front passivation layer in p-type and n-type c-Si solar cells, respectively are documented. The typical values of fixed oxide charge and interface density that results in good passivation of silicon surface using AlO_x are also documented.

As discussed in section 2.3.3, the AlO_x film deposited using RS technique have already shown its applicability as surface passivation layer in solar cells. Since the technique uses Al metal target reactively sputtered in high purity Ar and O_2 gases, makes it more viable for industrial application due to simple setup. As also discussed the RS AlO_x film is capable of passivating both n-type and p-type surface very effectively with S_{eff} of 8 cm.s^{-1} and 35 cm.s^{-1} , respectively [75,78]. The η of 20.1 % was measured on p-type PERC cell with rear surface passivated using RS AlO_x [79]. Hence with considering the applicability of this technique on solar industries, we have explored the development of high quality AlO_x film for

surface passivation of p-type c-Si. To further achieve the cost factor of the processing, the RS system with pulsed-DC power supply was used in this work. The details on the system will be discussed in the chapter 3. The work involves process development and optimization to achieve the good quality of surface passivation in terms of higher number of negative Q_f and low D_{it} , which are the most basic requirements to achieve the field-effect and chemical passivation, respectively by the film. Various characterization techniques viz. electrical, material and optical discussed in this chapter were used to access the film property.

In the next chapter, we will discuss the proposed work on the development and optimization of AlO_x films by using pulsed-DC RS technique. The various characterization and analysis of the results will be presented in chapter 3.

Chapter 3. Pulsed-DC Reactive Sputter Deposited AlO_x Film

3.1 Introduction

In RS PVD technique, a high purity metal is sputtered by heavy ions in reactive gas ambient for deposition of compound film on the substrate [74]. This technique may have a remarkable importance in the field of solar cell industries due to the goals set to achieve green energy and provide cheaper energy to the peoples. The PECVD system was widely used in solar cell industries, as high-quality of surface passivation was reported by AlO_x films deposited using this technique. However the PECVD technique used for film deposition may not full-fill the green energy criteria, as the TMA precursor with chemical composition of Al(CH₃)₃ has carbon in it [96,97]. This chemical precursor is expensive and requires extra equipment for safe handling of such hazardous chemical. Hence adding all this to the cost of passivated solar cell. In one of the report by Dingemans et al., a cost-cutting solution to make ALD AlO_x films cheaper was proposed by using low purity solar grade TMA precursor for solar cells [12]. Whereas the well-known RS technique uses pure metal and elemental gases for film deposition, could be advantageous due to potentially low cost for processing. As discussed in chapter 2, the RS AlO_x films were also successfully implemented as surface passivation layer of c-Si solar cells [33,75,78]. The RS deposition systems discussed in reports are with RF power source that work at high frequency of 13.56 MHz and hence require an impedance matching network. While in this work we propose to use pulsed-DC

power supply source in RS deposition system, which works at relatively low frequencies and hence does not need an impedance matching network.

Even though ALD AlO_x films have shown the better surface passivation quality with $S_{\text{eff}} < 6 \text{ cm.s}^{-1}$ as compared to RS AlO_x films with $S_{\text{eff}} < 35 \text{ cm.s}^{-1}$ on p-type surface. These films were implemented and tested on the PERC solar cell structures as rear-surface passivation layer, that resulted in the V_{oc} of 662 mV and 651 mV, with corresponding cell η of 21.4 % and 20.1 % for ALD AlO_x and RS AlO_x film, respectively [33,98]. The advantage of RS technique, is high deposition rate and hence the processing would be faster as compared to ALD technique. In the subsequent sections of this chapter we will discuss in detail the pulsed-DC RS deposition technique with the process development to achieve high quality AlO_x film.

3.2 Pulsed-DC reactive sputter deposition technique

In this work, AlO_x film was deposited by sputtering of high purity aluminum target with 99.9995 % purity using Ar as sputtering gas and O₂ as reactive gas. Ar is used here as plasma source to generate heavy Ar⁺ ions for sputtering of metal atoms from the target. Figure 3.1 (a) and (b) shows schematic diagram of typical sputter deposition system, and the pulsed-DC waveform of the power supply used this system, respectively.

The high purity Al target is connected to the cathode, where pulsed-DC power source supplies continuous negative and positive voltage pulses (V_p) and the substrate is connected to the anode which is grounded. For this RS system during the negative voltage supply the target surface is sputtered in the reactive gas ambient for τ_{ON} time, hence the compound film gets deposited on the substrate. Having a small positive voltage (i.e., pulse reversal) during the τ_{OFF} time, causes neutralization of the built-up charges which is created due to the formation of dielectric compound layer on the metal target surface. With pulse reversal a continuous reactive sputtering of metal target is possible in an arc free environment, which is another advantage of using the pulsed-DC power supply [99,100]. The negative peak amplitude of V_p is 80 % of total V_p during τ_{ON} time, whereas positive peak amplitude of V_p is 20 % of total applied voltage during τ_{OFF} time. The voltage and current are the measure of applied process power, which is reported to determine the plasma condition inside chamber [74].

This system also has magnet connected to the chamber near the cathode that is used for the proper confinement of the plasma close to the substrate, hence deposition rate improves through secondary ionizations [101].

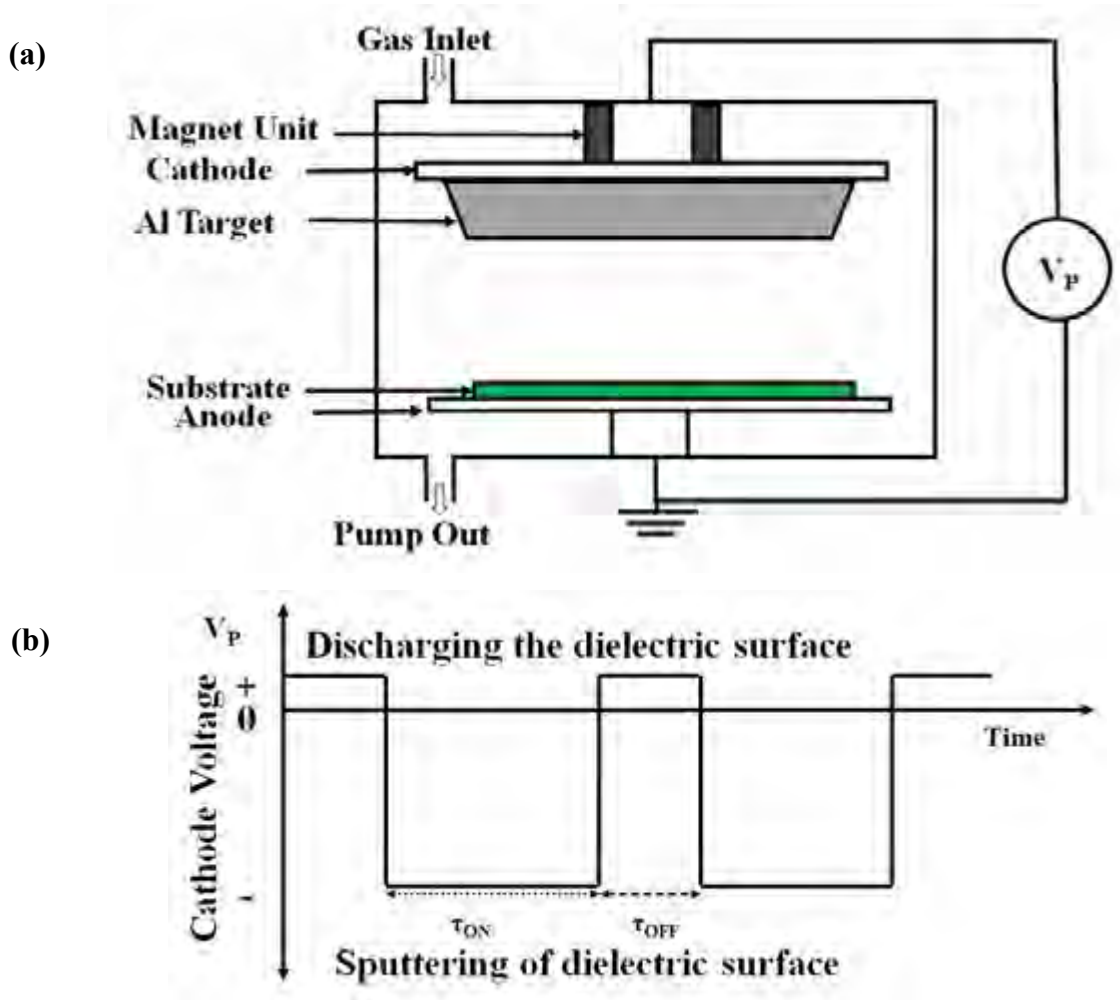


Figure 3.1 (a) Schematic diagram of the reactive sputtering system and (b) waveform of pulsed-DC power supply with V_p . Time τ_{ON} is target surface sputtering time and τ_{OFF} is the time when charges at the target surface get neutralized.

The pulsed-DC RS system with applied V_p is shown in Figure 3.1, the process development and optimization involves understanding the effect of various process variables in the system to achieve the required film quality by fine tuning them. In the following we will discuss various process parameters of the system with their impact on the film quality from the available reports.

(a) Process power

The applied power during film deposition, cause direct impact on the rate of sputtering. With high process power, the rate of Ar^+ ions hitting the target surface are high and cause more atoms to sputter off the target surface, hence increases the deposition rate. However with high power the roughness on the substrate surface also increases as the high energy accelerated Ar^+ ions hit the surface as well [74]. In this report the process power is also referred as power density (PD) in W.cm^{-2} , i.e., applied power per unit area.

(b) Process time

The process time is a measure of time during which the process power is applied to the metal target with process gas for reactive sputtering. Usually in PVD processes more process time is preferable as it allows the reactive species to settle down at the substrate surface and the incoming species could fill up the voids. The less process time may lead to porous film structure, which again depends on the applied process power [74].

(c) Process pressure

The property of the reactive sputtered film may be varied by changing the process pressure during deposition. The process pressure is the measure of reactive O_2 and sputter Ar gas flow rates inside chamber. In the reactive sputter deposition system, the gas composition (i.e., partial pressure) is very crucial element, as very low flow of O_2 gas may lead to non-stoichiometric film while very high flow of O_2 gas may lead to decrease in deposition rate due to poisoning of target [99]. The study also shows, for low process pressure the deposited film can have high compressive stress whereas with high process pressure this stress can be tensile [102].

(d) Substrate temperature

In the pulsed-DC RS system the substrate temperature can be varied between the room temperature to $320\text{ }^\circ\text{C}$. The property of the film can also be changed with high temperature deposition, as with heated surface the knock-on atoms penetrates deep into the film and trapped into interstitial and vacancies which results in the denser film [74,103]. However at very high temperature the back-sputtering of the deposited film may also occur which may results in peeling-off of the film from substrate after deposition [74].

(e) Pulsed-DC power supply

As shown in Figure 3.1 (b), the pulsed-DC type power supply used in this system, also has several variables for process optimization such as, pulse frequency, pulse reversal time and duty cycle. The optimal pulse frequency depends on the type of material to be sputtered. Keeping very low pulse frequency may damage the deposited film due to arcing in the chamber by formation of thick insulating layer at the metal target surface. The term τ_{ON} is the time corresponds to sputtering of the target surface with negative power supplied to cathode and τ_{OFF} is the time corresponds to positive power supplied to the cathode to compensate the surface charges which built-up during the reactive sputtering. The τ_{OFF} is also known as reverse time. The optimal value of pulse reversal should be selected, since large duration of τ_{OFF} , may cause the Ar^+ ions to get repelled from the cathode and cause damage in deposited film on substrate [99,100]. The term duty cycle (%) is defined as the ratio of τ_{ON} to total time ($\tau_{ON} + \tau_{OFF}$). The pulsed-DC power supply variables are kept constant as pulse frequency = 100 kHz, reverse time = 3 μs and duty cycle = 70 %, for all the experiments carried out in this work.

The development and optimization of process was carried out by varying various parameters as discussed above for good quality AlO_x film deposition. The quality of the film for different process variables are assessed using material characterization and electrical characterization, which will be discussed in subsequent sections.

3.3 Experimental details

The AlO_x film was deposited on 5 Ω .cm p-type CZ c-Si (100) wafers by pulsed-DC RS technique in PVD chamber of Applied Materials ENDURA cluster tool. The wafers were cleaned using standard RCA cleaning process before film deposition, as discussed in chapter 2, section 2.4.1. The process chamber was pumped down to the base pressure of 7×10^{-8} torr before film deposition. For electrical characterization, the MOS capacitor structures were fabricated with the thermally evaporated Al using shadow mask of diameter of 200 μm as top metal gate and blanket Al was evaporated on backside for back contact. These MOS capacitors were subsequently subjected to FGA (5 % H_2 in N_2) at 420 $^{\circ}C$ for 20 min to improve the metal-semiconductor contact resistance and also the film quality may improve with reduction of dangling bonds using hydrogen atoms. This process is also known as post-metallization annealing (PMA). During the AlO_x film deposition certain power supply

parameters were kept constant as discussed in previous section. The process variable such as process power, gas flow and deposition time for experiments are mentioned explicitly in the respective section of this chapter.

3.4 Hysteresis behaviour

The behaviour of the cathode voltage in the RS system was observed as the reactive O_2 gas flow rate was varied from minimum to a certain value and subsequently retracing the flow to the minimum value. Figure 3.2 shows the hysteresis behavior observed at three different applied process PD namely: 0.69, 1.3 and 2.07 $W.cm^{-2}$. The O_2 flow was varied from 5 sccm onwards by keeping Ar flow rate constant at 10 sccm during these process. The cathode voltage was monitored directly from the system. This process was carried out at room temperature. The plot of cathode voltage versus O_2 flow rate is shown in Figure 3.2 for different PD.

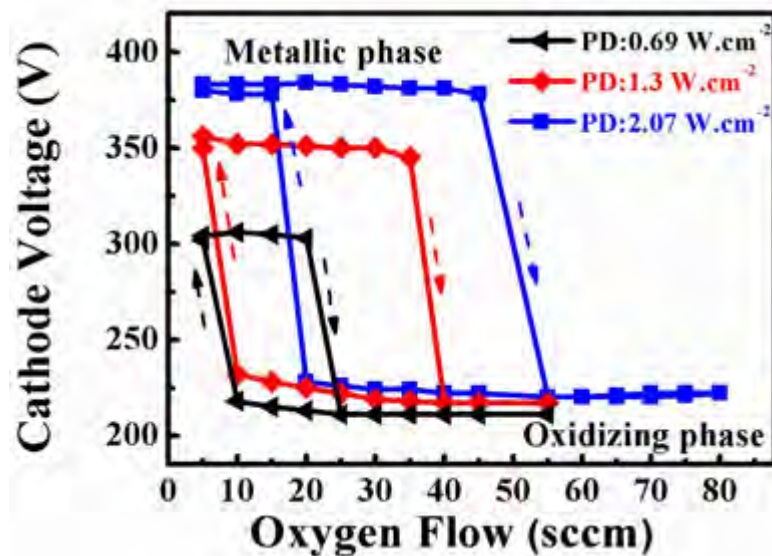


Figure 3.2 Hysteresis behaviour of cathode voltage as a function of oxygen (O_2) flow rate for different PD conditions in pulsed-DC RS system. The arrows indicate the forward and reverse direction of variation of O_2 flow.

In the pulsed-DC RS system the metal target retains its metallic property at low O_2 flow as the reactive species concentration in the chamber is still low. As the O_2 flow increases, the target surface starts to react with O_2 resulting in the formation of compound oxide layer at the target surface. This oxide layer would be charged by electrons from the plasma and hence causes a sudden drop in the cathode voltage. The initial target condition

with high cathode voltage is called “metallic phase” and sudden drop in the cathode voltage is called “oxidized phase” in forward direction of O₂ flow as shown in Figure 3.2. During the retrace, i.e., lowering of the O₂ flow rate in reverse direction, it is observed that the cathode voltage remains low until the oxide layer on the target surface gets completely sputtered-off. As the O₂ flow becomes sufficiently low the cathode voltage rises back to the initial high value, i.e., the target surface regains the metallic property with very low or almost no availability of any reactive gas species [100,101,104]. Since the critical O₂ flow for the reverse direction in the hysteresis curve is less than the forward direction, a hysteresis behavior is observed.

In the RS system, the AlO_x film deposition is carried out in the oxidized phase with low cathode voltage value in the forward direction of the hysteresis curve, where the O₂ flow rate value is chosen close to the knee point for stable film deposition [99,101]. As shown in Figure 3.2, the critical O₂ flow required for film deposition is observed to be different for different process power. At high deposition power a high rate of O₂ flow is required to get the oxide film deposition.

3.5 Material characterization

To obtain the material characteristics, the following systems were used: Sentech SE-800 for thickness and RI measurement, Bruker D8 discover diffractometer used in XRR mode to obtain film density, thickness and surface roughness of the film, Thermo VG scientific make Multilab 2000 XPS was used in the surface scanning mode to obtain the film composition, Veeco-Digital Instruments (Nanoscope IV) AFM was used for measuring surface roughness of the film in contact mode. The results of these analysis are discussed in the subsequent sections.

3.5.1 Film density and surface morphology

The film density and morphology were obtained for the AlO_x film deposited at three different PD viz. 0.69, 1.3 and 2.07 W.cm⁻². The deposition time for these are kept same at 300 s for all the experiments. These films are annealed in RTP system at 900 °C in oxygen ambient for 1 min. Figure 3.3 (a) and (b), shows the thickness and RI of films measured using SE, respectively.

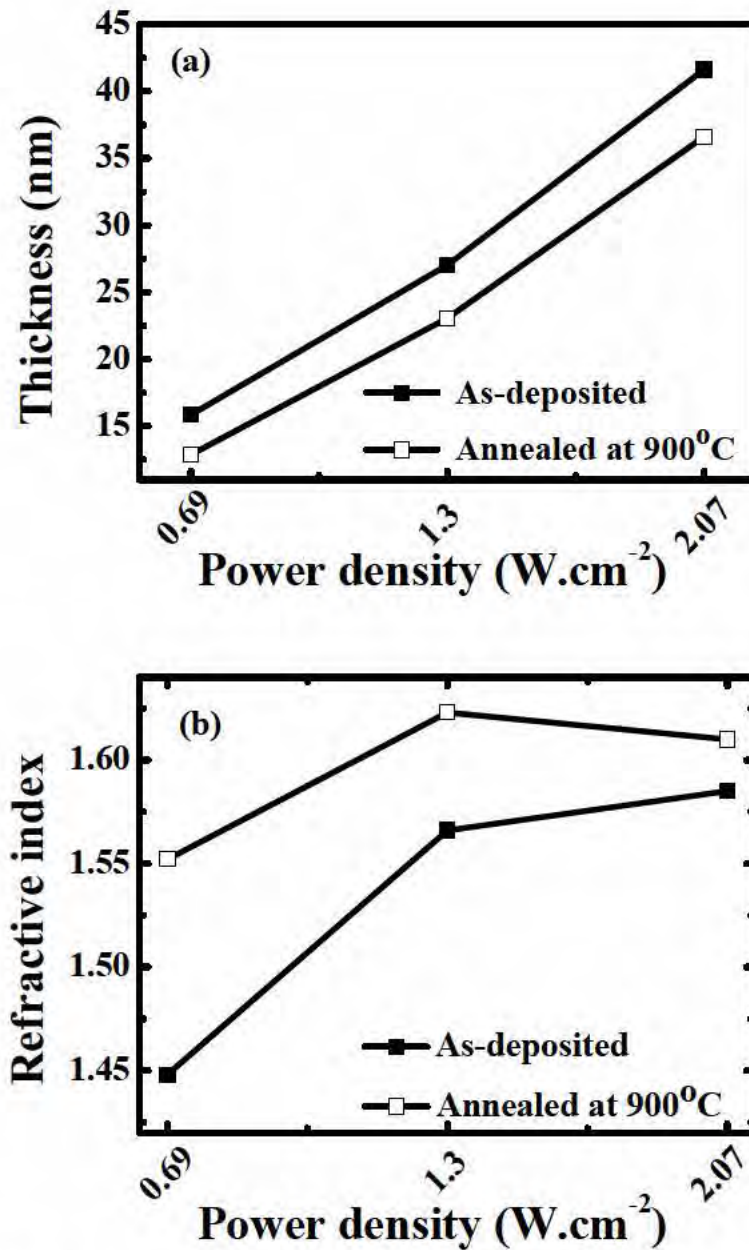


Figure 3.3 (a) Thickness and (b) RI of as-deposited and annealed AlO_x film deposited at different PD.

From Figure 3.3 (a), the deposition rate can be deduced using film thickness which shows a linear increase in deposition rate with process power. The high deposition rate of $8 \text{ nm}\cdot\text{min}^{-1}$ was obtained for film deposited at high PD of $2.07 \text{ W}\cdot\text{cm}^{-2}$. The thickness of the annealed film is reduced by 4 nm than as-deposited film, which is consistent for each process PD depositions. In Figure 3.3 (b), the RI of these films increases after annealing, which signifies an increase in film density. After annealing the value of $\text{RI} = 1.62$ was measured at a wavelength of 632.8 nm using SE, on high PD deposited film. The RI observed here is lower

than that reported for crystalline Al_2O_3 film, i.e., $\text{RI} = 1.76$ at 632.8 nm [105]. However for solar cell applications the value of $\text{RI} = 1.62$ that is typical value for amorphous AlO_x films, is acceptable [12].

The film density and surface roughness for different film deposited at different PD were assessed using XRR system using $\text{Cu K}\alpha$ energy source ($E = 8047 \text{ eV}$). The result was further analysed using Parratt formalism to extract the surface roughness and thickness of as-deposited AlO_x film from the reflectivity graph [90], are shown in Figure 3.4.

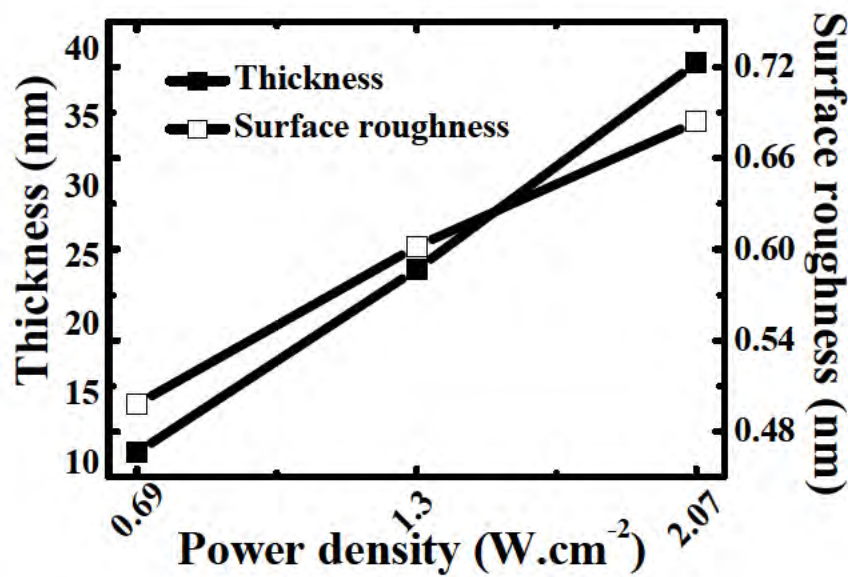


Figure 3.4 Surface roughness and thickness of as-deposited AlO_x film measured by XRR and extracted using Parratt formalism for different PD conditions.

The AlO_x film thickness and surface roughness seem to increase almost linearly with process power. The increase in surface roughness with power, may be due to the fact that high power cause fast collisions of the ions onto the substrate with high energy and hence leads to more damage on the film surface [74]. We have noticed here, the thickness of film measured by XRR shows about 3 nm less value as compared to the thickness obtained by SE measurement, as in Figure 3.3 (a). Such difference in thicknesses measured using these techniques was also reported by Wasserman et al. [106]. The thickness measured using SE is obtained from the shape and intensity of elliptically polarized light reflected from the interface separating the two mediums with different RI and in XRR technique, the difference in two interfaces separated by different electron densities were measured [107].

The film density for pulsed-DC RS AlO_x film deposited at different PD conditions, obtained using XRR measurement for as-deposited and annealed film in RTP at $900\text{ }^\circ\text{C}$ for 1 min, are shown in Figure 3.5.

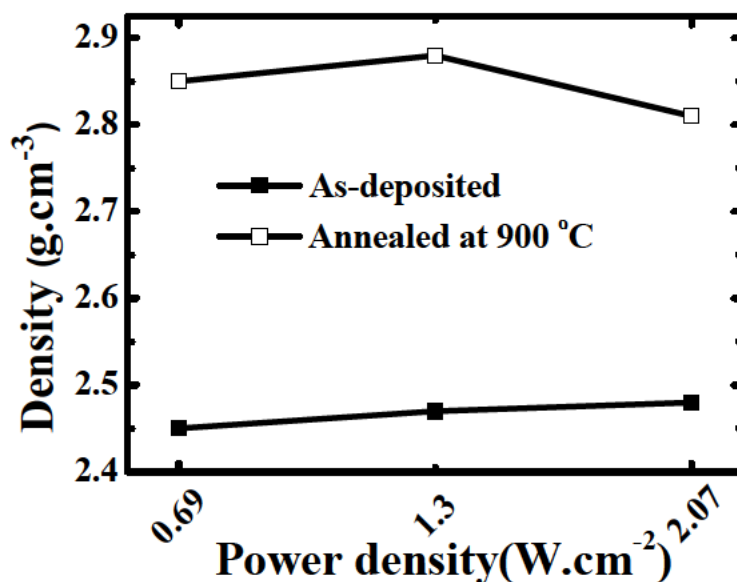


Figure 3.5 The film density for AlO_x obtained by XRR measurement using Parratt formulism for film deposited at different PD.

The value of film density seems independent of process power, however the density seems to increase after annealing. The film density for as-deposited $\text{AlO}_x = 2.45\text{ g.cm}^{-3}$, increases to 2.88 g.cm^{-3} after annealing. This result is in line with the RI values obtained for the annealed film as shown in Figure 3.3 (b), i.e., an increase in RI values relating to improvement in the film density after annealing. The value of film density for this film is relatively lower than the reported values for crystalline stoichiometric Al_2O_3 film which is between $3.95\text{-}4.1\text{ g.cm}^{-3}$ [108].

The surface morphology for this film was also obtained using Veeco-Digital Instruments (Nanoscope IV) make AFM for film deposited at low PD of 0.69 W.cm^{-2} . The surface roughness measured in contact mode for films deposited at different gas flow ratios, viz. with $\text{Ar}:\text{O}_2$ flow ratios of 2:5 and 3:5, are shown in Figure 3.6 (a) and (b), respectively.

The film deposited at low power shows very good surface with roughness value of root mean square (RMS) = 3.2 \AA , as shown in Figure 3.6 (a), for $\text{Ar}:\text{O}_2$ flow ratio of 2:5, i.e., $\text{Ar} = 10\text{ sccm}$ and $\text{O}_2 = 25\text{ sccm}$.

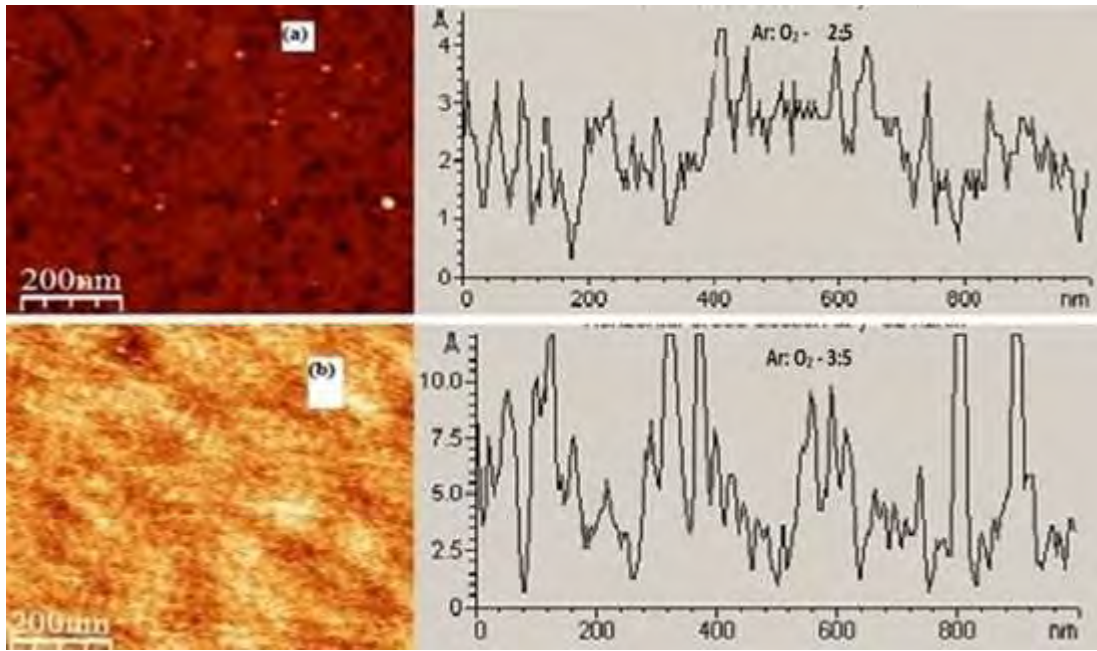


Figure 3.6 Contact mode AFM measurement of AlO_x films deposited with Ar: O_2 flow ratio of (a) 2:5 and (b) 3:5, and PD of 0.69 W.cm^{-2} .

In Figure 3.6 (b), an increase in surface roughness to RMS value of 10 \AA with increase in Ar: O_2 flow ratio of 3:5, i.e., Ar = 15 sccm and $\text{O}_2 = 30 \text{ sccm}$, is observed. Since an increase in Ar flow, may cause more Ar^+ ions bombarding the surface, hence may results in relatively higher roughness of the deposited film. The roughness values obtained using AFM technique is lower as compared to result obtained from XRR measurement, since the surface morphology obtained by AFM is in contact mode whereas by XRR measurement the extracted roughness values depend mostly on the Parratt model fitting, hence the surface morphology obtained using AFM technique is more reliable.

3.5.2 Film composition

The composition of the film was measured by Thermo VG Scientific make Multilab 2000 XPS using Mg $K\alpha$ radiation source (1253.6 eV). The XPS measurement was done on AlO_x film deposited at low PD of 0.69 W.cm^{-2} for different O_2 gas flow of 25 sccm and 30 sccm, keeping Ar flow of 10 sccm constant for both experiments. The Al 2p and O 1s spectra of XPS measurements are shown in Figure 3.7 (a) and (b), respectively. Al 2p and O 1s spectra along with Gaussian curve fitting for single peak after baseline correction are shown in Figure 3.7. The fitted curve is shown as smooth blue colored lines in both the figures.

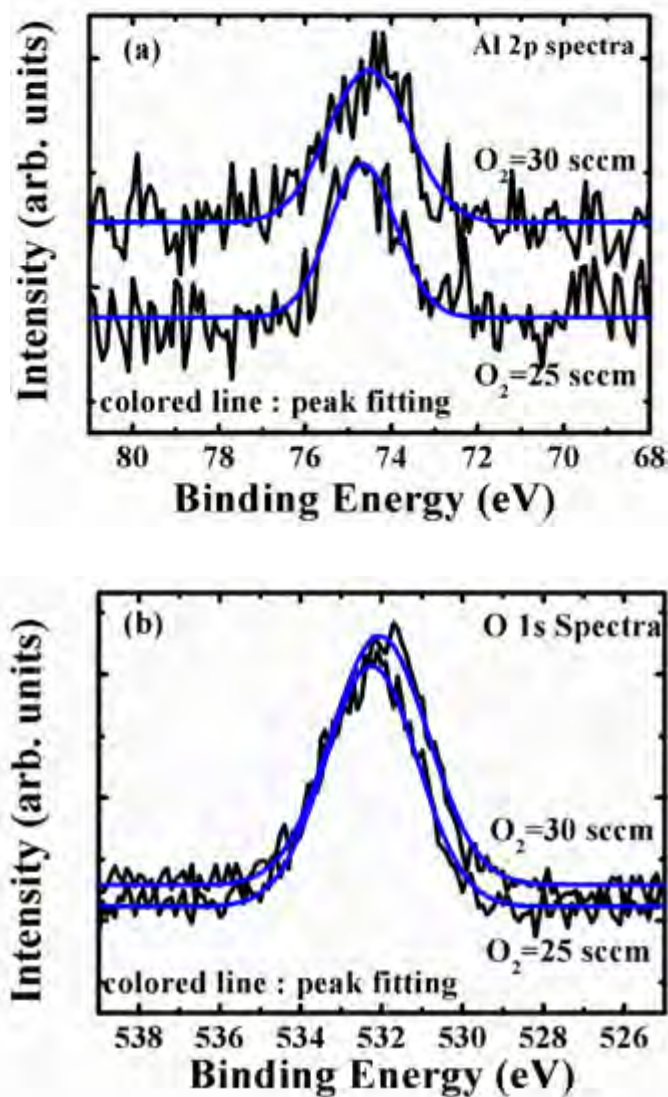


Figure 3.7 (a) Al 2p spectra (b) O 1s spectra of Al_xO_y films for different O_2 flow ratio measured using XPS.

The O/Al ratio of 1.48 was observed for AlO_x film deposited using Ar: O_2 ratio of 2:5 (i.e., $O_2 = 25$ sccm and Ar = 10 sccm) which seems to be closer to stoichiometric Al_2O_3 film. This value of $O_2 = 25$ sccm, is slightly higher than the knee point in the forward direction of O_2 flow on the hysteresis curve for film deposited at low PD of 0.69 W.cm^{-2} , as shown in Figure 3.2. The O/Al ratio of 1.7 was observed for Ar: O_2 ratio of 1:3 (i.e., $O_2 = 30$ sccm and Ar = 10 sccm), this means the film became O rich with higher O_2 flow rate during deposition.

In conclusion the deposited film would achieve stoichiometric Al_2O_3 , if the O_2 flow rate is chosen close to the knee point in the forward sweep of hysteresis plot. A similar trend

was also reported by Olsson et al., with stoichiometric Al_2O_3 film was achieved when deposition was carried out in oxidized mode close to knee point [109].

3.5.3 Deposition rate and optical property

The thickness and RI of the film were measured using Sentech SE-800 followed by curve fitting using SpectraRay software by Sentech GmbH. Figure 3.8 shows, the deposition rate and RI obtained for AlO_x film deposited at PD of 0.69 W.cm^{-2} with different O_2 flow.

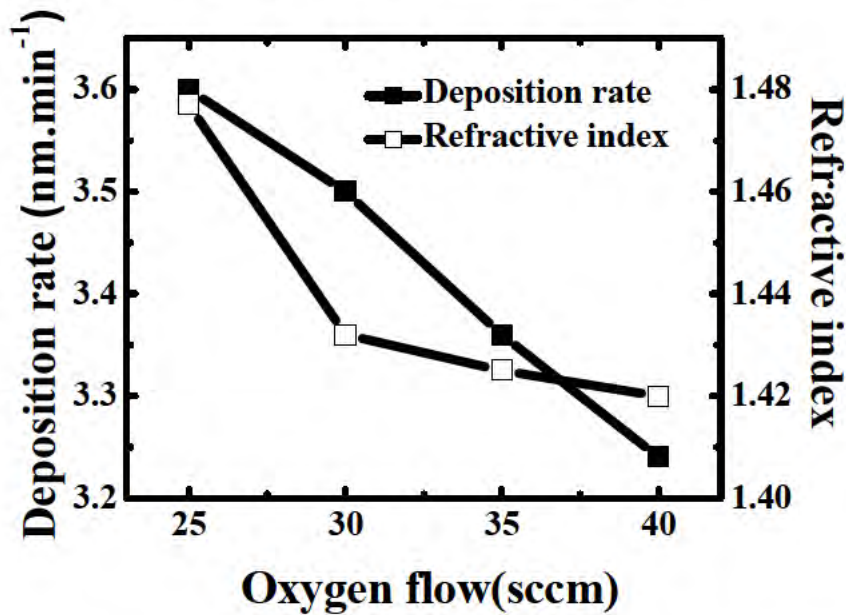


Figure 3.8 Deposition rate and RI of AlO_x film for different O_2 flow rate, keeping the Ar flow constant at 10 sccm and PD at 0.69 W.cm^{-2} .

The deposition rate is observed to be decreasing with increase in O_2 flow rate. The increase in reactive gas flow increases the process pressure inside the chamber during deposition, which causes a decrease in mean free path and hence the rate of sputtering. Another reason also supports result of the decrease in deposition rate, as the high reactive gas (O_2) inside the chamber makes the metal target surface to oxidize by formation of compound layer and hence secondary electron emission coefficient is higher, which further decrease the sputtering of metal surface as the compound surface lowers the reaction at the target [74,101]. The RI of 1.478 is observed for Ar: O_2 of 2:5, whereas the value of RI goes down a little for higher O_2 flow. This may be due to changes in the composition of the film or the density of the film.

3.6 Electrical characterization

To assess the electrical properties of the film, MOS capacitors were fabricated with AlO_x film deposited under the process conditions mentioned in section 3.3. The high frequency C-V measurements (at $f = 100$ kHz) of MOS capacitors were carried out using Keithley 4200 semiconductor characterization system, and the results are shown in Figure 3.9. The AlO_x film T_{ox} of 18 nm was measured using SE for film deposited at PD of 0.69 W.cm^{-2} with Ar: O_2 of 2:5 and deposition time of 300 s.

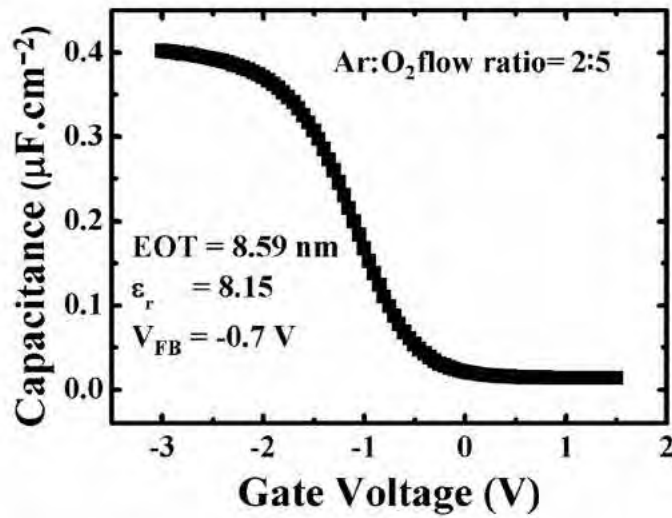


Figure 3.9 High frequency C-V characteristics curve of a typical MOS capacitor for AlO_x film deposited at PD of 0.69 W.cm^{-2} and Ar: O_2 flow of 2:5.

Various parameters extracted from the high frequency C-V plot, are dielectric constant of AlO_x film $\epsilon_{r-\text{AlO}_x} = 8.15$ and EOT = 8.59 nm, obtained using eq. (2.5) and eq. (2.7), respectively [86]. The value of $V_{\text{FB}} = -0.7 \text{ V}$ is extracted using different parameters of high frequency C-V using eq. (2.12) to eq. (2.14), in chapter 2.

The high frequency C-V measurement of AlO_x film deposited at two different PD of 0.69 W.cm^{-2} and 1.3 W.cm^{-2} are shown in Figure 3.10. The film deposited at $\text{O}_2 = 25 \text{ sccm}$ for PD of 0.69 W.cm^{-2} and $\text{O}_2 = 55 \text{ sccm}$ for PD of 1.3 W.cm^{-2} , i.e., close to knee point on hysteresis curve for respective power as shown in Figure 3.2, while keeping Ar flow = 10 sccm for both conditions. The deposition time was kept 300 s for both the experiments. The inset in Figure 3.10, shows the normalized C/C_{acc} curves. The shift in V_{FB} values is observed more towards the positive value for high process power (i.e., PD of 1.3 W.cm^{-2}) as compared to PD of 0.69 W.cm^{-2} for AlO_x film deposition.

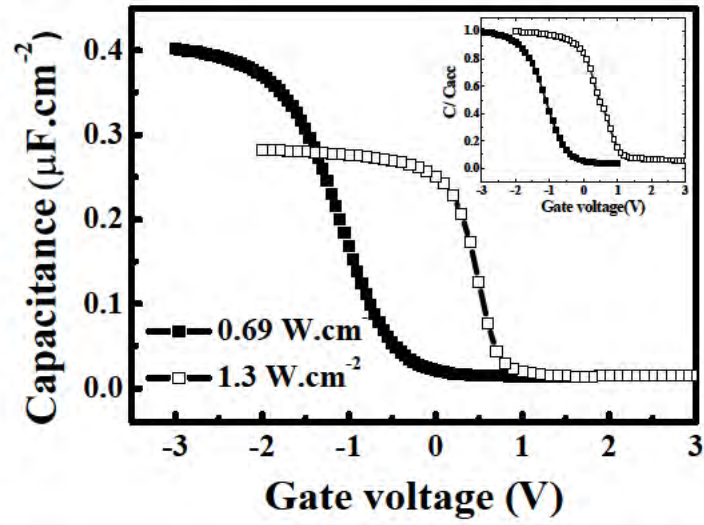


Figure 3.10 High frequency C-V plot of AlO_x MOS capacitor with films deposited at PD of 0.69 W.cm^{-2} and 1.3 W.cm^{-2} . The inset shows the normalised C/C_{acc} curve for both conditions to assess shift in V_{FB} .

The Q_f values can be extracted using eq. (2.15) from high-frequency C-V curve, by assessing the ΔV_{MG} [86], as discussed in chapter 2, section 2.4.1. The values of EOT, $\epsilon_{r-\text{AlO}_x}$, V_{FB} and negative Q_f extracted from the high frequency C-V measurement at different PD conditions are given in Table 3.1.

Table 3.1 The extracted values of EOT, $\epsilon_{r-\text{AlO}_x}$, V_{FB} and Q_f from high frequency C-V measurement for AlO_x film deposited at different PD.

Power density (W.cm^{-2})	EOT (nm)	$\epsilon_{r-\text{AlO}_x}$	V_{FB} (V)	Negative Q_f (cm^{-2})
0.69	8.59	8.15	-0.7	3.5×10^{11}
1.3	12.44	8.93	0.8	2.88×10^{12}

The as-deposited film at high PD of 1.3 W.cm^{-2} has more negative Q_f of $2.88 \times 10^{12} \text{ cm}^{-2}$ as compared to low PD deposited film which has negative Q_f of $3.5 \times 10^{11} \text{ cm}^{-2}$. The value of negative Q_f of $1.7 \times 10^{12} \text{ cm}^{-2}$ for as-deposited Al_2O_3 film by PECVD process was reported by Kania et al. [67]. The increased Q_f to $3.1 \times 10^{12} \text{ cm}^{-2}$ was shown after annealing in FGA at $425 \text{ }^\circ\text{C}$ for 25 min for this PECVD AlO_x film. In our case the as-deposited film deposited at PD of 1.3 W.cm^{-2} shows negative Q_f of $2.88 \times 10^{12} \text{ cm}^{-2}$, which is comparable to

those reported by PECVD AlO_x film after PDA. Hence pulsed-DC RS AlO_x film deposited at PD of 1.3 W.cm^{-2} , shows an applicability as surface passivation layer on p-type surface of c-Si solar cells by field-effect passivation mechanism.

The film was also tested for robustness and leakage using I-V measurement of MOS capacitors, by application of gate voltage sweeps. The film was deposited at PD of 0.69 W.cm^{-2} with Ar: O_2 flow ratio of 2:5 and deposited time of 300 s. The I-V measurements were performed on 20 different devices on the same wafer and the breakdown voltage was noted for each device. The Weibull distribution plot of E_{BD} is shown in Figure 3.11 (a). In Figure 3.11 (b), the gate current density versus gate voltage (J-V) plot is shown for one of the MOS capacitors to assess the leakage current.

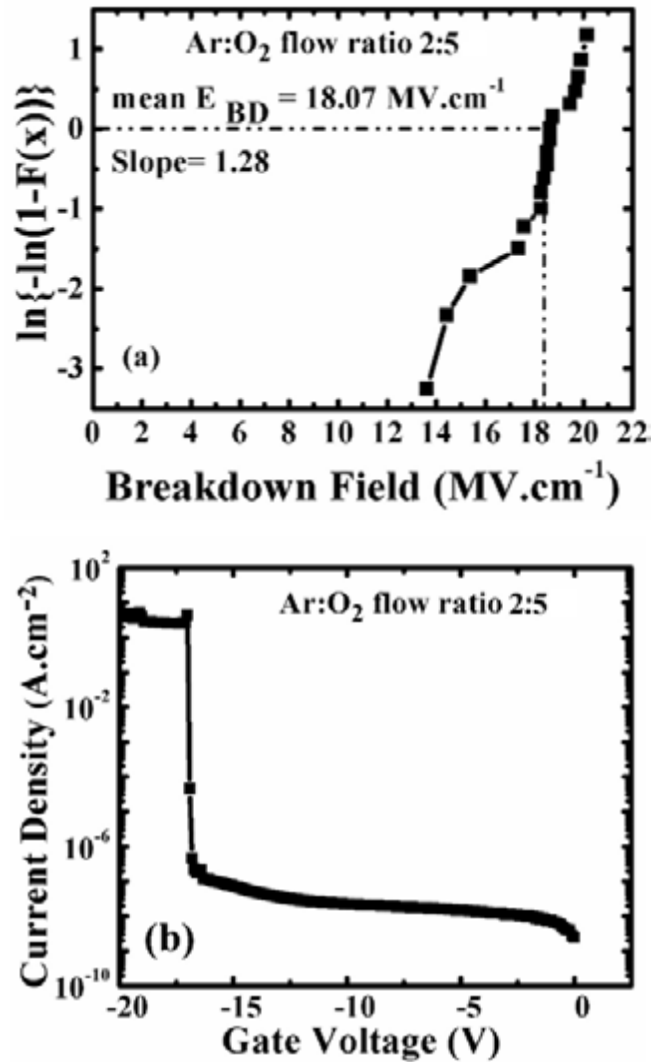


Figure 3.11 (a) Weibull distribution plot of E_{BD} and (b) J-V plot for MOS capacitor with AlO_x film deposited using Ar: O_2 gas flow ratio of 2:5.

In this work with the film deposited using 70 % O₂ flow ratio, we have obtain mean E_{BD} of 18.07 MV.cm⁻¹ for film thickness of 17.97 nm (EOT = 8.59 nm), as shown in Figure 3.11 (a). An E_{BD} of 7.4 MV.cm⁻¹ was reported by Seino et al. for pulsed-DC RS AlO_x film, with film physical thickness of 50 nm and deposited using 70% O₂ flow ratio [110]. The comparison of E_{BD} values for respective EOT obtained and reported by various RS deposition techniques and metal-organic chemical vapor deposition (MOCVD) technique are given in Table 3.2 [111,112].

Table 3.2 Comparison of the E_{BD} for AlO_x film deposited using different methods from the published report.

Reference	Deposition method	EOT (nm)	E _{BD} (MV.cm ⁻¹)
[112]	MOCVD	5.5	19.3
	RF reactive sputtering	6.3	14.1
[110]	Pulsed-DC reactive sputtering	*50	**7.4
This work	Pulsed-DC reactive sputtering	8.59	18.07

*Physical thickness

**Breakdown field = breakdown voltage/physical thickness

The E_{BD} obtained by our optimized process with low power deposition is comparable to the values reported for films deposited by MOCVD Al₂O₃ film and is better than the RS deposited Al₂O₃ film [111,112]. From Figure 3.11 (b), low leakage current density of 3 × 10⁻⁹ A.cm⁻² is observed at gate voltage of -5 V for the film with EOT of 8.59 nm, which is similar to the leakage current obtained for MOCVD deposited stoichiometric Al₂O₃ films [111]. This film was applied as inter-poly dielectric (IPD) layer in the flash memory applications [111]. Thus the film developed during the thesis and reported in this chapter may be also implemented as IPD layer for flash memory applications [113].

3.7 Summary

In this chapter we have reported the development and optimization of process for deposition of AlO_x film using a pulsed-DC RS technique. The various material and electrical characteristics were used towards the optimization of the process. The electrical properties measured for the film indicate its potential to be applied as surface passivation layer on p-type

c-Si surface with high negative Q_f of $2.88 \times 10^{12} \text{ cm}^{-2}$ when deposited at high power (i.e., PD = 1.3 W.cm^{-2}). With the low PD optimized process, a stoichiometric Al_2O_3 film were obtained at O_2 flow rate chosen close to knee point at forward hysteresis behaviour of the system. The same process have shown mean E_{BD} of 18.07 MV.cm^{-1} and dielectric constant $\epsilon_{r-\text{AlO}_x}$ of 8.15 for EOT of 8.59 nm for this AlO_x film. The film may be also applied as IPD layer in flash memory applications due to low leakage and high breakdown field. The high deposition rate at high PD deposition, makes pulsed-DC RS technique a suitable choice for industrial purpose. This technique makes an attractive low cost option. In the subsequent chapters we will discuss in detail the pulsed-DC RS AlO_x film applicability for the surface passivation of p-type c-Si using suitable characterization techniques. The impact of various process parameters and PDA process on the film and interface quality will be analysed and discussed with the use of more sophisticated measurement tools.

Chapter 4. Optimization of Post-Deposition Annealing for the Improvement of Passivation

4.1 Introduction

One of the mechanisms for surface passivation by AlO_x film on p-type silicon is the repulsion of electrons from the surface by the negative Q_f present in the AlO_x film, causing field-effect passivation. An improvement in interface quality during deposition or after PDA process leads to reduction in number of D_{it} , causing chemical passivation and hence further improves the surface passivation quality [35,45]. The origin of negative Q_f in Al_2O_3 film was proposed by Kimoto et al., which says the presence of both T and O coordinated Al in the $\gamma\text{-Al}_2\text{O}_3$ film and T coordinated Al are present at the $\text{Al}_2\text{O}_3/\text{c-Si}$ interface [42]. The films were deposited by ALD process on c-Si wafer and the Al-coordination was probed using EELS [42]. On the other hand Hoex et al. reported, an increase in negative Q_f in PA-ALD Al_2O_3 film after PDA, due to the formation of a very thin (~ 2 nm) interfacial oxide (SiO_2) layer at $\text{Al}_2\text{O}_3/\text{c-Si}$ interface [44]. From the published reports, the necessity of PDA process for enhancing the passivation effect by AlO_x film synthesized using different techniques was very clear, since the PDA process cause an improvement in field-effect passivation and/or chemical passivation [34,35,58,70,75,76,114,115]. The PDA was mainly carried out in N_2 , forming gas (forming gas anneal-FGA) or air ambient at the temperature range of 300-550 °C for annealing time between 10-60 min [34,35,39,70,76,115-117].

For PA-ALD and PECVD Al₂O₃ films an improvement in surface passivation with $S_{\text{eff}} < 5 \text{ cm.s}^{-1}$ was reported after annealing of film. However as discussed in chapter 2, these films contain 2-7 % hydrogen [52]. Hence the improvement in surface passivation quality after PDA was related to diffusion of hydrogen from the film to the interface, that improves chemical passivation [36,72,117]. For RS AlO_x film, Li et al. reported S_{eff} of 16 and 14 cm.s⁻¹ after PDA in N₂ and FGA ambient at 400 °C, respectively [75]. Since the RS deposited AlO_x film was not expected to contain hydrogen as discussed in earlier chapter, hence hydrogen may be introduced into the film during the PDA process to improve the surface passivation quality.

In this chapter we will discuss the impact of different PDA conditions on pulsed-DC RS AlO_x film for surface passivation application. The film and interface quality is assessed through electrical characterization of the MOS capacitor and material characterizations like cross-sectional TEM and depth resolved XPS. The surface passivation quality was measured using minority carrier life-time tester. The details of the instruments were provided in chapter 2.

4.2 Experimental details

As discussed in chapter 3, the AlO_x film deposited at PD of 1.3 W.cm⁻² has shown high density of negative Q_f compared to low PD deposited film. Hence we have optimized different PDA conditions on the film deposited at high PD of 1.3 W.cm⁻². The other process parameters for film were set as: Ar flow = 15 sccm, O₂ flow = 55 sccm, and deposition time = 300 s. The film deposition was carried out at room temperature. For electrical characterization MOS capacitors were fabricated on 5 Ω.cm p-type (100) CZ c-Si wafer. The AlO_x films were deposited on RCA cleaned wafers as discussed in chapter 2, section 2.4.1. Subsequently the samples were subjected to PDA in a quartz furnace in three different ambients: (i) high purity N₂ gas, (ii) mixture of N₂ + O₂ gas (in 79:21 ratio to mimic dry air), and (iii) FGA with 8 % hydrogen in N₂, and three different temperatures set at: 420 °C, 470 °C and 520 °C. The annealing time of 20 min was used for all the experimental conditions. The MOS capacitors fabrication steps with AlO_x dielectric film were discussed in chapter 2, section 2.4.1.

For these AlO_x films surface passivation quality was assessed by minority carrier life-time measurements by Sinton Consulting WCT-120 life-time tester. Symmetrical structures were prepared with film deposited on both sides of RCA cleaned p-type FZ c-Si (100) wafers

with resistivity of 7.8 Ω .cm. The material characterization of these films were carried out using, JEOL make JEM 2100F cross-sectional TEM and elemental analysis of the film using Thermo Scientific make MultiLab 2000 XPS. The Sentech SE-800 SE was used for thickness and RI measurement. Keithley 4200 SCS was used for C-V and G-V measurements.

4.3 Electrical characterization

The high frequency C-V and G-V characteristics of the MOS capacitor with as-deposited film and film annealed in FGA are shown in Figure 4.1 (a) and (d), N_2 are shown in Figure 4.1 (b) and (e) and $N_2 + O_2$ ambient are shown in Figure 4.1 (c) and (f) at different temperatures namely 420 °C, 470 °C and 520 °C, respectively. The annealing time for all the PDA conditions are 20 min. The measurement frequency was $f = 100$ kHz.

The different parameters extracted from the high frequency C-V characteristic plot as discussed in chapter 2. The EOT of AlO_x film in the range of 12.7-13.6 nm were extracted using eq. (2.7), for all the PDA conditions which is in line with the process control of the deposition process. Figure 4.1 (a), (b) and (c) shows after annealing the C-V curve shifts to the right, i.e., positive shift in V_{FB} value. This indicates an increase in negative Q_f after PDA of AlO_x film.

From the G-V curve in Figure 4.1 (d), (e) and (f) shows the peak conductance is observed to reduce after annealing, indicating a decrease in value of D_{it} . This implies that the interface quality has improved after annealing in a way suitable for passivation of p-type c-Si surfaces.

The negative Q_f and D_{it} are extracted using C-V and G-V characteristics, respectively, are quantified using methods described in section 2.4 of chapter 2. The value of Q_f is extracted from ΔV_{MG} of C-V plot, using eq. (2.15) and the D_{it} is extracted from the G-V plot using eq. (2.20) [87].

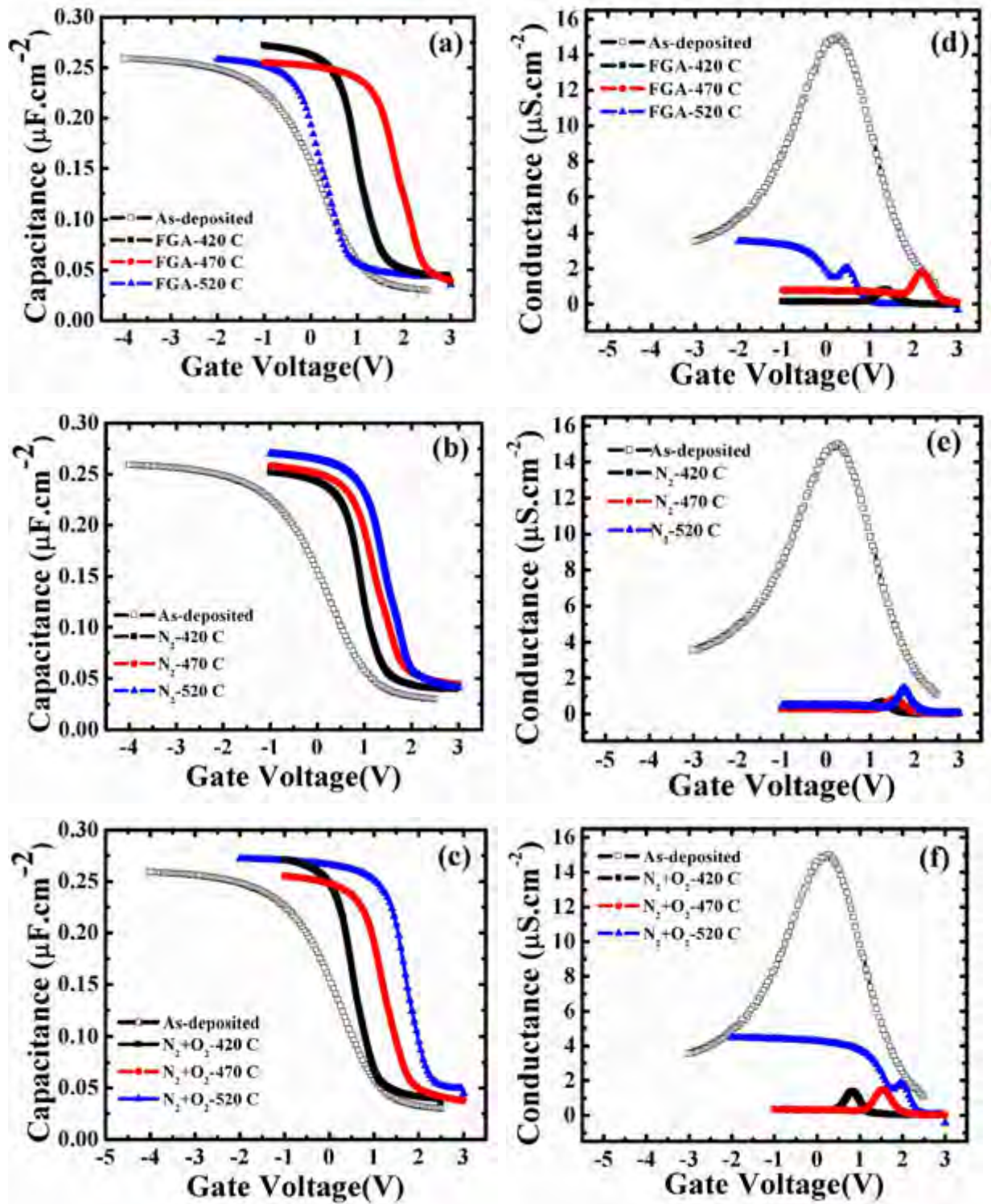


Figure 4.1 The C-V and G-V characteristics plot of MOS capacitors measured at $f = 100$ kHz for as-deposited AlO_x film and after annealing in FGA {(a), (d)}, N_2 {(b), (e)} and $\text{N}_2 + \text{O}_2$ {(c), (f)} ambient at 420 °C, 470 °C and 520 °C for 20 min.

Figures 4.2 (a) and (b) shows the extracted values of the negative Q_f and D_{it} for as-deposited and annealed AlO_x film at different conditions, respectively. The error-bar shows the spread of data over a sample for at least five devices from each experimental split. The centreline of the box shows the mean value while the upper and lower ends of the boxes are high and low values of the parameters. As shown in Figure 4.2 (a), the negative Q_f of $4 \times 10^{12} \text{ cm}^{-2}$ is obtained for as-deposited AlO_x film. While after annealing, the value of negative Q_f increases and saturates to $6 \times 10^{12} \text{ cm}^{-2}$ for PDA temperature of 470°C and above in N_2 and $N_2 + O_2$ ambient. The negative Q_f of these films are comparable to the value reported for PA-ALD Al_2O_3 film [34,58,116] and slightly higher than that reported for RF reactive sputtered AlO_x films [75].

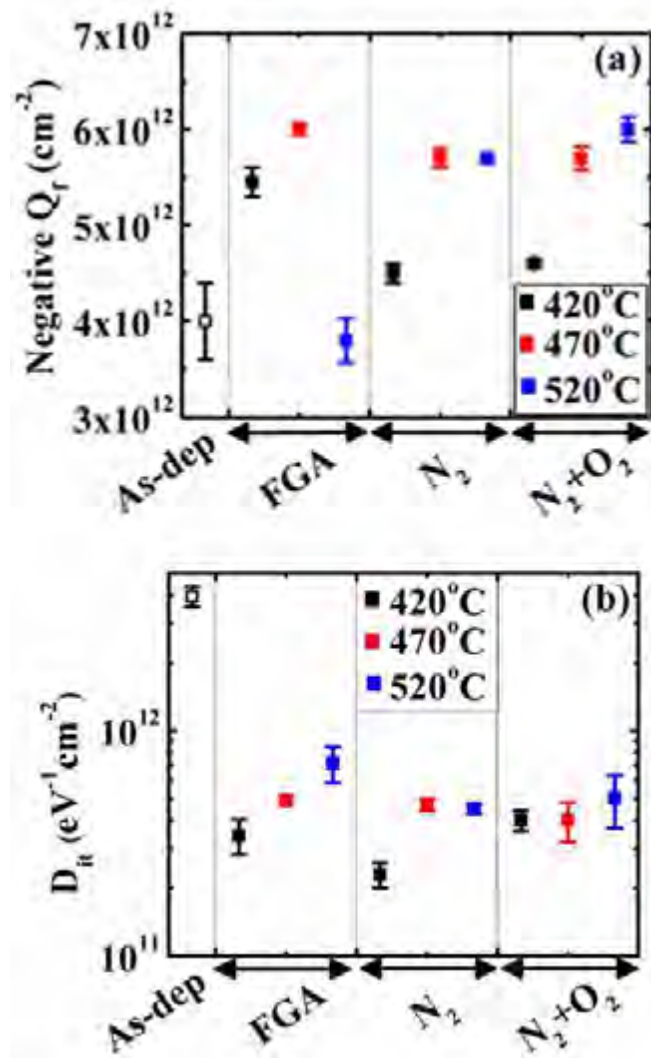


Figure 4.2 Extracted value of (a) negative Q_f and (b) D_{it} from MOS capacitors for as-deposited and annealed AlO_x film in different PDA conditions.

In report by Krugel et al. only marginal difference in the negative Q_f values were shown after annealing of RF reactive sputtered AlO_x films [79]. For FGA annealed film, the value of negative Q_f is observed to drop down significantly for higher temperature (520 °C) annealing, whereas at low temperatures the trend looks similar to that of other annealing ambients. In fact the value of negative Q_f for FGA film at 520 °C is slightly lower than that observed for as-deposited film. The trend of negative Q_f values after annealing in FGA is quantitatively similar to that reported by Benick et al. in PA-ALD Al_2O_3 films [116]. The report also showed that the value of negative Q_f obtained at 425°C annealing temperature is higher than that for higher temperature annealing at 550 °C, the ambient for annealing was air [116]. The presence of Al vacancies or O interstitials in the film causes negative Q_f in the film, according to Miyajima et al. [76]. Kimoto et al. [42], shows the Al atoms occupy T coordinated Al sites and hence results in negative Q_f in the film. These results along with the results by Benick et al. suggests that the structural modification may be responsible for the suppression or reduction of negative Q_f at high annealing temperatures (~ 500 °C) due to the presence of hydrogen in the film [116]. The source of hydrogen in the PA-ALD Al_2O_3 film is the hydrogen from precursor. However in our work, the PDA with FGA is the only source of hydrogen that could diffuse through the AlO_x film during annealing.

The values of D_{it} extracted from the G-V plot of AlO_x film annealed in different PDA conditions are shown in Figure 4.2 (b). The value of D_{it} is observed to decrease nearly by one order of magnitude after annealing, resulting in improved AlO_x/c -Si interface. The D_{it} values observed here were less than the values reported for RF reactive sputtered films used as surface passivation application [75]. For PDA in N_2 ambient, the lowest D_{it} of $2 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ is obtained at an annealing temperature of 420 °C, whereas for high temperature annealing a slight increase in the value of D_{it} to $4 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ is observed. Similar behaviour is observed for PDA in $N_2 + O_2$ ambient with the mean D_{it} value appearing to be independent of annealing temperature. The improvement in D_{it} after PDA in N_2 and $N_2 + O_2$ ambients, can be attributed to oxidation of interface by diffusion of oxygen from the AlO_x film or oxygen from PDA ambient during the annealing [75]. With FGA annealing the reduction in D_{it} values can be explained by the passivation of dangling bonds at the interface using atomic hydrogen. However, the high temperature (520 °C) annealing, cause degradation of the interface quality with increase in D_{it} value, which can be related to the effusion of hydrogen from the interface [116].

4.4 Surface passivation

The τ_{eff} was measured using WCT-120 lifetime tester and corresponding value of S_{eff} was calculated using eq. (2.29), in section 2.4.3 of chapter 2. The τ_{bulk} of 1.4 ms is measured on p-type FZ (100) wafer of resistivity 7.8 $\Omega\cdot\text{cm}$ (2 inch) by immersing the RCA cleaned wafer in iodine-methanol (IM) solution (i.e., 1.18 g of iodine in 50 mL of methanol) [95]. Other method includes application of PECVD SiN_x film as passivation layer, was proposed by Schmidt et al., to accurately determine the value of τ_{bulk} on mono-Si wafers with doping density of 10^{14} - 10^{17} cm^{-3} [118].

Kerr et al. proposed the generalized parameterization method to calculate the upper limit of τ_{bulk} for mono-Si with specific doping density [119]. Here the FZ wafers of resistivity 7.8 $\Omega\cdot\text{cm}$ (measured using 4-probe) with doping density of 1.75×10^{15} cm^{-3} , estimated from the resistivity versus doping concentration plot by Thurber et al. [120]. Hence in this work upper limit of $\tau_{\text{bulk}} = 30$ ms at excess minority carrier density, Δn of 4×10^{14} cm^{-3} was calculated using generalized parameterization method. Since the value of τ_{bulk} estimated using generalized parameterization method by Kerr et al. is different than the measured $\tau_{\text{bulk}} = 1.4$ ms for same specification of silicon substrate [119], hence we have also investigated the sensitivity of S_{eff} value to τ_{bulk} value for different τ_{eff} values, extracted using eq. (2.29). The results are shown in Figure 4.3.

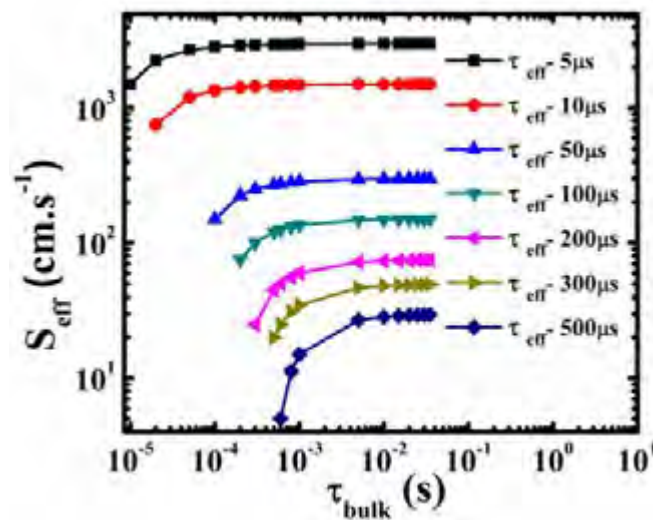


Figure 4.3 Study of relation between S_{eff} and τ_{bulk} for different values of τ_{eff} , extracted using eq. (2.29).

The result shows that the value of S_{eff} is most sensitive to the value of τ_{bulk} in lower range < 10 ms for $\tau_{\text{eff}} = 300 \mu\text{s}$ and above, whereas at higher range of $\tau_{\text{bulk}} > 30$ ms the value of S_{eff} seems to be nearly independent of τ_{bulk} .

The measured τ_{eff} on as-deposited and annealed AlO_x film in different PDA conditions using life-time tester are shown in Figure 4.4 (a) and the corresponding calculated value of S_{eff} using eq. (2.29) are shown in Figure 4.4 (b).

As shown in Figure 4.4 (a), as-deposited AlO_x the τ_{eff} of $0.1 \mu\text{s}$ at $\Delta n = 4 \times 10^{14} \text{ cm}^{-3}$ is measured, while significant improvement in value of τ_{eff} is observed on annealed films. The best value of $\tau_{\text{eff}} = 0.35$ ms is observed on $\text{N}_2 + \text{O}_2$ annealed film at 520°C for 20 min, at $\Delta n = 4 \times 10^{14} \text{ cm}^{-3}$. The film annealed in FGA ambient at 520°C , has shown very poor $\tau_{\text{eff}} < 0.1 \mu\text{s}$.

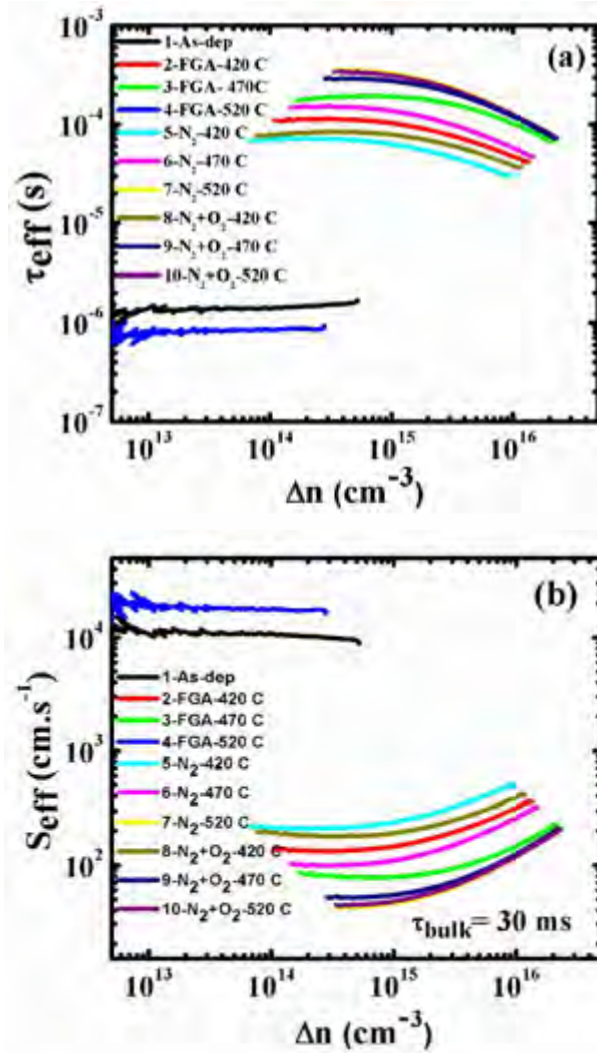


Figure 4.4 (a) The τ_{eff} measured and (b) corresponding calculated value of S_{eff} on as-deposited AlO_x film and after annealing in different PDA conditions.

Based on the hypothesis explained before, the value of S_{eff} calculated using eq. (2.29) with upper limit, $\tau_{\text{bulk}} = 30$ ms on p-type c-Si wafer with resistivity $7.8 \Omega\cdot\text{cm}$ [119], shown in Figure 4.4 (b). The result shows an improvement in the surface passivation after annealing, with the reduction of S_{eff} by 2 orders of magnitude compared to as-deposited film.

The comparison of S_{eff} values calculated for τ_{bulk} measured in IM solution using life-time tester and for upper limit of τ_{bulk} using generalized parameterization reported by Kerr et al., is given in Table 4.1 [95,119]. The AlO_x film is annealed in $\text{N}_2 + \text{O}_2$ ambient at 520°C for 20 min. The $\tau_{\text{eff}} = 0.35$ ms is measured on the symmetrical structure of AlO_x film passivated p-type c-Si using life-time tester.

Table 4.1 The value of S_{eff} for AlO_x film annealed in $\text{N}_2 + \text{O}_2$ ambient at 520°C , with τ_{bulk} measured in IM solution [95] and estimated using upper limit by generalized parameterization [119] at $\Delta n = 4 \times 10^{14} \text{ cm}^{-3}$.

Methods	τ_{bulk} (ms)	Measured* τ_{eff} (ms)	Calculated S_{eff} ($\text{cm} \cdot \text{s}^{-1}$)
Measured* on p-type FZ ($7.8 \Omega\cdot\text{cm}$) wafer by immersing in IM solution	1.4	0.35	32
Upper limit of τ_{bulk} using generalized parameterization by Kerr et al. [119]	30	0.35	42

*Measured using life-time tester

In Figure 4.5, the minimum value of S_{eff} at Δn of $4 \times 10^{14} \text{ cm}^{-3}$ calculated using the upper limit of $\tau_{\text{bulk}} = 30$ ms and measured τ_{eff} on as-deposited film and film annealed in different PDA conditions are shown.

As shown in Figure 4.5, the minimum S_{eff} of $42 \text{ cm}\cdot\text{s}^{-1}$, is observed on annealed AlO_x film in $\text{N}_2 + \text{O}_2$ or N_2 ambient at temperature 520°C for 20 min. For PDA in $\text{N}_2 + \text{O}_2$ ambient, the S_{eff} is observed to decrease with annealing temperature. The improvement in surface passivation can be further related to an increase in negative Q_f hence field-effect passivation, as shown in Figure 4.2 (a). Similar trend in minimum S_{eff} value to annealing temperature is observed for PDA in N_2 ambient as well.

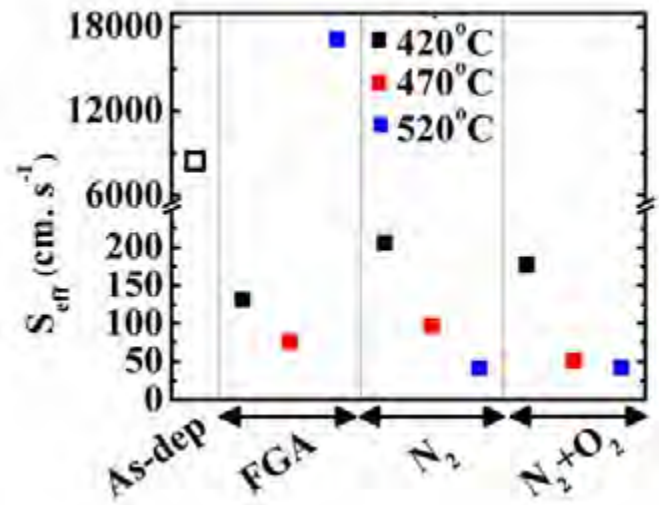


Figure 4.5 Minimum value of S_{eff} at Δn of $4 \times 10^{14} \text{ cm}^{-3}$ for as-deposited AlO_x film and after PDA of AlO_x film in different conditions.

However PDA in FGA ambient, shows improvement in S_{eff} value for annealing temperature upto 470°C and further at higher temperature (i.e., 520°C), a significant degradation is observed. As discussed in section 4.3, this sample shows the lowest negative Q_f of $4 \times 10^{12} \text{ cm}^{-2}$ and the highest D_{it} of $3.8 \times 10^{12} \text{ eV}^{-1}\text{cm}^{-2}$ at high temperature annealing among the PDA samples. The poor surface passivation can be attributed to the effusion of hydrogen from film at such high temperature and hence increase of dangling bonds [46,61,121]. In subsequent section the material characterization and interfacial property will be discussed to infer the reason for differences in passivation quality for different PDA conditions.

4.5 Material characterization

4.5.1 Cross-sectional imaging by TEM

Cross-sectional TEM images of these films were obtained to gain better insight into $\text{AlO}_x/\text{c-Si}$ interface. Figure 4.6 (a) and (b) shows the cross-sectional TEM images of as-deposited AlO_x film and annealed AlO_x film in $\text{N}_2 + \text{O}_2$ ambient at 520°C for 20 min.

Figure 4.6 (a), shows thick interfacial layer (IL) at $\text{AlO}_x/\text{c-Si}$ interface with thickness of 8.2 nm, and the AlO_x layer on IL with thickness of 21.4 nm is observed on as-deposited film. After annealing the film, thickness of IL = 8.4 nm and the AlO_x layer on IL with

thickness of 19.9 nm are observed, in Figure 4.6 (b). Thus no significant effect of PDA is observed on the thickness of the IL and AlO_x layer. For ALD deposited Al_2O_3 film very thin (1-2 nm) IL was reported at the $\text{AlO}_x/\text{c-Si}$ interface after PDA [34]. Y. Jin et al. reported thick IL of 4 nm for electron cyclotron resonance (ECR) sputter deposited Al_2O_3 film, which is significantly thicker than ALD or PECVD Al_2O_3 film [34,121]. The thickness of IL observed in our experiment is significantly higher than those reported elsewhere.

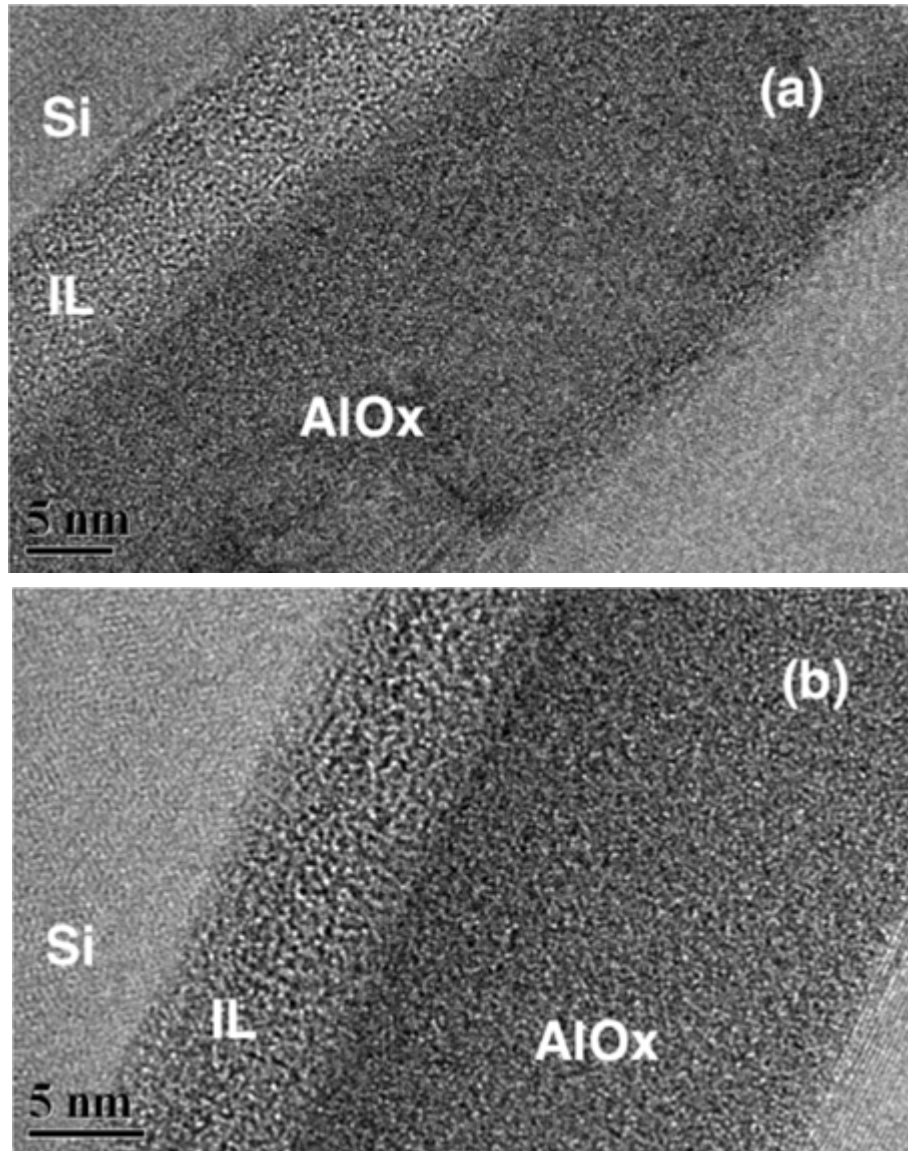


Figure 4.6 Cross-sectional TEM image of (a) as-deposited AlO_x film deposited on c-Si and (b) AlO_x film annealed in $\text{N}_2 + \text{O}_2$ gas at 520 °C for 20 min.

The presence of IL was suggested as the key to improvement in passivation quality by AlO_x film on the Si surface [34,122,123]. Dingemans et al. demonstrated the effect of

different thickness of interfacial SiO₂ layer intentionally deposited on c-Si and subsequently capped with ALD Al₂O₃ film, on the quality of surface passivation by ALD Al₂O₃ film [124]. The report shows the surface field was decreasing with an increase in SiO₂ layer thickness, as the positive Q_f in SiO₂ may screen a part of the negative Q_f at the SiO₂/Al₂O₃ interface [124].

4.5.2 Elemental analysis by XPS

The elemental depth-resolved profile using XPS measurement for AlO_x film annealed in N₂ + O₂ ambient at 520 °C for 20 min, is shown in Figure 4.7. Using elemental depth-resolved profile, the elemental profile and composition in IL and AlO_x layer can be obtained in terms of atomic concentration (%). As discussed in previous section, the IL = 8.4 nm was found on N₂ + O₂ annealed film, hence using the XPS depth-profile technique the composition of thick IL in AlO_x/c-Si interface will be analysed.

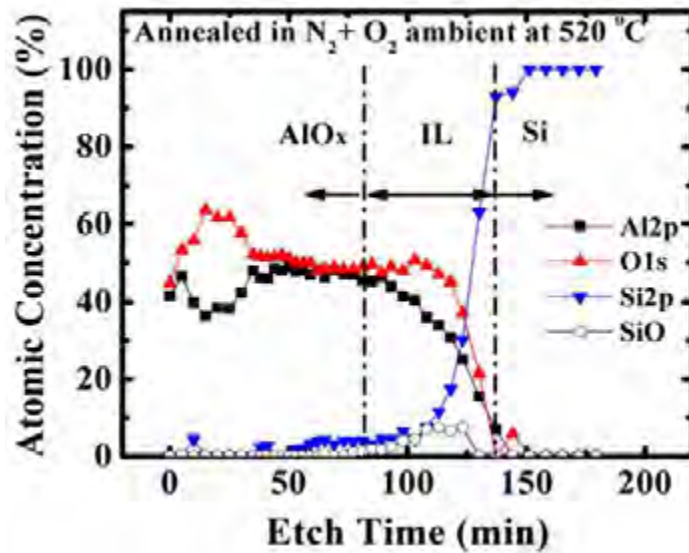


Figure 4.7 Atomic concentration of Al 2p, O 1s and Si 2p elemental depth-profiles of AlO_x film deposited on c-Si for annealing in N₂ + O₂ ambient at 520 °C for 20 min.

As shown in Figure 4.7, the atomic concentration (%) determined from Al 2p, O 1s and Si 2p emissions obtained using depth-resolved XPS measurement are plotted as a function of etch time. The film shows O concentration of approximately 60 atomic % and Al concentration of approximately 40 atomic %, near the top surface in the AlO_x layer, which indicates stoichiometry Al₂O₃ film with O/Al ratio of 1.5 after PDA. While in the bulk of AlO_x layer, the atomic concentrations of O and Al are almost equal and O/Al ratio became approximately 1. As we go deeper, a gradual decrease in Al concentration and increase in Si concentration are observed along with a constant O concentration. The oxidized state of Si

(SiO) is observed in this region. This transition region can be identified as the IL. Hence it can be concluded that the composition in IL is in the form of aluminum silicate.

Close to the c-Si/IL interface the aluminum silicate became Si rich and close to the IL/ AlO_x layer interface it became Al rich. The stoichiometric Al_2O_3 film close to the surface is due to re-oxidation of the surface during PDA in $\text{N}_2 + \text{O}_2$ ambient at 520 °C. Kimoto et al. analysed the composition of ALD deposited AlO_x film by using EELS and showed that the composition of IL is aluminum silicate (AlSiO_x) at the interface [42]. In the RS technique, two processes occur simultaneously during the initial stage of deposition (i) the oxidation of the Si surface by oxygen radicals and ions from the plasma and (ii) deposition of aluminum oxide compound. The intermixing of deposited layers and the layer already present on the substrate during the sputtering process are because of high energy particles arriving at the substrate and hence may lead to formation of AlSiO_x layer [125]. As the deposition proceeds, the oxidation of silicon stops beyond a certain IL thickness as the oxidants would have to penetrate through already deposited layer.

4.6 Summary

In this chapter we have investigated the role and importance of PDA process in the surface passivation quality of pulsed-DC RS AlO_x film deposited on p-type c-Si. The best value of $S_{\text{eff}} = 42 \text{ cm. s}^{-1}$ is obtained for the film annealed in N_2 or $\text{N}_2 + \text{O}_2$ ambient at high temperature of 520 °C for 20 min. The reasons for improved surface passivation is also assessed through electrical characterization of these films, which has shown an increase in negative Q_f to about $6 \times 10^{12} \text{ cm}^{-2}$ and decrease in D_{it} to about $4 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ after PDA. From the results we have also observed a degradation in surface passivation quality after high temperature annealing in FGA at 520 °C. The D_{it} remained similar to that of the as-deposited film. For the same condition, a significant decrease in Q_f is observed. That means that the passivation of low doped p-Si surface by pulsed-DC RS AlO_x film is dominantly field-effect passivation mechanism. The TEM and depth-resolved XPS analysis reveals the presence of thick IL with the composition of AlSiO_x for pulsed-DC RS AlO_x film deposited on c-Si. In the next chapter the origin and distribution of the Q_f in the AlO_x film will be explored using EELS and other measurement techniques. The reason for difference in passivation quality by AlO_x film after high temperature annealing in $\text{N}_2 + \text{O}_2$ and FGA ambients will be investigated using XPS analysis.

Chapter 5. Origin and Distribution of Charges in AlO_x Film Deposited on c-Si by Pulsed-DC Reactive Sputtering

5.1 Introduction

As discussed in the previous chapters, one of the mechanisms for surface passivation of p-type c-Si by pulsed-DC RS AlO_x film is field-effect passivation by repulsion of electrons from the surface using negative Q_f present in the film [35,45]. Further improvement in surface passivation is possible due to chemical passivation mechanism with reduction in D_{it} values after PDA [35,45]. The level of surface passivation is evaluated by estimating S_{eff} from the measured τ_{eff} on passivated wafers. Kimoto et al. studied the ALD Al₂O₃ film deposited on c-Si (001), using EELS to determine elemental coordination and interfacial property of the film [42]. The study, shows presence of both *T* and *O* coordinated Al in the γ -Al₂O₃ film. The bonding structure of the *T* (i.e., AlO₄) and *O* (AlO₆) coordinated Al, are shown in Figure 5.1 (a) and (b), respectively [126].

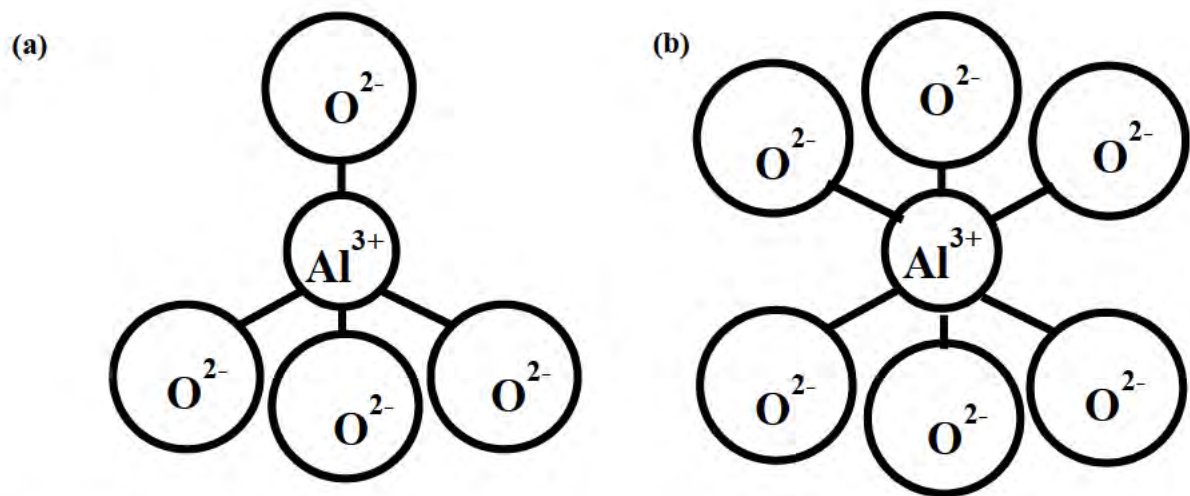


Figure 5.1 (a) Tetrahedral (*T*) structure of Al^{3+} coordinated with four O^{2-} ions and (b) octahedral (*O*) structure of Al^{3+} coordinated with six O^{2-} ions [126].

M. Mbila identified two basic soil clay mineral structures, known as silicon tetrahedron (SiO_4) and Al octahedron (AlO_6) [126]. The SiO_4 also known as orthosilicate anion, consists of all four oxygen ions shared equally with silicon ion while leaving behind excess negative charges. These negative charges will get neutralized after bonding of these oxygen ions with other silicon ions in the structure. During the soil weathering process, the Al^{3+} ion substitutes for Si^{4+} in the basic structure as shown in Figure 5.1 (a), which is also called isomorphous substitution. The *T* structure of soil which use to carry the effective positive charge, turns into net negative charged *T* coordinated structure after isomorphous substitution process of replacing Si^{4+} with Al^{3+} [126]. The study by S.W. Bailey, also reported an apical oxygen results in net negative charge for the *T* structure after Al^{3+} substitutes for Si^{4+} [127]. Figure 5.1 (b) shows, the *O* structure of AlO_6 , with each aluminum ion sharing positive 0.5 charge with bonded oxygen ions and each oxygen ions has remaining negative 1.5 charge to be neutralized by bonding with other Al ions [126].

Kimoto et al. showed EELS study for ALD deposited Al_2O_3 , where 5 nm thick Al_2O_3 film were deposited at 300 °C using TMA precursor and H_2O reactant on Si (001) wafer [42]. The film was annealed using RTA process at 750 °C in Ar + O_2 mixture (1 %). The EELS spectra shows the peak intensity of *T* coordinated Al at 78.2 eV was higher near the $\text{Al}_2\text{O}_3/\text{c-Si}$ interface, and decreases gradually towards the surface of Al_2O_3 layer [42]. The *O* coordinated Al peak at 79.7 eV was high towards the surface of Al_2O_3 layer. It was also reported that, near the interface Si $\text{L}_{2,3}$

peak was chemically shifted by 5 eV towards high energy. This peak was related to the silicate present in the form of SiO_4 (T) or amorphous SiO_2 . The intensity of peak at 105 eV, was decreasing towards the surface of Al_2O_3 layer. Hence the presence of Si in the form of silicate (SiO_4) at the interface, results in formation of aluminium silicate at the interfacial layer [42]. Similarly Hoex et al. studied the origin of negative Q_f in 30 nm thick Al_2O_3 film deposited using thermal ALD and PA-ALD at 200 °C on n-type c-Si (100) wafer. The film was annealed in N_2 ambient at 400 °C for 30 min to activate the surface passivation [128]. The result also confirmed the presence of peaks related to T and O coordinated Al in both thermal ALD and PA-ALD Al_2O_3 films. After annealing the T coordinated Al peak becomes quite significant near the interface, for both deposition methods, which supports the finding of increase in number of negative Q_f after PDA. The result also indicates the formation of about 0.8 nm thick interfacial SiO_2 for thermal ALD, while for PA-ALD the interfacial oxide layer thickness was about 2 nm [128]. Both the reports suggest that study of $\text{AlO}_x/\text{c-Si}$ interface is very important in analysing the origin and distribution of Q_f .

As discussed in chapter 4, the IL at $\text{AlO}_x/\text{c-Si}$ interface by pulsed-DC RS technique is thicker (8.4 nm) than ALD and PECVD Al_2O_3 interface. The IL was identified as AlSiO_x using XPS measurements. The good quality surface passivation with S_{eff} of 42 $\text{cm}\cdot\text{s}^{-1}$ was observed for film annealed in $\text{N}_2 + \text{O}_2$ ambient at 520 °C for 20 min, whereas in same condition with FGA ambient leads to degradation in the surface passivation quality. Dingemans et al., correlated degradation of surface passivation in FGA annealing at high temperature to the effusion of hydrogen from the PA-ALD Al_2O_3 film [72]. In this case, the film is not expected to contain hydrogen, as high purity Al target was sputtered using Ar and O_2 as sputtering and reactive gas in vacuum system [74].

In this chapter, we will explore the origin and distribution of Q_f in the pulsed-DC RS AlO_x film using spatially resolved EELS. We further study the interface quality in more detail by analysing the XPS data for different intermediate oxide states of Si 2p in different samples under study. The FTIR spectroscopy measurement of film will be discussed to analyse the type of chemical bonding between elements present in the film. The study of film property using EELS and UV-Vis-NIR spectroscopy will be presented to determine the E_{BG} of the film.

5.2 Experimental details

The pulsed-DC RS AlO_x films were deposited on RCA cleaned 5 Ω.cm p-type (100) CZ c-Si wafer, as discussed in chapter 2, section 2.4.1. The optimized process parameter as discussed in chapter 3, was used for AlO_x film deposition at room temperature, using PD of 1.3 W.cm⁻² and Ar flow rate of 15 sccm and O₂ flow rate of 55 sccm, with deposition time of 300 s. Subsequently two samples were annealed in N₂ + O₂ (79:21) ambient, and FGA ambient with 8 % hydrogen at 520 °C for 20 min.

High resolution EELS spectrum for these samples were collected using FEI TITAN 80-300 kV TEM operating at an extraction voltage of 300 kV. A gun monochromator was used to obtain a resolution as good as 180 meV in energy loss for a dispersion of 0.01 eV/channel. The Al L_{2,3} (onset ~ 73 eV) and Si L_{2,3} (onset ~ 99 eV) energy loss near edge spectra (ELNES) were measured using a dispersion of 0.03 eV/channel. The plural scattering background was removed by using power law method. The measurement was done at 12 different spots in the samples starting from the c-Si substrate, IL and AlO_x region in the sample. The EELS spectra were collected in the low-loss region to study the E_{BG} of the film. A dispersion of 0.01 eV/ channel was used for low-loss EELS acquisition. The zero-loss peak was removed by subtracting the reflected tail of the negative part of the zero-loss intensity. The single scattering distribution was then extracted by Fourier-log deconvolution method.

The distribution of intermediate oxidation states of Si in the IL for different annealing samples were studied using depth-resolved XPS measurement. The ULVAC-PHI make XPS measurements system with model PHI 5000 Versa Probe-II was used in this work. The XPSPEAK 4.1 software was used for curve fitting and Shirley background correction was applied before the analysis of the XPS spectrum [129].

The optical absorption coefficient (α) was calculated using Kramers-Kronig analysis [130]. The Perkin Elmer make Lambda 950 model UV-Vis-NIR spectroscope with an integrating sphere was used in transmission mode, to measure the E_{BG} of AlO_x film deposited on quartz wafer [131,132]. Perkin Elmer make (Spectrum BX II) FTIR spectroscope was used to analyze chemical

properties in terms of chemical bonding and coordination by measuring the absorbance spectra in the wide wavelength range in normal transmission mode.

5.3 EELS measurements

The cross-sectional TEM image with different sampling spots for EELS measurements with corresponding EELS intensity spectra at each sampling spot of pulsed-DC RS AlO_x film are shown in Figure 5.2 (a,b,c) and Figure 5.2 (d,e,f), respectively. The TEM image and EELS spectra of as-deposited AlO_x film is shown in Figure 5.2 (a) and (d), respectively. The TEM image and EELS spectra of annealed AlO_x film in $\text{N}_2 + \text{O}_2$ ambient is shown in Figure 5.2 (b) and (e), respectively and similarly for FGA annealed AlO_x film is shown in Figure 5.2 (c) and (f), respectively.

For as-deposited film the *T* and *O* peaks of Al $L_{2,3}$ signal spectra are positioned at 70 and 74 eV respectively, in the AlO_x region as shown in Figure 5.2 (d) [133]. While the *T* and *O* peaks of Al $L_{2,3}$ signal spectra are shifted to higher energy values and positioned at 73.3 and 76.3 eV, in the IL region, respectively as shown in Figure 5.2 (d), which can be attributed to an increase in oxidation state [134]. As noticed the *T* and *O* peaks are seen separately in this sample. The Si $L_{2,3}$ signal is present at 99.4 eV which also extends till about 2 nm in the IL region [44,128,134,135]. Whereas no strong signal corresponding to SiO_2 , is seen on as-deposited AlO_x film spectra, since the film was deposited at room temperature and film obtained is a sub-stoichiometric oxide of Al [136]. The XPS analysis will be presented later in this chapter to support this observation.

The EELS spectra for annealed film in $\text{N}_2 + \text{O}_2$ is shown in Figure 5.2 (e). For annealed films the *T* and *O* signal peaks are inseparable in the bulk of the AlO_x region, and the *T* coordinated Al $L_{2,3}$ peak is positioned at 70 eV. Whereas in the IL region, the *T* and *O* peaks are seen separately with shift in energy to high value at 75 eV and 76.9 eV, respectively [44,128,134,135]. A peak at 106.2 eV corresponds to the oxidation state of Si is present throughout the IL region and the Si $L_{2,3}$ signal peak at 99.2 eV is present in c-Si region [44,128]. The formation of SiO_2 at IL region is due to the diffusion of excess O from annealing ambient through the AlO_x region at high temperature exposure [134,135].

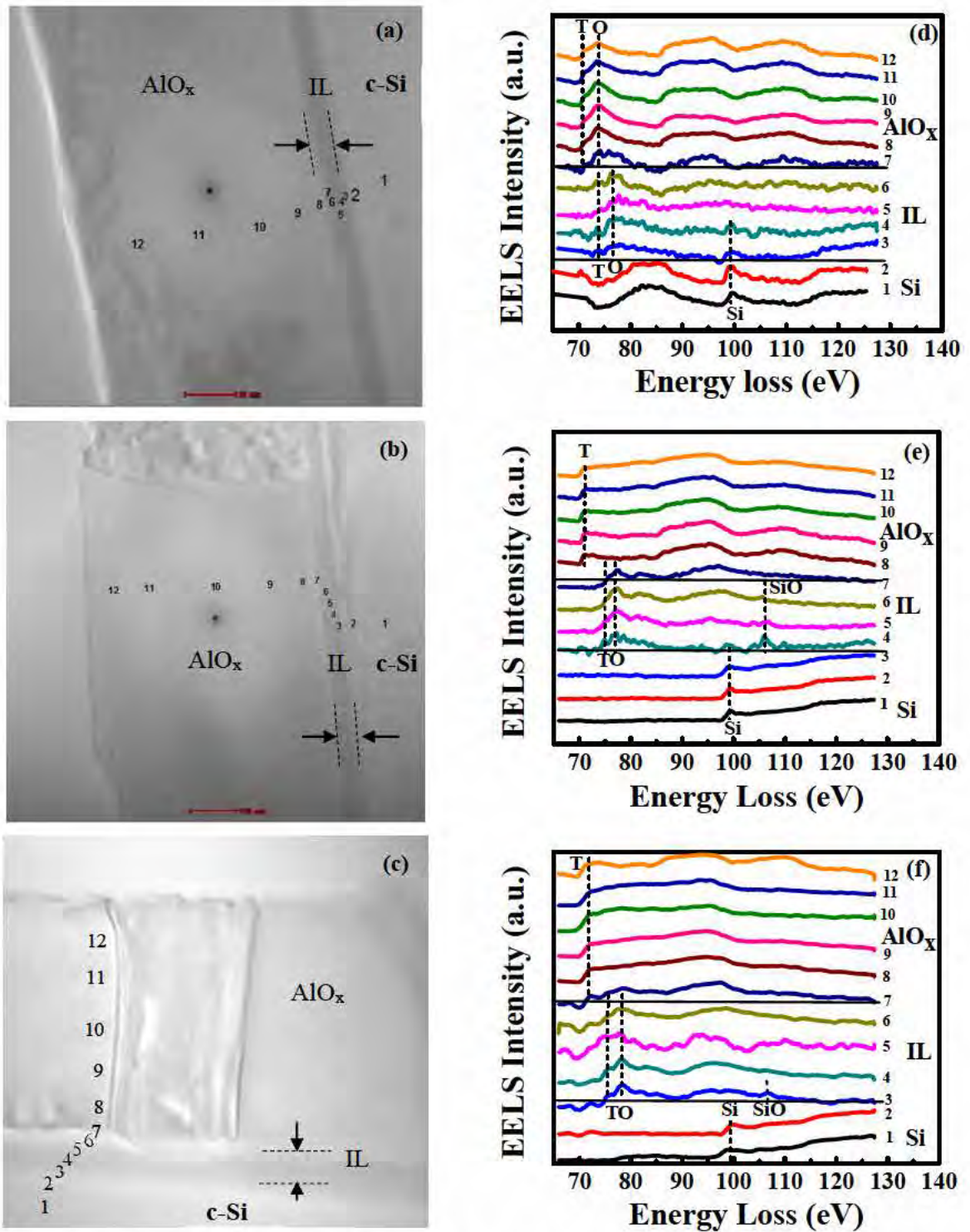


Figure 5.2 (a,b,c) Cross-sectional TEM image of AlO_x films with different scanning spots and (d,e,f) corresponding EELS spectrum. (a,d) as-deposited film, (b,e) film annealed in N₂ + O₂ ambient, and (c,f) in FGA ambient at 520 °C.

The EELS spectra for FGA annealed film is shown in Figure 5.2 (f). As also discussed above, the T and O signal peaks are inseparable in the bulk of the AlO_x region for this annealing condition as well. The T coordinated Al $L_{2,3}$ peak is positioned at 71.6 eV in bulk of AlO_x region, while in the IL region, the separate T and O peaks are seen to be shifted to higher energy and positioned at 75.6 eV and 77.9 eV respectively [44,128,134,135]. A peak corresponding to SiO_2 at 106.2 eV is present at IL only for about 1 nm from the c-Si surface and Si $L_{2,3}$ signal is present in c-Si [44,128]. A very thin SiO_2 layer at c-Si/IL interface can be attributed to the diffusion of oxygen from AlO_x layer to the interface during high temperature annealing [134,135].

The T/O peak intensity ratios at different sampling points in the AlO_x and IL region of as-deposited film and in IL region of annealed film is plotted for three samples to assess the distribution of Q_f at the interface, as shown in Figure 5.3.

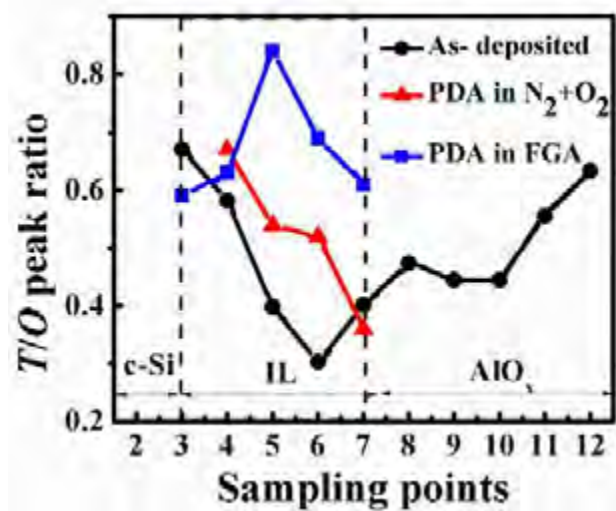


Figure 5.3 The T/O peak intensity ratios at different sampling points in the AlO_x and IL regions of the as-deposited film, and in IL region of the annealed AlO_x film.

It is observed that the value of T/O peak intensity ratio is increasing for annealed films in the IL region, the similar trend was also reported by Hoex et al. for PA-ALD Al_2O_3 film deposited on c-Si [44,128]. An increase in T/O peak intensity ratio signifies that the T coordinated Al is dominating at the IL region. For the FGA annealed sample, the T/O ratio is seen to peak in the middle of the IL region and then decreases towards the c-Si surface. For the $\text{N}_2 + \text{O}_2$ annealed sample, the T/O ratio is seen to be consistently increasing towards the c-Si surface. At the IL/ AlO_x

interface, the T/O ratio for the FGA annealed sample is seen to be marginally lower than both the as-deposited and $N_2 + O_2$ annealed sample. As proposed by Kimoto et al., the increase in T/O ratio is attributed to the increase in negative Q_f [42], these observations are consistent with the trends in the negative Q_f presented in Figure 4.2.

5.4 Exploration of intermediate oxidation states using XPS

The depth-profile of Al 2p, O 1s and Si 2p elements using XPS measurement of as-deposited AlO_x film and films annealed in $N_2 + O_2$ and FGA ambient at 520 °C are shown in Figure 5.4 (a), (b) and (c), respectively.

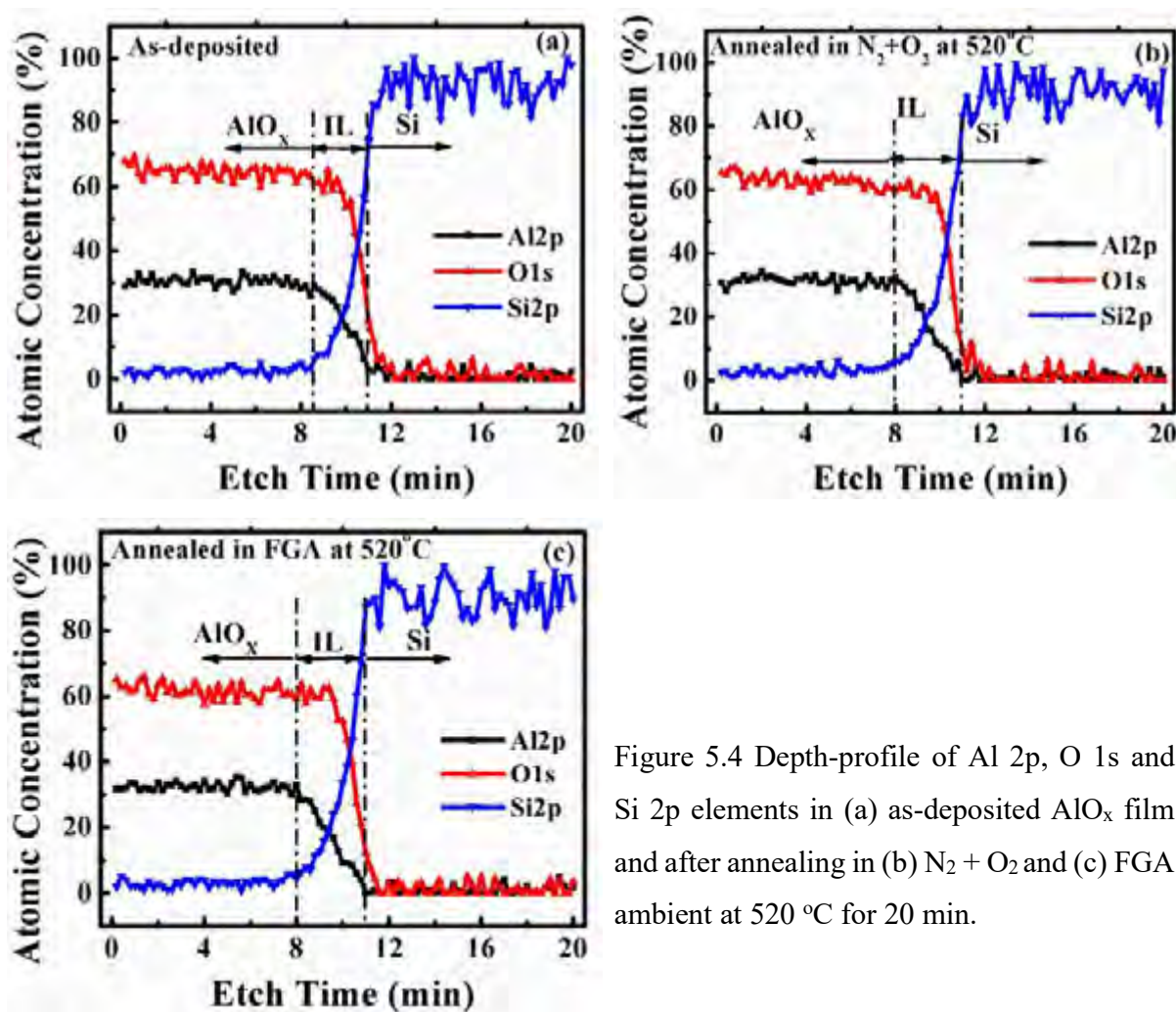
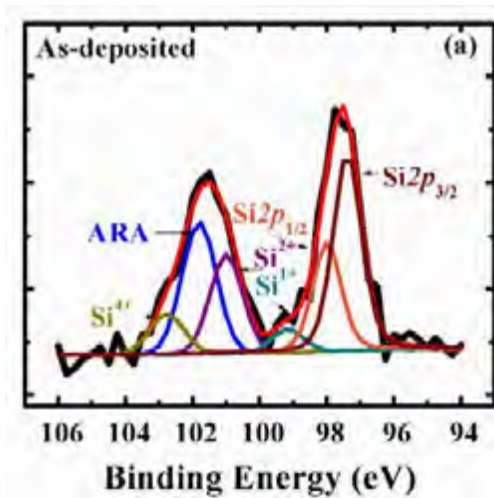


Figure 5.4 Depth-profile of Al 2p, O 1s and Si 2p elements in (a) as-deposited AlO_x film and after annealing in (b) $N_2 + O_2$ and (c) FGA ambient at 520 °C for 20 min.

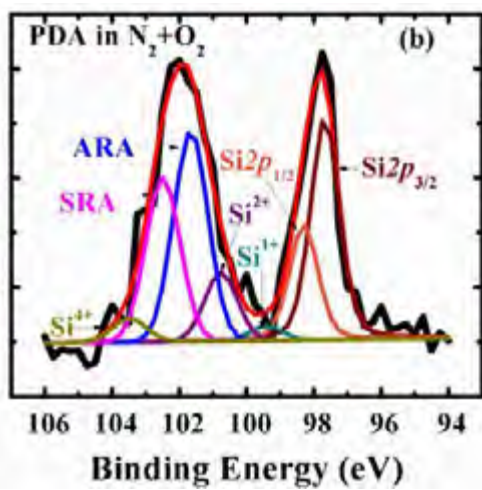
In the bulk of the AlO_x region near top surface, the concentration of O is between 60-70 atomic (%) and Al concentration is between 35-38 atomic (%), this indicates a sub-stoichiometric, oxygen rich film. In the IL region, a gradual decrease in Al and O concentration and increase in Si concentration are observed. As also discussed in chapter 4, the composition in the IL is in the form of aluminum silicate.

To gain better insight on the chemical composition w.r.t. distribution of intermediate oxidation states of Si $2p$ in the IL region of these films, XPS data were studied in more details. Different intermediate oxidation states are termed as Si^{n+} , where $n = 1, 2, 4$, i.e., Si^{1+} as Si_2O , Si^{2+} as SiO , and Si^{4+} as SiO_2 are used here to fit the Si $2p$ signal [137]. The XPS spectra of Si $2p$ fitted for different intermediate oxidation states in the IL region (at 46_Depth Level) of $\text{AlO}_x/\text{c-Si}$ for as-deposited film and film annealed in $\text{N}_2 + \text{O}_2$ and FGA ambients at 520 °C are shown in Figure 5.5 (a), (b) and (c), respectively. The Si $2p$ spectra was fitted using XPSPEAK 4.1 software, where the baseline correction was applied using Shirley integration method and the FWHM and GL was kept constant during the peak fitting [129]. As shown in Figure 5.5, the spectra of Si $2p$ for as-deposited and films annealed in $\text{N}_2 + \text{O}_2$ and FGA were fitted for 46_depth level at IL region of $\text{AlO}_x/\text{c-Si}$, while the other depth level spectra fitting are not shown here.

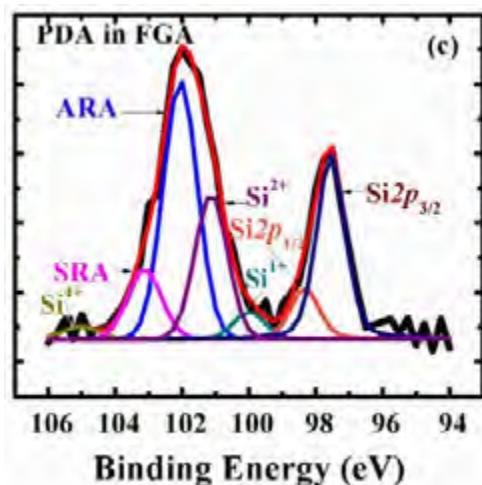
As shown in Figure 5.5, the Si $2p$ spectra for different samples are fitted with different peaks which are identified as Si^0 (bulk Si), Si^{1+} , Si^{2+} and Si^{4+} . While the peaks marked as aluminium-oxygen rich aluminosilicate (ARA) and silicon-oxygen rich aluminosilicate (SRA) are also identified in between the binding energy of 101.5 to 103 eV, as different forms of aluminosilicate [138]. It was also reported by Zhang et al. that the Si $2p$ peak at 102.66 eV may appear either due to SiO_x or Si-O-Al [139]. The peak position (eV) and corresponding peak area fitted by XPSPEAK 4.1 software is also given in Table next to Figure 5.5 (a), (b) and (c). The core level Si $2p$ spectrum, i.e., Si^0 (bulk Si) state can be further decomposed into two peaks Si $2p_{1/2}$ and Si $2p_{3/2}$ with the intensity ratio 1:2 and a spin-orbit splitting of 0.63 eV. The same FWHM of 1 eV with Gaussian-Lorentzian (GL) of 25 % for fitting these peaks [137,140,141]. The silicon intermediate oxide states are fitted using pure Gaussian peak with full width at half maximum (FWHM) of 1.1, 1.15 and 1.2 eV for Si^{1+} , Si^{2+} and Si^{4+} , respectively and GL of 0 %. The oxide peaks named as ARA and SRA in between Si^{2+} and Si^{4+} was fitted using FWHM of 1.2 eV and GL of 0 %.



Peak	Position (eV)	Area
Si 2p _{3/2}	97.357	1059.288
Si 2p _{1/2}	97.959	666.101
Si ¹⁺	99.128	135.494
Si ²⁺	100.942	521.225
ARA	101.762	835.331
Si ⁴⁺	102.745	254.974



Peak	Position (eV)	Area
Si 2p _{3/2}	97.67	1214.813
Si 2p _{1/2}	98.300	630.897
Si ¹⁺	99.420	79.487
Si ²⁺	100.760	382.564
ARA	101.660	1231.724
SRA	102.490	963.232
Si ⁴⁺	103.490	139.202



Peak	Position (eV)	Area
Si 2p _{3/2}	97.545	1574.969
Si 2p _{1/2}	98.324	438.768
Si ¹⁺	99.989	229.070
Si ²⁺	101.129	1280.476
ARA	102.050	2376.485
SRA	103.118	644.394
Si ⁴⁺	105.041	120.117

Figure 5.5 The Si 2p XPS spectra fitted for different intermediate oxidation states in the IL region of AlO_x/c-Si for as-deposited and annealed AlO_x films. The spectra is shown for only at one depth level (46_Depth Level) for clarity.

As shown in Figure 5.5, the core-level peak of Si 2*p* spectrum, i.e., Si⁰ (bulk Si), was decomposed into two peaks Si 2*p*_{1/2} and Si 2*p*_{3/2} present at different binding energy (eV). Such decomposition of Si⁰ at various depth level in the bulk of Si, IL and AlO_x region was performed for different samples. In Figure 5.6, the peak position of Si 2*p*_{3/2} was obtained through fitting at different #_Depth Level in AlO_x film, IL and c-Si region are shown for different samples.

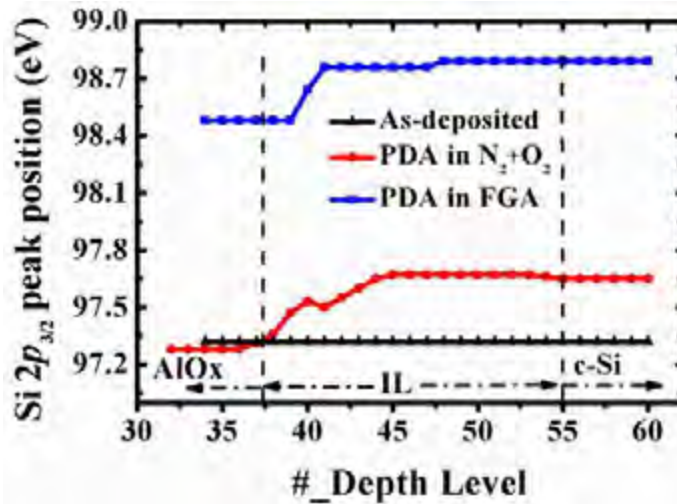


Figure 5.6 The Si 2*p*_{3/2} peak position of Si⁰ (bulk) for core level Si 2*p* at different #_Depth Level for as-deposited AlO_x film and after annealing in N₂ + O₂ and FGA ambients at 520 °C.

As shown in Figure 5.6, the peak position of Si 2*p*_{3/2} seems to be shifting to high energy value for annealed samples. The abrupt shift of entire Si 2*p*_{3/2} spectrum by 0.3 eV was observed for FGA annealed sample in the IL region, which may be related to the presence of atomic H from the annealing ambient [142]. The similar result was reported by Gunther et al., which shows a shift in core-level Si 2*p* by 0.3 eV towards higher energy as atomic H saturates dangling “Si-” bonds, from the atomic deuterium annealing of SiO₂ film (5 nm) grown on Si [142]. Another report by Himpsel et al., studied the effect of H₂ ambient annealing in 3 nm SiO₂ film grown on Si substrate, which shows the distribution of intermediate oxidation states remains un-affected by H₂ annealing [141]. As shown in Figure 5.6, for N₂ + O₂ annealed film, the shift of Si 2*p*_{3/2} spectrum is not as abrupt as FGA annealed film and while the overall shift is also low, the reason behind this difference is not very clear at this point. The observation on core-level shift to improvement in interface quality after annealing is consistent with the result of D_{it} reduction for annealed films as shown in Figure 4.2 in previous chapter.

Similarly, in the IL region of as-deposited and annealed AlO_x films, the position of intermediate oxidation states in-terms of shift in binding energy with respect to reference peak Si 2p_{3/2} at various #_Depth Level are shown in Figure 5.7 (a), (b) and (c), respectively.

Figure 5.7 shows, the binding energy peak shift are in the range of 2-6.5 eV for different intermediate oxidation states with respect to core-level Si 2p_{3/2} peak, for all the samples. This shift to higher energy was related to oxidation of Si [143]. As shown in Figure 5.7 (b) and (c), the distribution of oxide states are relatively smooth for annealed films as compared to as-deposited AlO_x film which is more scattered, in Figure 5.7 (a). The smooth distribution of oxide states can be attributed to saturation of dangling “Si-” bonds by hydrogen present in FGA ambient and oxygen present in N₂ + O₂ ambient after annealing in 520 °C, as also discussed earlier.

Figure 5.7, the distribution of Si⁴⁺ (i.e., SiO₂) state is present throughout IL for as-deposited and FGA annealed samples, whereas in N₂ + O₂ annealed film the Si⁴⁺ is seen only in smaller segment of the IL. This may partly explain the reason for less number of negative Q_f in as-deposited and FGA annealed film. Since the SiO₂ has positive Q_f which compensates the negative Q_f in AlO_x film and hence decreases the net negative Q_f in AlO_x film for as-deposited and FGA annealed samples [144].

The relative contribution of individual intermediate oxidation states present in the IL region of as-deposited and annealed AlO_x films, are given in Table 5.1. The data shows, contribution of Si⁰ (i.e., Si 2p_{3/2}) in as-deposited AlO_x film is relatively higher by ~ 2 % as compared to both the annealed films. This support the result of EELS spectra in Figure 5.2 (d), which shows the presence of Si L_{2,3} signal at 99.4 eV throughout the IL of as-deposited film. The Si¹⁺ (i.e., Si₂O) oxidation state contribution is observed to be slightly higher by 1-2 % in as-deposited and FGA annealed AlO_x film as compared N₂ + O₂ annealed film. The contribution of Si²⁺ (i.e., SiO) is about 4 % higher in as-deposited and N₂ + O₂ annealed film as compared to FGA annealed film. The contribution of Si⁴⁺ (i.e., SiO₂) is about two times higher in as-deposited and FGA annealed AlO_x film as compared to N₂ + O₂ annealed AlO_x film, as discussed earlier, the contribution of Si⁴⁺ leads to reduction of net negative Q_f. The sub-oxides states known as ARA and SRA, the contribution of ARA higher in N₂ + O₂ annealed film by ~ 5 % and the contribution of SRA is higher in FGA annealed film by ~ 15-20 % as compared to N₂ + O₂ annealed and as-deposited films.

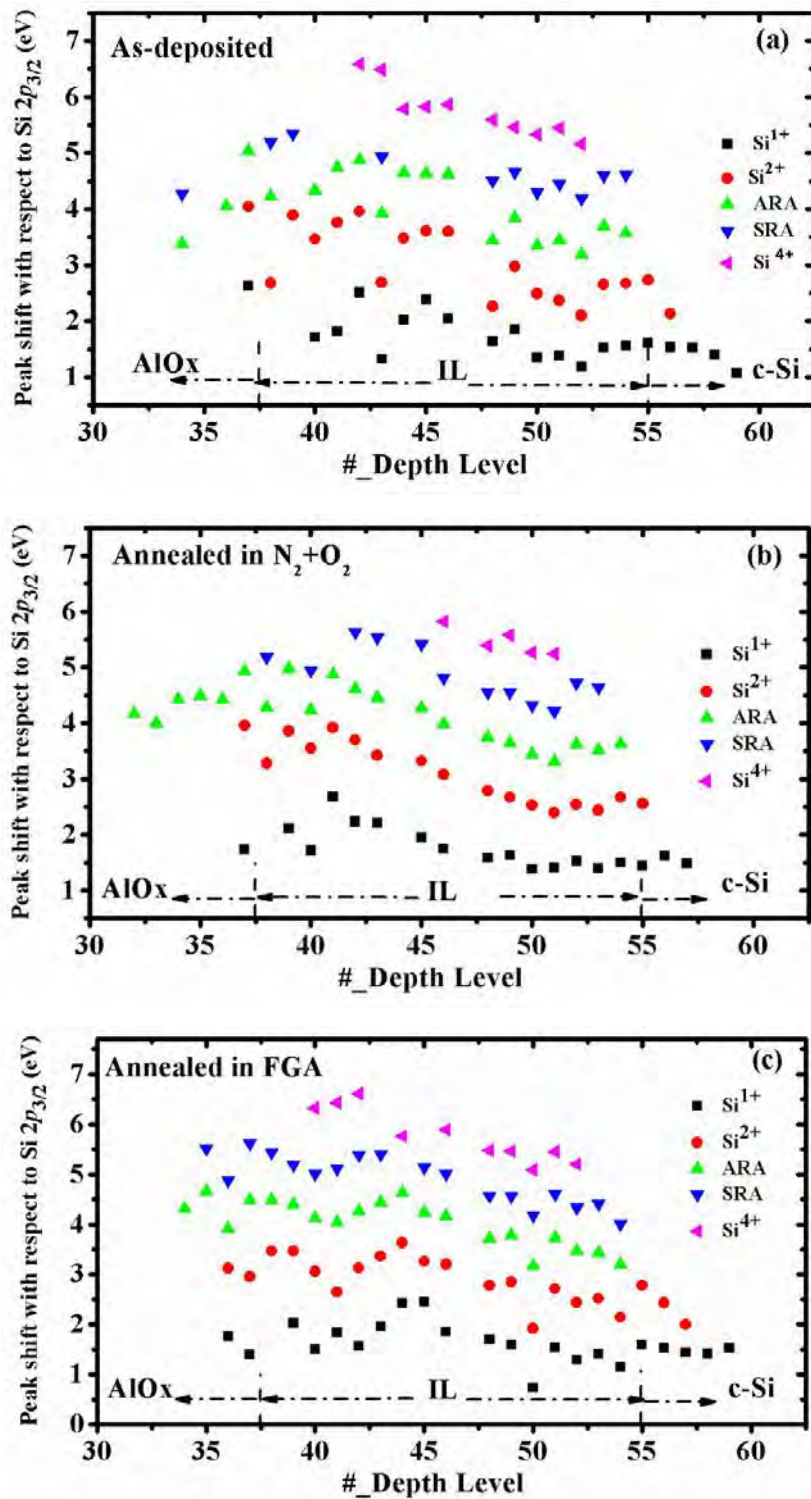


Figure 5.7 Different intermediate oxidation states in-terms of shift in binding energy (eV) with respect to Si 2p_{3/2} peak at #_Depth Level in IL of (a) as-deposited AlO_x film and AlO_x film (b) annealed in N₂ + O₂ ambient and (c) FGA ambient at 520 °C.

Table 5.1 The relative contribution of intermediate oxidation states for different samples.

Samples	Relative contribution of intermediate oxidation states for different samples (%)					
	Si ⁰	Si ¹⁺	Si ²⁺	ARA	SRA	Si ⁴⁺
As-deposited	34.95	33.02	34.57	24.8	30.03	40.16
PDA in N ₂ + O ₂	32.63	32.7	34.72	39.7	25.54	20.47
PDA in FGA	32.42	34.29	30.71	35.5	44.43	39.37

Figure 5.8 (a) and (b), shows the relative contribution and distribution of ARA and SRA sub-oxide states in different samples at #_Depth Level in the IL region, respectively. For N₂ + O₂ annealed AlO_x film, ARA is enhanced and the SRA states is suppressed at IL near AlO_x region. The presence of aluminum silicate at the interface of AlO_x/c-Si was also discussed in chapter 4.

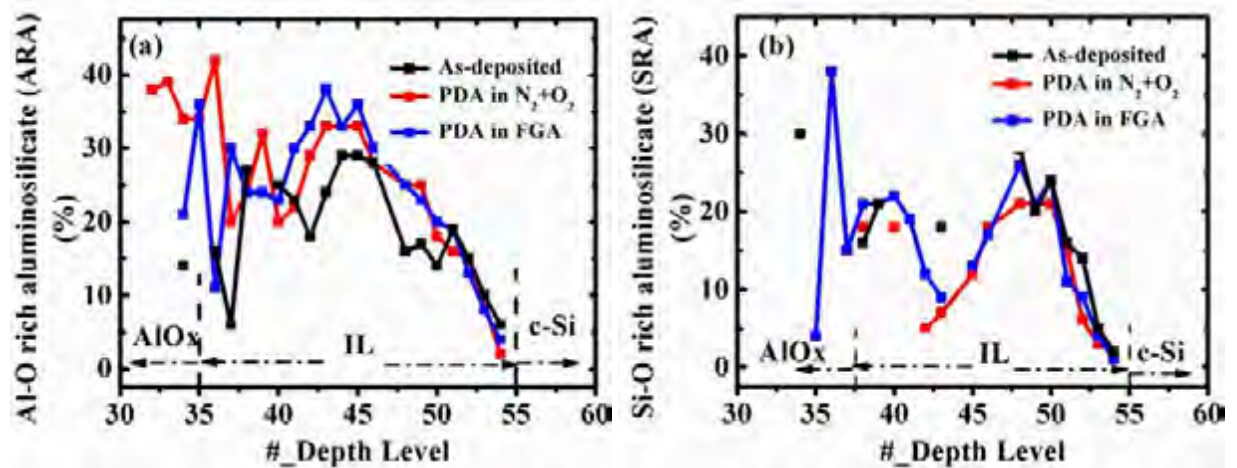


Figure 5.8 The presence (%) and distribution of (a) Al-O rich aluminosilicate (ARA) and (b) Si-O rich aluminosilicate (SRA) sub-oxide states in different samples at #_Depth Level in the IL region.

5.5 FTIR investigation of the films

The absorbance spectra are obtained using FTIR spectroscope in the normal transmission mode at the 4000-450 cm^{-1} wave number range for different samples, as shown in Figure 5.9.

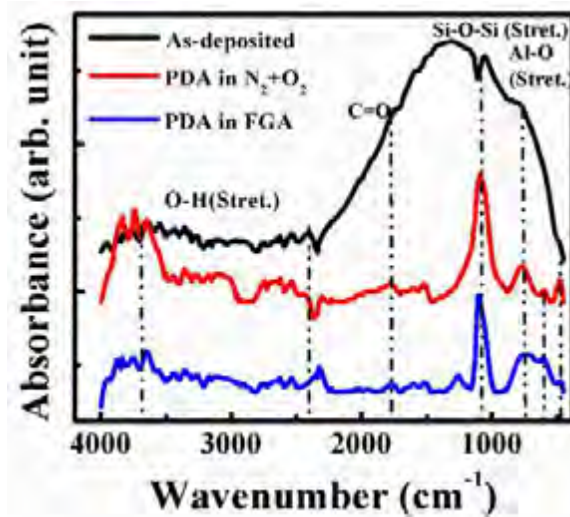


Figure 5.9 Absorbance spectra for as-deposited and annealed AlO_x film in $\text{N}_2 + \text{O}_2$ and FGA ambient at 520 $^\circ\text{C}$, using FTIR measurement. “Stret.” stands for stretching mode.

The background spectra was subtracted using same un-deposited c-Si wafer prior to measurement, so that the absorbance spectra shows vibration peaks related to deposited film only. The peak position and corresponding peak assignment for as-deposited and annealed samples are given in Table 5.2.

The broad peak at 480 cm^{-1} corresponds to Al-O stretching are present in all three samples, with asymmetrical structure for as-deposited and FGA annealed AlO_x film, while it is symmetrical and sharp for $\text{N}_2 + \text{O}_2$ annealed AlO_x film [145]. The broadness in the spectra is related to motion of both Al and O elements, whereas the sharpness of spectra is related to O motion only [146-150]. An asymmetrical peak at 600 cm^{-1} corresponding to Si is also present in all samples [135]. The feature peak positioned at 630 cm^{-1} are present in both the annealed samples, which are related to O-Al-O bending mode [135,146,151]. The peak at 750 cm^{-1} corresponds to Al-O stretching mode of condensed AlO_4 tetrahedra, present in $\text{N}_2 + \text{O}_2$ annealed AlO_x film and the asymmetrical and broader peak for as-deposited and FGA annealed films is seen [147,148].

Table 5.2 The peak position and respective chemical bonds associated with it, for as-deposited and annealed AlO_x film in N₂ + O₂ and FGA ambient at 520 °C.

Peak position (cm ⁻¹)	Chemical bond	Sample and peak type			References
		As-deposited	N ₂ + O ₂	FGA	
480	Al-O Stret. mode	Asym	Sym	Asym	145
630	O-Al-O bending mode	No	Sym	Asym	135,146,151
750	Al-O Stret. mode [‘condensed’ Tetrahedral AlO ₄]	Asym	Sym	Asym	135,144,147,148
1090	Si-O-Si	No	Sym	Sym	135,144
1062	Si-O-Si	Asym	No	No	135,144

*Stret. : stretching mode, Asym.: asymmetric peak, Sym.: symmetric, No: not present.

A sharp and symmetrical peak at 1090 cm⁻¹ corresponds to Si-O-Si stretching mode is observed for annealed films. The appearance of peak at 1090 cm⁻¹ (Si-O-Si stretching mode), shows that an interfacial oxide is found at the AlO_x/c-Si interface, as a result of diffusion of oxygen from AlO_x film or diffusion of excess oxygen present in PDA ambient which reacts with the c-Si surface [135]. For as-deposited AlO_x film, the broad asymmetric peak is positioned at 1060 cm⁻¹ can be attributed to the lack of formation of Si-O bond at the interface [134,135]. From the FTIR measurement the presence of interface in the form of silicate is confirmed and the peak positioned at 750 cm⁻¹ related to Al-O stretching mode of condensed AlO₄ tetrahedra for all the three samples are evident from this experiment.

5.6 Band-gap energy measurement using low-loss EELS spectra

The EELS can be used to assess the E_{BG} of the film in low-loss regime < 10 eV with a high spatial resolution, as shown in Figure 5.10 [131,132]. Since the EELS spectra consists of zero-loss peak at 0 eV, which seems more intense due to elastically scattered electrons through atomic nuclei interaction causing very small energy loss. The intense energy distribution at zero-loss peak was mainly due to electron source, hence need to be removed by subtracting the reflected tail of the

negative part of the zero-loss intensity [130]. The single scattering distribution was then extracted by Fourier-log deconvolution method [91]. This energy distribution at low energy are due to inelastic scattering by electrons from conduction and valance bands. The E_{BG} is calculated by the equation used for traditional semiconductors, as shown in eq. (5.1) [132],

$$\alpha = A(E - E_{BG})^n/E \quad (5.1)$$

where, α is optical absorption coefficient which was calculated using Kramers-Kronig analysis [130], A is a constant, $E = h\nu$ represents photon energy and $n = 1/2$ for allowed direct transition. The E_{BG} for different samples can be obtained from the x-axis intercept of the linear fit between $(\alpha.E)^2$ versus E plots, are shown in Figure 5.10 [132,152].

Figure 5.10 (a,b,c), shows the low-loss EELS spectra for E_{BG} measurement in AlO_x bulk region, whereas Figure 5.10 (d,e,f), shows low-loss EELS spectra for E_{BG} measurement in IL region of as-deposited AlO_x film and film annealed in $N_2 + O_2$ and in FGA at 520 °C, respectively. It was reported that the low-loss EELS measurement may underestimate the value of E_{BG} due to the Cerenkov radiation effect [153-155]. To negate the effect of Cerenkov radiation, Gu et al. reported E_{BG} values for film thicknesses $< 0.5 \lambda$, here λ is the mean free path of the electron in the material [131]. In these experiments the low-loss EELS spectra was acquired for thickness between 0.2λ to 0.4λ , hence the Cerenkov radiation effects will not be very significant. The same method and experimental conditions were also tested successfully in ZnO and $ZnO_{1-x}S_x$ alloys to obtain accurate E_{BG} values [156,157].

For the as-deposited AlO_x film the E_{BG} of 2.6 eV is measured at AlO_x region by low-loss EELS method, as shown in Figure 5.10 (a). After annealing of AlO_x film in $N_2 + O_2$ and FGA ambient, an increase in the E_{BG} value of AlO_x region to 4.4 eV is shown in Figure 5.10 (b,c). This value of E_{BG} measured is relatively lower than the reported E_{BG} of 8.7 eV for $\alpha-Al_2O_3$ [158]. However trends similar to those shown in Figure 5.10 were reported by Rose et al., which showed a low E_{BG} of 2.6 eV for ultra-thin amorphous Al_2O_3 film formed by Ar/ O_2 plasma exposure on Al film grown on CoAl (100) substrate and an increase in E_{BG} value to 4.5 eV for well-ordered Al_2O_3 film, after annealing at elevated temperature in the oxygen ambient [159,160]. This may suggest a structural modification of the AlO_x film after annealing at high temperature.

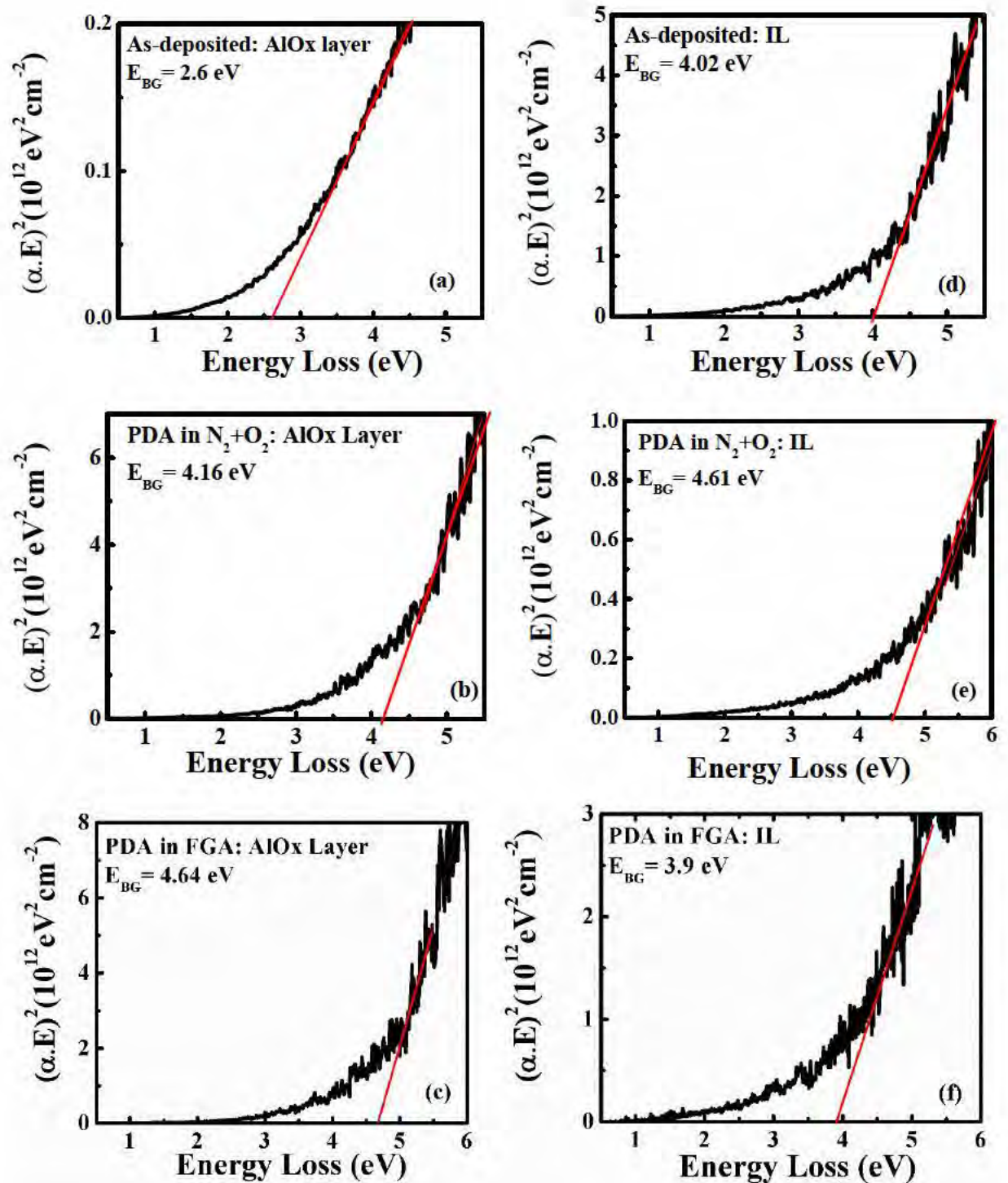


Figure 5.10 The E_{BG} measured using low-loss EELS spectra at the AlO_x layer (a,b,c) and IL region (d,e,f) for: (a,d) as-deposited film, (b,e) film annealed in N₂ + O₂ and (c,f) FGA ambient at 520 °C.

While the value of low E_{BG} for RS AlO_x film to 4.4 eV as compared to E_{BG} of 8.7 eV for $\alpha-Al_2O_3$ may be related to the defects induced in band-gap of the film [160]. As discussed in chapter 3, section 3.5, the film density of 2.88 g.cm^{-3} were obtained using XRR measurement technique after annealing, i.e., also low as compared to crystalline stoichiometric Al_2O_3 film density ($3.95\text{-}4.1\text{ g.cm}^{-3}$) [108]. Hence low film density may be related to the porosity of the film which results in low E_{BG} for this film [161].

The E_{BG} is also obtained for the IL using the low-loss EELS measurement technique with high spatial resolution, shown in Figure 5.10 (d,e,f). The E_{BG} of IL (i.e., 4.02 eV) is relatively higher as compared to the E_{BG} of AlO_x layer for as-deposited film. This can be explained by bonding between Al, O and Si that may results in band gap widening, as reported by Reiche et al. [162].

5.7 Band-gap energy measurement using UV-Vis-NIR spectroscope

The UV-Vis-NIR measurements were performed on AlO_x films deposited on quartz wafer in normal transmission mode. Figure 5.11 (a,b,c), shows the Tauc plot of $(\alpha E)^2$ versus E to acquire the E_{BG} value of the as-deposited and annealed AlO_x film in $N_2 + O_2$ and FGA ambients at $520\text{ }^\circ\text{C}$ [94]. It should be noted that the E_{BG} obtained using UV-Vis-NIR spectroscopy gives detail of complete dielectric film deposited on quartz wafer, unlike the EELS technique where the E_{BG} can be assessed in different regions of the dielectric film as discussed earlier. However since the film is deposited in quartz for UV-Vis-NIR analysis, the IL layer in this case would be different from that in the sample analysed using EELS. So we would compare only the E_{BG} of the AlO_x obtained by the two techniques. From Figure 5.11, the E_{BG} for different samples can be obtained from the x-axis intercept of the linear fit between $(\alpha.E)^2$ versus E plots.

As shown in Figure 5.11 (a), for the as-deposited AlO_x film, an E_{BG} of 3.5 eV is obtained. Similar to the result of EELS, the UV-Vis-NIR measurement also shows an increase in the E_{BG} value to 4.3-4.4 eV after annealing of AlO_x film in $N_2 + O_2$ and FGA ambients, as shown in Figure 5.11 (b) and (c), respectively. The discussion on structural modification of the AlO_x film after annealing at high temperature, stand here as well.

The E_{BG} values obtained using the techniques mentioned for as-deposited film and the film annealed in $N_2 + O_2$ and FGA ambients are given in Table 5.3, for comparison. The as-deposited film shows low E_{BG} of 2.5 eV as compared to annealed film, which also suggest the modification of the film after annealing and so as the improvement in the film quality. With the low-loss EELS spectra the E_{BG} between 4-4.5 eV is obtained for individual regions, i.e., AlO_x and IL. The E_{BG} between 4.2-4.4 eV is measured by UV-Vis-NIR spectroscopy for the AlO_x film after PDA, which is lower than the value reported for stoichiometric amorphous Al_2O_3 film, i.e., 8.7 eV [163].

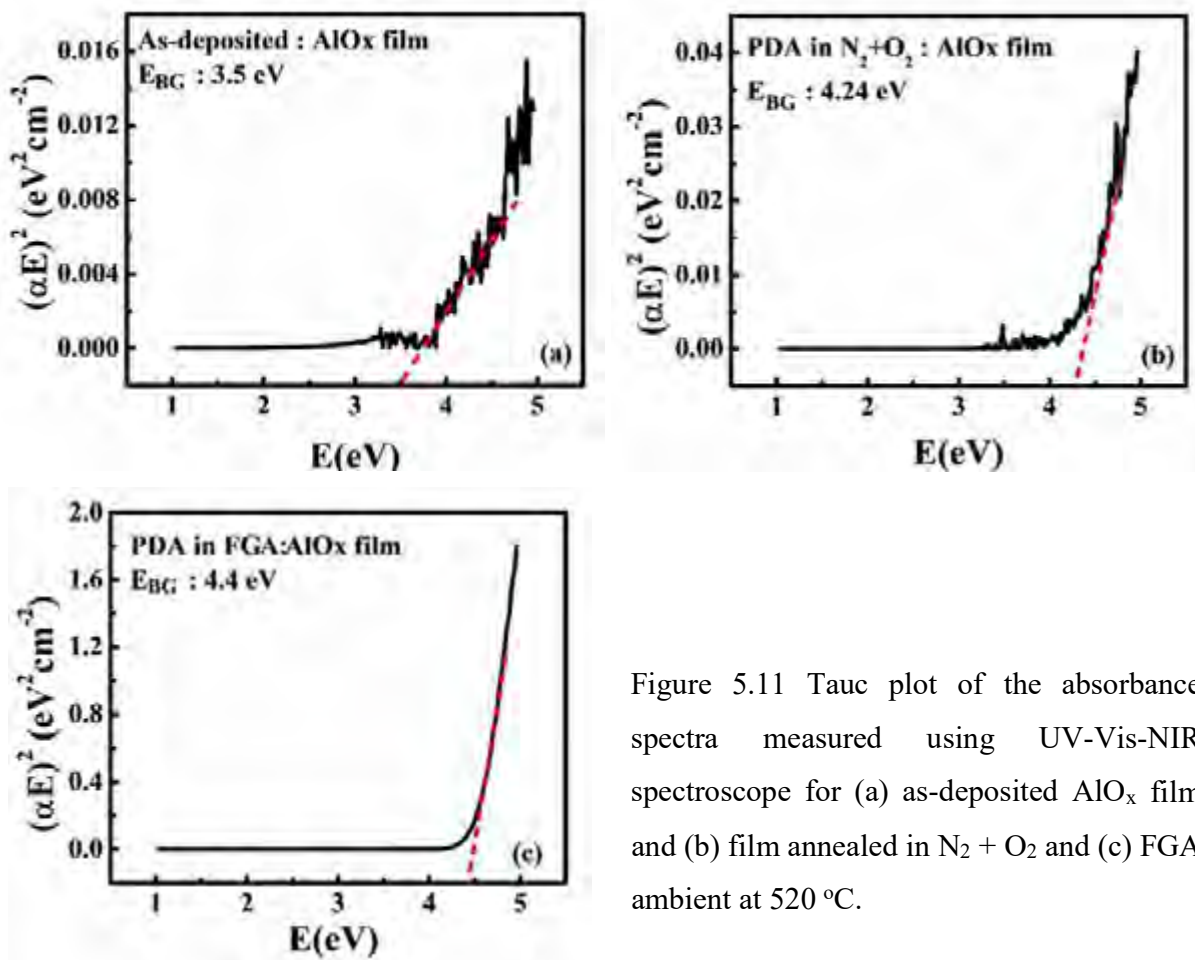


Figure 5.11 Tauc plot of the absorbance spectra measured using UV-Vis-NIR spectroscope for (a) as-deposited AlO_x film and (b) film annealed in $N_2 + O_2$ and (c) FGA ambient at 520 °C.

Table 5.3 Values of AlO_x film E_{BG}, measured using low-loss EELS spectra and UV-Vis-NIR spectroscope for as-deposited and annealed films in N₂ + O₂ and FGA ambients at 520 °C.

Samples	Low-loss EELS measurement	UV-Vis-NIR measurement
As-deposited	2.6 eV	3.5 eV
PDA in N ₂ +O ₂	4.0 eV	4.2 eV
PDA in FGA	4.6 eV	4.4 eV

5.8 Conclusion

In this chapter we have studied the origin and distribution of Q_f in the pulsed-DC RS AlO_x film deposited on p-type c-Si, using EELS measurement technique. It is observed that *T* and *O* coordinated Al L_{2,3} peaks are present in this AlO_x film. From the EELS measurement, the shift in *T* and *O* peaks of Al L_{2,3} to higher energy for all the three samples are observed in the IL region of at AlO_x/c-Si interface. The peak at 106.2 eV is present throughout the IL region, which is corresponding to the oxidation state of Si. In this films, the *T/O* peak intensity ratio in the IL region is observed to increase after annealing, which signifies an improvement in negative Q_f values. Similar observation was also reported by Hoex et al. on PA-ALD Al₂O₃ film deposited on c-Si [44,128]. However in our case, the increase in *T/O* peak intensity ratio is higher in the middle of the IL region for FGA annealed film, as compared to N₂ + O₂ annealed film. While the *T/O* peak intensity ratio is higher at the IL/c-Si interface for the N₂ + O₂ film. From this result, it may be concluded that the fixed charge distribution in the FGA and N₂ + O₂ films are significantly different.

Through XPS measurement, the distribution of intermediate oxidation states of Si 2*p* in the IL region of these films are studied in detail. The following intermediate oxidation states are identified at the IL region: Si¹⁺ (Si₂O), Si²⁺ (SiO) and Si⁴⁺ (SiO₂) with the peak shifts between 2 to 6.5 eV with respect to core-level (Si⁰), i.e., Si 2*p*_{3/2} for all the samples, as a result of oxidation of the Si elements. Two significant peaks are identified between the binding energy of 102 eV-103 eV, named as ARA and SRA, can be a combination of Al-O-Si elements. The presence of Si⁴⁺ (i.e., SiO₂) related peak in as-deposited and FGA annealed AlO_x films are higher as compared to

$N_2 + O_2$ annealed film, which may partly explains the reason of reduction in net negative Q_f in AlO_x film.

From the FTIR measurement the peak positioned at 750 cm^{-1} related to Al-O stretching mode of condensed AlO_4 tetrahedra are present in all the three samples. A sharp and symmetrical peak at 1090 cm^{-1} , corresponding to Si-O-Si stretching mode, is observed for annealed films. For as-deposited AlO_x film, the broad asymmetric peak positioned at 1060 cm^{-1} can be attributed to the lack of formation of Si-O bond at the interface.

The E_{BG} obtained for these films using both low-loss EELS spectra and UV-Vis-NIR spectroscopy, which shows a relatively low E_{BG} of 2.6 eV for as-deposited AlO_x . After annealing, the E_{BG} of the film improves to 4.5 eV, which also suggest the modification and improvement of the film quality after annealing. However the value of E_{BG} measured is relatively lower than the 8.7 eV reported for $\alpha-Al_2O_3$ [163], which may be related to low film density of 2.88 g.cm^{-3} for this film and hence the porosity in the film results in low E_{BG} [161].

In the next chapter we will discuss the optimization of different process conditions by varying different process parameters in the pulsed-DC RS system, and assess the film behaviour by applying the optimized PDA conditions which is proved as most important process to activate the passivation quality of these films.

Chapter 6. Impact of Deposition Process Conditions on the Quality and Interface between Pulsed-DC Reactive Sputtered AlO_x and Silicon

6.1 Introduction

In this chapter we have investigated the impact of various process conditions on the AlO_x film deposited on p-type c-Si towards the application as surface passivation layer after optimized PDA process. As stated in earlier chapters, high quality of surface passivation is related to activation of both field-effect and chemical passivation, which is achieved after the PDA process. Hence the optimized PDA condition as discussed in chapter 4, i.e., annealing in N₂ + O₂ ambient at 520 °C for 20 min was applied on the AlO_x film for different process conditions. The process parameters investigated are (i) the power density, (ii) substrate temperature, and (iii) the process gas used during film deposition.

The experimental details are as follows: the films were deposited on RCA cleaned p-type silicon wafers as discussed in chapter 2, section 2.4.1. The electrical and material characterization were performed on the film deposited on p-type (100) CZ c-Si wafers with resistivity of 5 Ω.cm. For life-time measurements the films were deposited on both the sides of double-sided polished p-type (100) FZ c-Si wafer with resistivity of 7.8 Ω. cm. The τ_{eff} was measured using Sinton WCT-120 life-time tester. Sentech SE-800 was used for thickness and

RI measurement. The cross-sectional imaging was carried out using JEOL make JEM 2100F TEM. The elemental analysis of the film was carried out using Thermo Scientific make MultiLab 2000 XPS. The MOS capacitors fabrication steps with AlO_x dielectric film were discussed in chapter 2, section 2.4.1. Keithley 4200 SCS was used for C-V and G-V measurements.

6.2 Impact of process power density

The AlO_x films were deposited at PD between 0.13 and 1.3 W.cm⁻², keeping the gas flow rate constant at Ar of 10 sccm and O₂ of 55 sccm for these depositions. Since the variable for this experiment was PD, i.e., varied from 0.13 and 1.3 W.cm⁻², the O₂ flow = 55 sccm was selected based on knee point of forward hysteresis curve for maximum PD of 1.3 W.cm⁻², as discussed in chapter 3, section 3.4. The Ar flow rate = 10 sccm was selected, based on the observation of good quality AlO_x film with low surface roughness as discussed in chapter 3 section 3.5.1. The T_{ox} of the AlO_x films measured using SE for various PD conditions are between 17-20 nm. The deposition time set for PD = 0.13 W.cm⁻² as 40 min, for PD = 0.27 W.cm⁻² as 25 min, PD = 0.41 W.cm⁻² as 20 min, PD = 0.69 W.cm⁻² as 8 min and PD = 1.3 W.cm⁻² as 4 min. Figure 6.1(a), (b) and (c), shows the thickness of the film, deposition rate and RI of the film for different PD conditions.

Figure 6.1 (a) shows, the T_{ox} measured using SE for different PD conditions for as-deposited and annealed films. The value of T_{ox} = 16.8 nm is obtained on low PD = 0.13 W.cm⁻² deposited AlO_x film and high PD = 1.3 W.cm⁻² deposition results in T_{ox} = 20 nm. Since for this experiment, our focus was to obtain same thickness for all PD conditions, hence the deposition time was set as mentioned earlier. The effect of annealing on these shows almost same thickness for as-deposited and PDA films for all PD values.

Figure 6.1 (b) shows deposition rate for different PD conditions. In this case, as the thickness of the film is almost same for all the PD conditions, while the deposition time is varied. Hence the deposition rate was obtained as T_{ox} divided by the deposition time for each PD conditions. The deposition rate is observed to increase with process power, as similar trend was also discussed in chapter 3 for pulsed-DC RS technique. The highest deposition rate of 5 nm.min⁻¹ was observed for film deposited at high PD of 1.3 W.cm⁻².

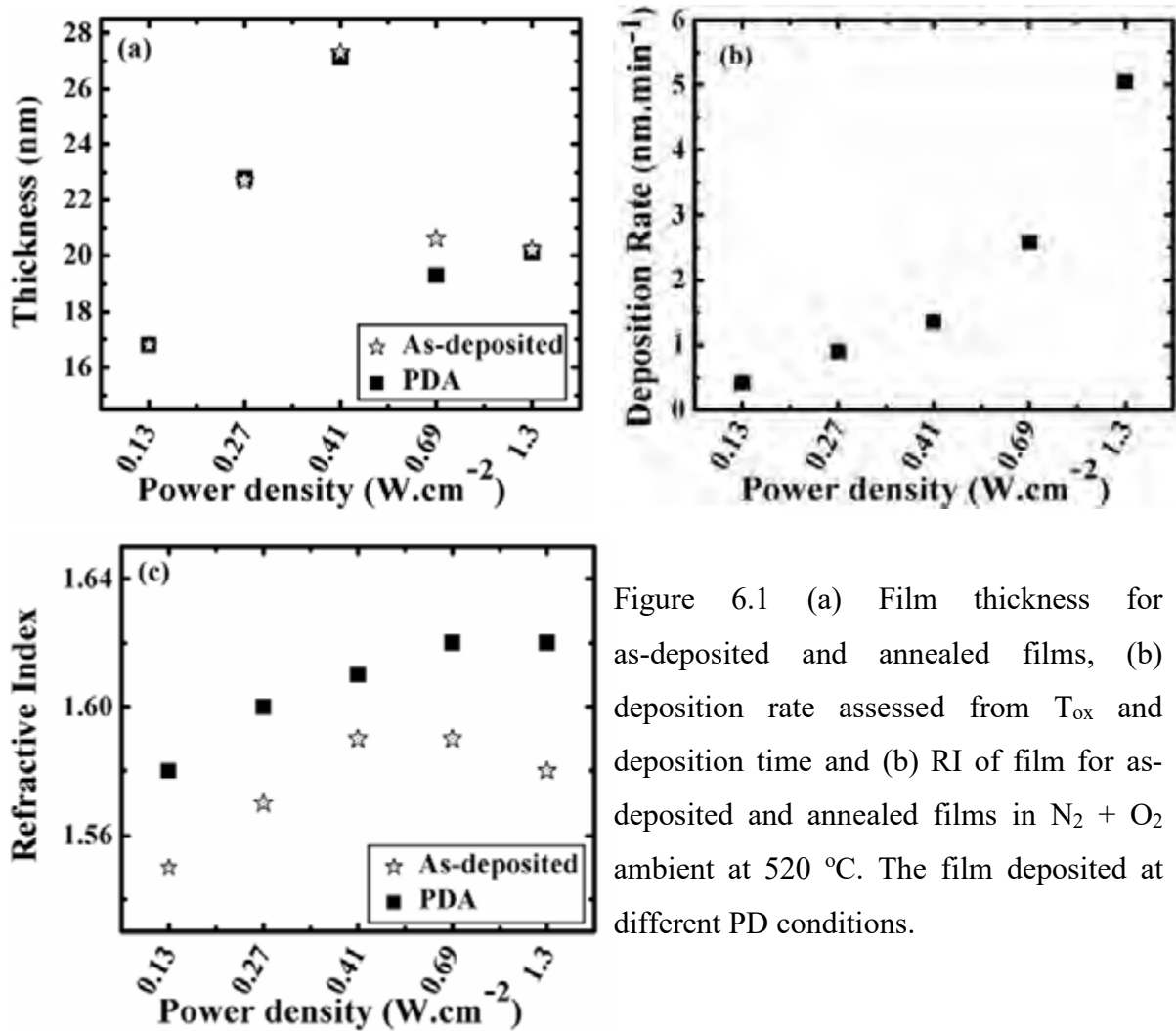


Figure 6.1 (a) Film thickness for as-deposited and annealed films, (b) deposition rate assessed from T_{ox} and deposition time and (b) RI of film for as-deposited and annealed films in $N_2 + O_2$ ambient at 520 °C. The film deposited at different PD conditions.

This deposition system shows reasonably high rate of deposition with cost-effective film deposition. Dingemans et al. reported that AlO_x thickness in the range of 3 nm is adequate for passivation of p-type c-Si surfaces [12]. From this perspective, high power deposition looks attractive as high throughput could be used in an industrial application. However, Zang et al., reported that high power deposition in RF reactive sputtering process degrades the passivation performance of RS AlO_x films [78].

Figure 6.1 (c) shows the value of RI is improving with applied power. Since the high power process, results in Ar^+ ions to accelerate with high energy, so that more atoms are sputtered from the target surface and deposited on the substrate. Further improvement in the RI value to 1.6 was observed after PDA of these films, due to improvement in film density or change in film composition, as discussed in chapter 3.

6.2.1 Electrical characterization

The films are characterized electrically for different PD conditions, to obtain the values of negative Q_f and D_{it} for as-deposited and annealed samples using MOS capacitors. Figure 6.2 (a) and (b) shows the C-V characteristics of the AlO_x film deposited at different PD conditions and after annealing in $N_2 + O_2$ ambient at 520 °C for 20 min, respectively. Figure 6.2 (c) and (d) shows, G-V characteristics of the as-deposited and annealed AlO_x film deposited at different PD conditions, respectively. These measurements was carried out at a frequency of 100 kHz.

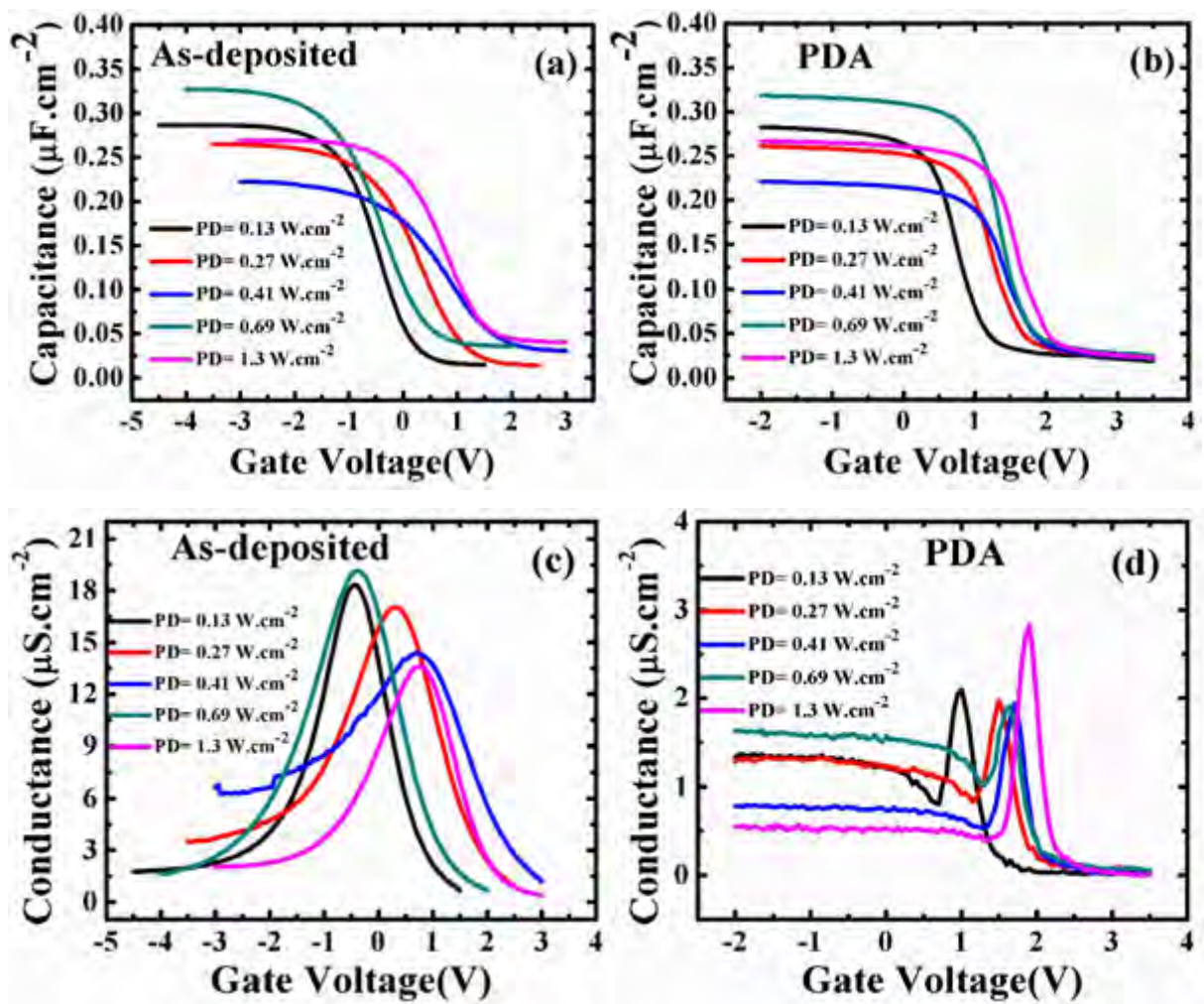


Figure 6.2 (a,b) The C-V and (c,d) G-V characteristics of MOS capacitor with film deposited at different PD between 0.13-1.3 $W \cdot cm^{-2}$. Film are annealed in $N_2 + O_2$ ambient at 520 °C for 20 min.

As shown in Figure 6.2 (a) and (b), the C-V plot for as-deposited films and annealed films deposited at different PD conditions, respectively. The difference in the C_{acc} is observed

due to difference in T_{ox} of the film. Figure 6.2 (a), shows positive shift of V_{FB} value by 0.33 V for film deposited at high PD = 1.3 W.cm⁻² as compared to low PD = 0.13 W.cm⁻² deposition, attributed to increase in negative Q_f with process power for as-deposited condition. Whereas in Figure 6.2 (b), the more positive shift of V_{FB} for annealed films was observed after annealing. As shown in Figure 6.2 (c) and (d), the conductance peak is observed to reduce significantly after annealing, which signifies an improvement in interfacial quality with reduction of D_{it} values.

The values of negative Q_f obtained from C-V plot using eq. (2.15) and the D_{it} extracted from G-V plot using eq. (2.20), are shown in Figure 6.3 (a) and (b), respectively for both as-deposited and annealed films deposited at different PD conditions.

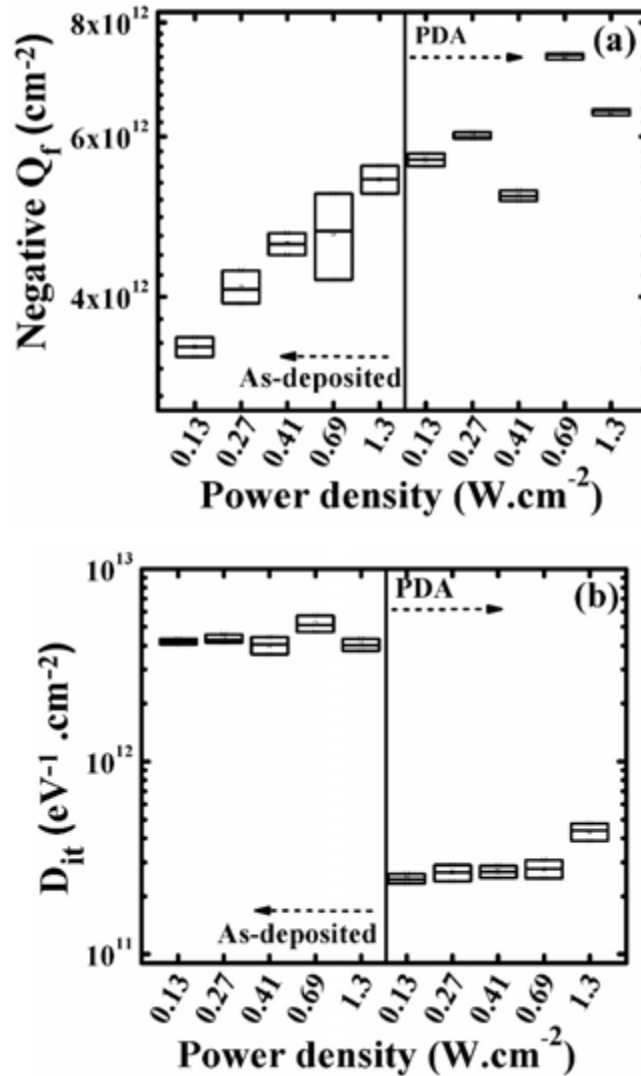


Figure 6.3 Extracted values of (a) negative Q_f and (b) D_{it} for AlO_x film deposited at different PD conditions. The film was annealed in $N_2 + O_2$ ambient at 520 °C for 20 min.

As shown in Figure 6.3 (a), the negative Q_f value is observed to be increasing monotonously with process power for as-deposited film, with high value of negative $Q_f = 5 \times 10^{12} \text{ cm}^{-2}$ is observed at high PD deposition. After PDA the value of negative Q_f increases further to $5.5 \pm 1.5 \times 10^{12} \text{ cm}^{-2}$ with the tighter distributions for all PD conditions. Figure 6.3 (b) shows, the values of D_{it} is in the range of $3 \pm 1 \times 10^{12} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ for as-deposited AlO_x film and after annealing the D_{it} decreases to $2 \pm 3 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ shows an improvement in interfacial quality. However a small increase in value of D_{it} is observed at high PD deposition of $1.3 \text{ W} \cdot \text{cm}^{-2}$ as compared to low PD deposition after annealing.

6.2.2 Surface passivation

The impact of process power on the quality of surface passivation is assessed using life-time tester by measuring τ_{eff} and calculating S_{eff} using eq. (2.29), where upper limit of $\tau_{\text{bulk}} = 30 \text{ ms}$ is used from generalized parameterization proposed by Kerr et al. [119] as discussed in chapter 4. Figure 6.4 (a) and (b) shows the measured τ_{eff} and calculated S_{eff} in as-deposited and annealed AlO_x films. The film was deposited at PD of $0.13 \text{ W} \cdot \text{cm}^{-2}$ and $1.3 \text{ W} \cdot \text{cm}^{-2}$, with process time of 40 min and 4 min, respectively. The annealing of film was carried out in $\text{N}_2 + \text{O}_2$ ambient at $520 \text{ }^\circ\text{C}$ for 20 min.

As shown in Figure 6.4 (a) and (b), the result shows significant improvement obtained in terms of surface passivation quality with very low value of $S_{\text{eff}} = 30 \text{ cm} \cdot \text{s}^{-1}$ for film deposited at high PD of $1.3 \text{ W} \cdot \text{cm}^{-2}$ after annealing, whereas low PD of $0.13 \text{ W} \cdot \text{cm}^{-2}$ deposited film seems not so effective with value of $S_{\text{eff}} = 107 \text{ cm} \cdot \text{s}^{-1}$ after annealing. These result of surface passivation improvement with increase in power is contradictory to the surface passivation results shown for RF reactive sputtered AlO_x film by Zhang et al. [78]. The report shows a degradation in surface passivation quality with increase in process power, where the AlO_x film was deposited at 220 W (i.e., PD of $4.82 \text{ W} \cdot \text{cm}^{-2}$) [78]. The results presented in this work indicates that good surface passivation quality can be achieved with high deposition rate by using pulsed-DC RS technique with high PD deposition of AlO_x film.

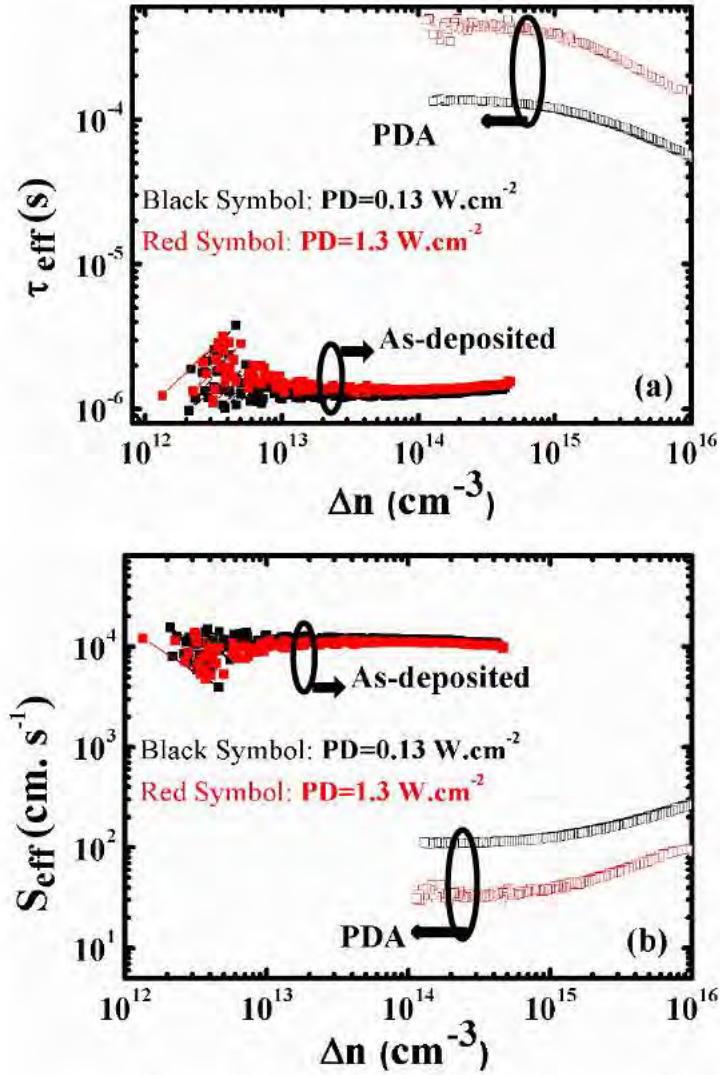


Figure 6.4 (a) Measured τ_{eff} and (b) corresponding S_{eff} on as-deposited and annealed films deposited at $\text{PD} = 0.13 \text{ W.cm}^{-2}$ and 1.3 W.cm^{-2} .

6.2.3 Physical characterization of the films

The cross-sectional TEM image of as-deposited AlO_x film deposited at low $\text{PD} = 0.13 \text{ W.cm}^{-2}$ is shown in Figure 6.5. In this case the film deposited at low $\text{PD} = 0.13 \text{ W.cm}^{-2}$, and result show the IL thickness of 5.8 nm and AlO_x region thickness of 10.9 nm. A significantly thick IL is seen for as-deposited film at the interface of $\text{AlO}_x/\text{c-Si}$ for low PD deposition. The IL layer is formed by the oxidation of the Si by the oxygen species present in the plasma. The intermixing of silicon oxide and deposited aluminum oxide due to ion bombardment leads to formation of thick IL [125]. Since the low PD deposition shows, lower deposition rate as compared to others condition, hence the time available for oxidation of Si at the interface is large, which may result in formation of relatively thick IL.

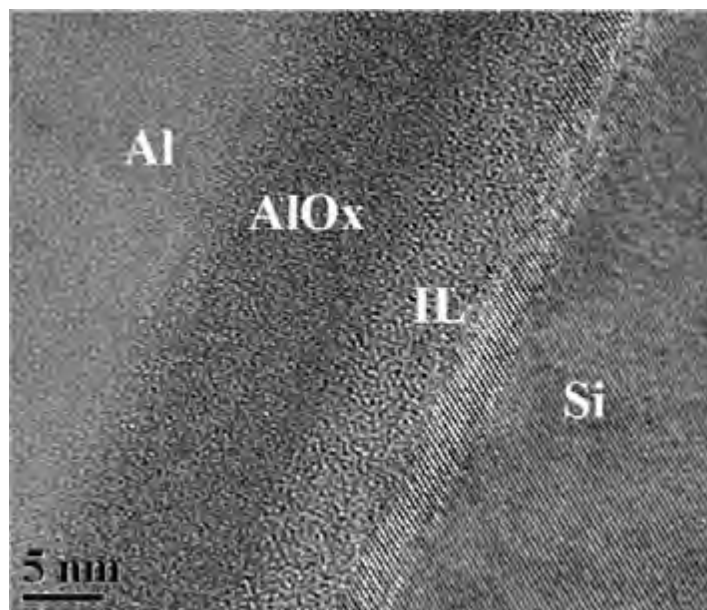


Figure 6.5 Cross-sectional TEM image of as-deposited AlO_x film deposited at low PD of 0.13 W.cm^{-2} .

The depth-profile of Al 2p, O 1s and Si 2p elemental measured using depth-resolved XPS measurement technique for as-deposited and annealed AlO_x films, deposited at low PD = 0.13 W.cm^{-2} and high PD = 1.3 W.cm^{-2} are shown in Figures 6.6 (a,c) and (b,d), respectively. The atomic concentration (%) is plotted as a function of etch time (min).

Figure 6.6 (a) and (c) shows the depth-profile of as-deposited films deposited at low PD = 0.13 W.cm^{-2} and high PD = 1.3 W.cm^{-2} , respectively. It is found that the atomic ratio of O/Al is approximately 1 in the AlO_x region for these films. In Figure 6.6 (b) and (d), the depth-profile of annealed films in same deposition conditions, respectively, shows the atomic concentration of O 1s found to be increasing at the AlO_x region, hence the atomic ratio of O/Al increases for annealed films. Since the annealing was done in $\text{N}_2 + \text{O}_2$ ambient at 520°C , the O from the annealing ambient may diffuse into the film during the process and hence results in increase of O/Al atomic ratio. The annealed film at high PD of 1.3 W.cm^{-2} also shows stoichiometric Al_2O_3 is achieved with atomic O/Al ratio ~ 1.5 in the AlO_x region. In the IL region, a peak corresponding to SiO at 103 eV was observed in all the samples. The concentration of SiO profile for low PD deposition in the IL region is increasing significantly after annealing. In the IL region of all samples, the gradual decrease in Al and O atomic concentration with increase in Si atomic concentrations suggests the IL is in the form of aluminum silicate.

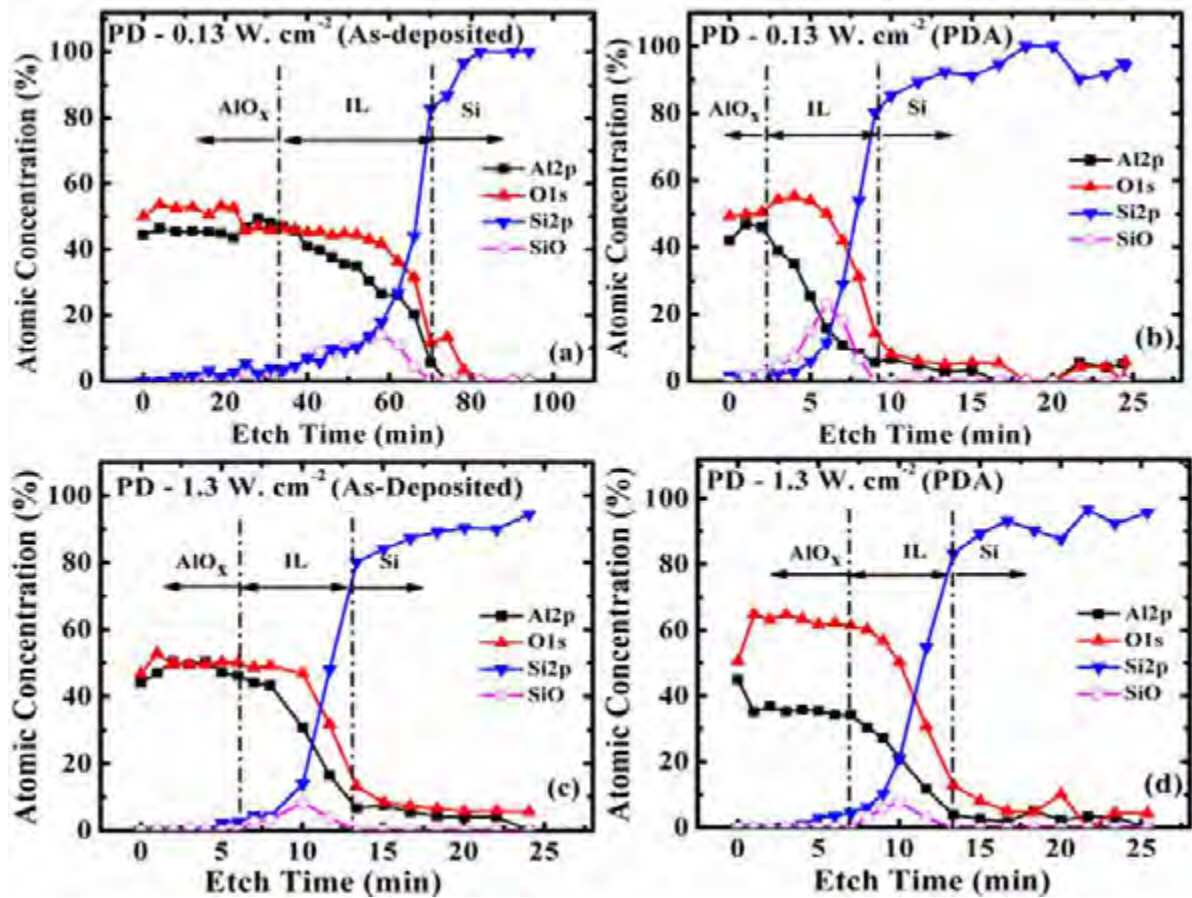


Figure 6.6 Atomic concentration of Al 2p, O 1s and Si 2p elemental depth-profiles for (a) as-deposited and (b) annealed AlO_x films deposited at low PD of 0.13 W. cm^{-2} and (c) as-deposited and (d) annealed AlO_x films deposited at high PD of 1.3 W. cm^{-2} .

In the IL region, relatively higher concentration of SiO bonding = 20 % atomic concentration is observed at low PD deposited film, whereas high PD deposition leads to 8 % less SiO concentration. This shows consistency in result with relatively thick IL for low PD deposition that low deposition rate gives sufficient time for the growth of SiO_x and intermixing with the AlO_x in IL region. For high PD deposited film, the deposition rate is higher which may result in more abrupt transition in material composition and so result in relatively thin IL layer with higher Al than the low PD deposition.

Since the high PD = 1.3 W.cm^{-2} deposited AlO_x film gives best value of surface passivation after annealing, as presented in section 6.2.2 and with high deposition rate. This means that pulsed-DC RS technique is more appropriate for high throughput processing of high quality sputtered AlO_x film as compared to RF reactive sputtering system.

6.3 Impact of substrate temperature during deposition

The impact of different substrate temperatures during film deposition on the quality of AlO_x film was assessed through electrical characterization. In the pulsed-DC RS system used for the investigations in this thesis, the substrate temperature can be varied from room temperature (RT) to 320 °C. For this experiment the substrate temperature during deposition viz. RT, 100 °C, 200 °C and 320 °C, and different PD deposition viz.: 0.13, 0.69 and 1.3 W.cm^{-2} , was used for film deposition while keeping Ar flow of 10 and O_2 flow of 55 sccm. The deposition time for PD = 0.13 W.cm^{-2} was 40 min, PD = 0.69 W.cm^{-2} was 8 min and PD = 1.3 W.cm^{-2} was 4 min, to achieve similar thickness for all PD conditions. The film was annealed in optimized PDA condition in $\text{N}_2 + \text{O}_2$ ambient at 520 °C for 20 min, as discussed in chapter 4.

The film thickness and RI measured for different film with above experimental details using SE are shown in Figure 6.7 (a) and (b).

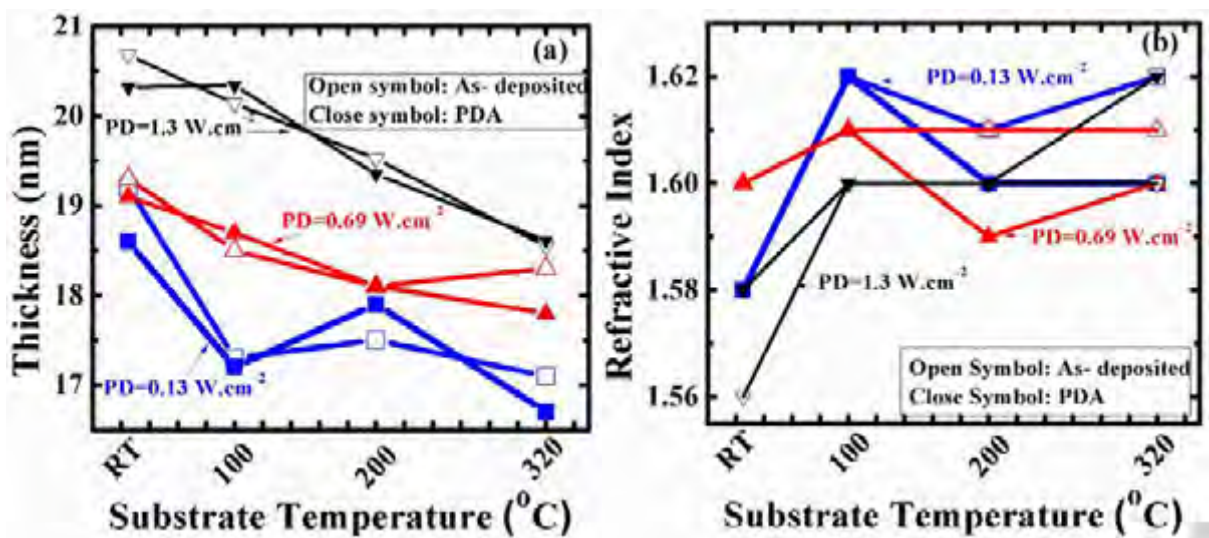


Figure 6.7 (a) Thickness and (b) RI measured by SE for film deposited with different PD conditions and substrate temperature of RT, 100 °C, 200 °C and 320 °C. Open symbol: as-deposited film and close symbol: annealed film.

From Figure 6.7 (a), it is observed that the thickness of film is decreasing with increase in substrate temperature, which is very significant for high PD deposition whereas at low PD deposition the difference seems less. With high temperature on the substrate, the knock-on atoms may penetrate deep into the film and gets trapped into interstitial and vacancies hence results in denser film [74,103]. The reduction in thickness can be related to densification of film [103].

Figure 6.7 (b) shows the value of RI is improved for film deposited at high substrate temperature as compared to RT deposition. The RI values for high temperature deposition films are in the range of 1.59-1.62, which signifies an improvement in film density. However no clear trend in value of RI is visible for substrate temperature > 100 °C.

The AlO_x film deposited at high PD of 1.3 W.cm^{-2} is electrically characterized for different substrate temperature depositions, the deposition time was 4 min, while keeping Ar flow of 10 sccm and O_2 flow of 55 sccm. The film was annealed in optimized PDA condition in $\text{N}_2 + \text{O}_2$ ambient at 520 °C for 20 min. Figures 6.8 (a) and (b) shows extracted values of negative Q_f and D_{it} using eq. (2.15) and (2.20), respectively for as-deposited films and Figures 6.8 (c) and (d) for annealed films.

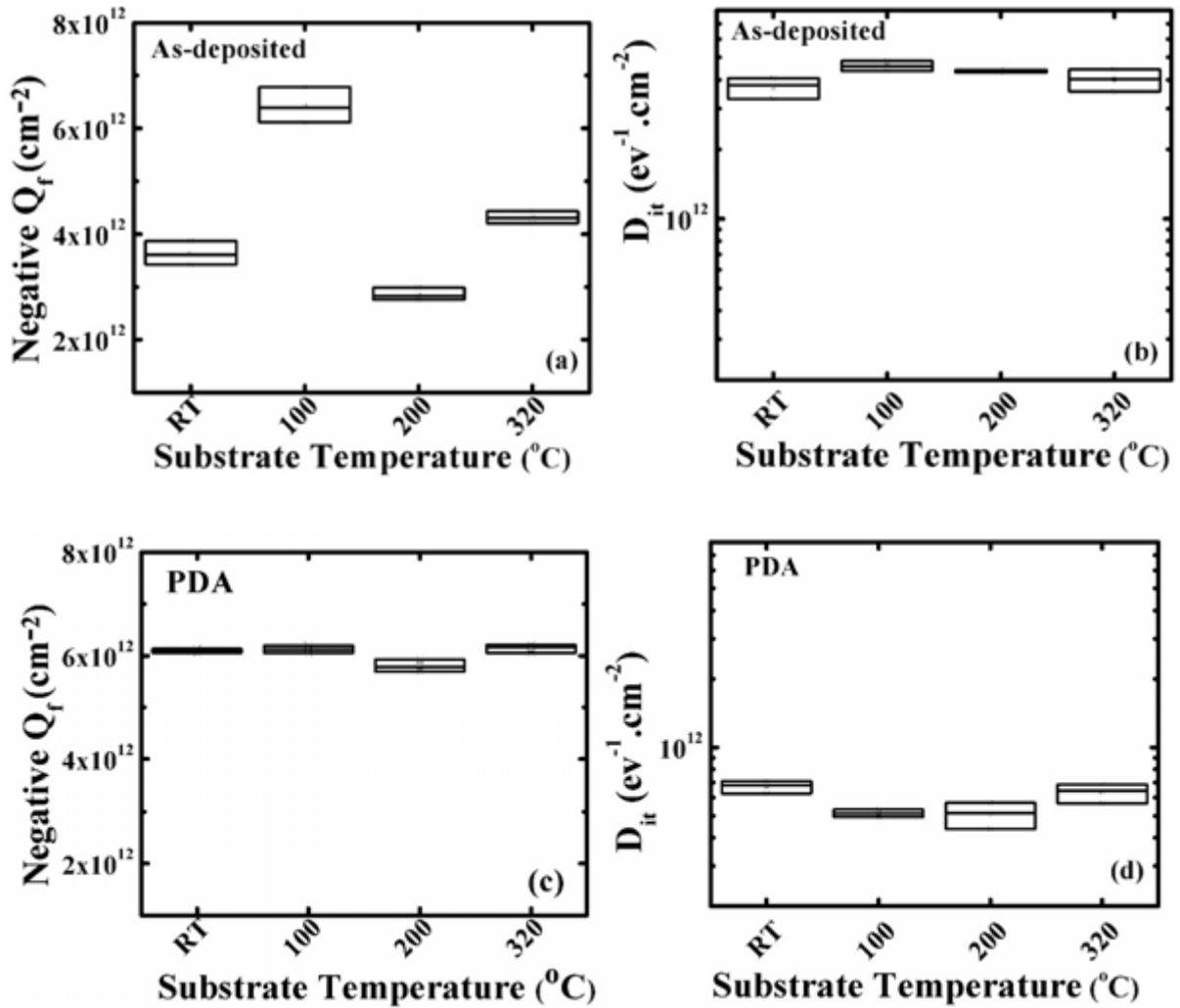


Figure 6.8 Extracted values of negative Q_f (a,c) and D_{it} (b,d) from C-V and G-V characteristics plot of MOS capacitor with AlO_x film deposited at different substrate temperature.

Figure 6.8 (a) shows, high value of negative Q_f in the range of $2.5 \pm 3.7 \times 10^{12} \text{ cm}^{-2}$ is observed in as-deposited film deposited at different substrate temperature. The negative Q_f increases to $5.8 \pm 0.3 \times 10^{12} \text{ cm}^{-2}$ after annealing in AlO_x film deposited at different substrate temperature, as shown in Figure 6.8 (c).

Figure 6.8 (b) and (d) shows the values of D_{it} extracted from G-V characteristics plot for as-deposited and annealed AlO_x film deposited at different substrate temperature, respectively. As shown in Figure 6.8 (b), the D_{it} values are in the range of $3 \pm 1 \times 10^{12} \text{ cm}^{-2} \cdot \text{eV}^{-1}$, for as-deposited films and improves significantly to $5 \pm 2 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$, after annealing for these films.

From the experiment, we can conclude that pulsed-DC RS film deposited at RT is good enough to maintain the film quality as desired for surface passivation of p-type c-Si wafer after activation of passivation using optimized PDA condition. This would result in a simpler system for commercial applications.

6.4 Impact of process gas

This experiment was performed to observe the impact of changing the process gas used during deposition, while keeping process pressure constant at 3.5 mTorr during deposition. Two experiments were carried out: (i) an optimized recipe with Ar of 10 sccm as sputter gas and O_2 of 55 sccm as reactive gas and (ii) only O_2 of 65 sccm used during film deposition. The film was deposited at $\text{PD} = 1.3 \text{ W} \cdot \text{cm}^{-2}$ with deposition time of 4 min for both the processes. The films were subjected to optimized PDA condition, i.e., in $\text{N}_2 + \text{O}_2$ ambient at 520°C for 20 min as discussed in chapter 4. Figures 6.9 (a) and (b) show the thickness and RI of the film for these process conditions, are measured by SE.

The result shows, the thickness for AlO_x film deposited using only O_2 gas is 1 nm less as compared to the process gas with Ar + O_2 mixture. The presence of excessive reactive gas (O_2) in the chamber leads to relatively slow reaction at surface of the Al target that lowers the deposition rate. As discussed in chapter 3, in the RS system the Al target forms a compound surface after O_2 exposure, which results in slow sputter rate as compared to the metal surface. The state of low deposition rate is called as poisoned surface at target with formation of thick oxidized layer [74,101,109].

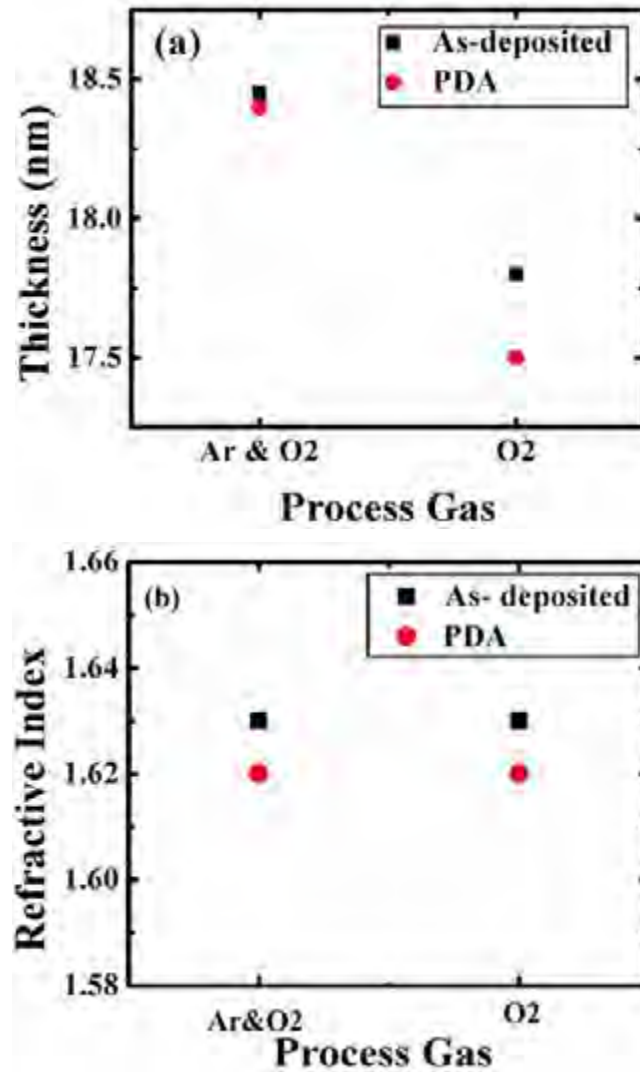


Figure 6.9 (a) Thickness and (b) RI values measured by using SE for different process gases used during film deposition.

For process with Ar used as sputter gas during deposition, make use of heavy Ar⁺ ions to sputter the metal surface and hence results in relatively high rate of deposition. Figure 6.9 (b), shows the value of RI = 1.63 for as-deposited film, which is independent of the process gas. The annealed film shows value of RI = 1.62 for both the process gases.

The films were characterized electrically using MOS capacitors fabricated using AlO_x film deposited by Ar + O₂ and only O₂ process gas. The negative Q_f extracted from C-V characteristics plot and D_{it} extracted from G-V characteristics plot for both as-deposited and annealed conditions are shown in in Figures 6.10 (a) and (b), respectively. The negative Q_f calculated using eq. (2.15) and D_{it} calculated using eq. (2.20), respectively from chapter 2.

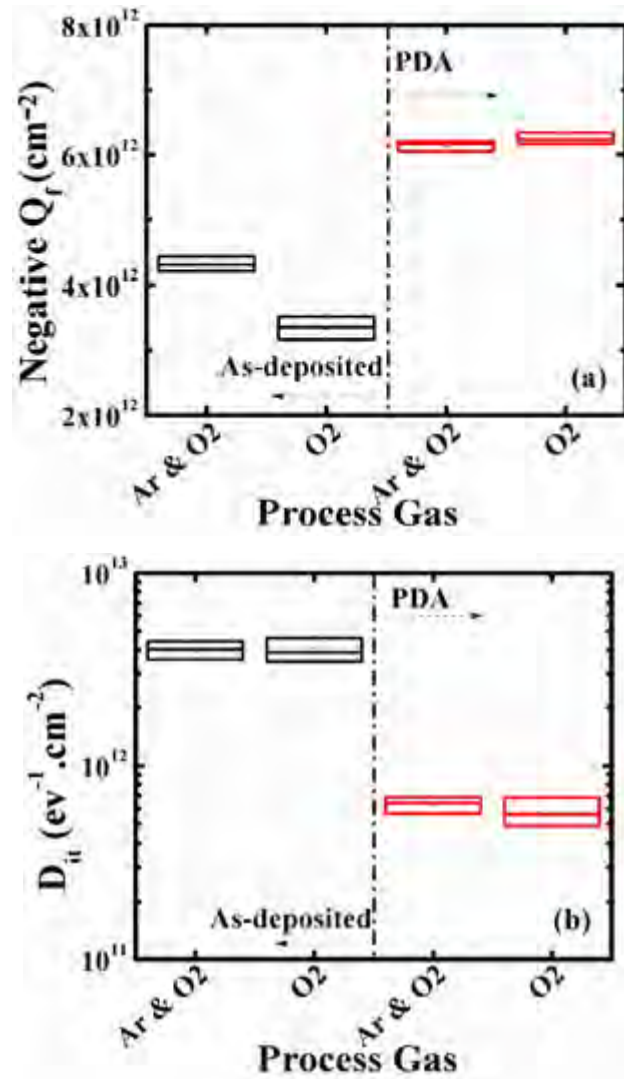


Figure 6.10 Extracted values of (a) negative Q_f and (b) D_{it} from C-V and G-V MOS characteristics plot for AlO_x films deposited using different process gas viz.: Ar & O_2 and O_2 only and keeping process pressure = 3.5 mTorr.

As shown in Figure 6.10 (a), the value of negative Q_f is slightly lower for the as-deposited film processed using O_2 gas only. However after PDA, the value is approximately the same $6.2 \times 10^{12} \text{ cm}^{-2}$ for both the process conditions. The value of $D_{it} = 3.5 \times 10^{12} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ seems to be independent of the process gas for as-deposited film, as shown in Figure 6.10 (b). An improvement in the value of D_{it} to $5 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ is observed for both the process conditions after annealing. From electrical characterization it is observed that the difference in value of negative Q_f and D_{it} is almost negligible after the annealing process, hence we may select the process with O_2 gas as Ar is much more expensive than O_2 , for the processes with for deposition time. For long deposition time the target poisoning may lead to low

deposition rate or arcing [74]. With only O₂ gas used as process gas for deposition periodic target conditioning, i.e., sputtering-off target surface with no reactive gas, may be required to avoid decrease in deposition rate during the processes [74].

6.5 Summary

In this chapter we have discussed the impact of various process parameters on the quality of pulsed-DC RS AlO_x film. The optimized PDA process were applied on these films for further characterization. The impact of following process parameters on the film was studied:

- i. Process power density: The PD was varied between 0.13 to 1.3 W.cm⁻², keeping the other parameters constant. The study shows that with high PD of 1.3 W.cm⁻² deposition rate as high as 5 nm.min⁻¹ was obtained. The values of negative Q_f obtained were in the range of $5.5 \pm 1.5 \times 10^{12}$ cm⁻² and D_{it} of $2 \pm 3 \times 10^{11}$ cm⁻².eV⁻¹ for various PD depositions. The films were characterized further to access the surface passivation quality, which shows very low value of S_{eff} = 30 cm.s⁻¹ for film deposited at high PD of 1.3 W.cm⁻² after annealing, whereas low PD deposited film seems not so effective with value of S_{eff} = 107 cm.s⁻¹ after annealing. Hence with high PD deposition we have found an improvement in the surface quality with higher rate of deposition (higher throughput).
- ii. Substrate temperature: For these study the deposition of the film was carried out at different substrate temperature between RT to 320 °C, while keeping the other process parameters constant. The thickness of the films seems to be decreasing with increase in substrate temperature, as higher mobility of the deposited particles was attained on the heated surface leading to an improvement in film density. The improvement in RI value of the film after high temperature deposition, also shows an improvement in film density. These films were electrically characterized for assessment of film property after as-deposited and annealed conditions. The film deposited at high PD of 1.3 W.cm⁻² and annealed in N₂ + O₂ at 520 °C for 20 min, gives the negative Q_f in the range of $5.8 \pm 0.3 \times 10^{12}$ cm⁻² and D_{it} values are in the range of $5 \pm 2 \times 10^{11}$ cm⁻².eV⁻¹ with high temperature depositions. These values are similar to values obtained for RT deposited film after annealing. Hence we can conclude that film deposited at RT is good enough to maintain the film quality as desired for surface passivation application on p-type c-Si after PDA.

iii. Process gas: Here we have studied the impact of process gas used for film deposition while keeping the process pressure constant at 3.5 mTorr during deposition. The optimized process with Ar and O₂ used as process gases was compared to process using only O₂ as process gas for film deposition. The process PD of 1.3 W.cm⁻² with deposition time of 4 min was used in both the conditions. The T_{ox} for AlO_x film deposited using only O₂ gas is 17.5 nm versus 18.5 nm for Ar + O₂ mixture, a decrease of 5%. The RI of the films were 1.62 and independent of the process gas. From electrical characterization it is observed that after PDA the difference in value of negative Q_f 6.2 × 10¹² cm⁻² and D_{it} 5 × 10¹¹ cm⁻².eV⁻¹ is almost negligible. Hence we may select the process with O₂ gas as Ar is much more expensive than O₂, with periodic target conditioning process to be carried out once a while to avoid target poisoning.

In this chapter the process optimization steps were discussed with changing the process parameters in the system. In the next chapter, we will discuss the high temperature stability of the film, as this is important property of the film in terms of application on c-Si solar cells. The solar cell process involve the firing process for activation of screen-printed contacts with high temperature exposure in the range of 800 °C for few seconds. Hence the film should show stability to high temperature as well. The study and behaviour of pulsed-DC RS AlO_x film for high temperature exposure will be presented in the next chapter.

Chapter 7. Thermal Stability of Passivation for Pulsed-DC Reactive Sputtered AlO_x Film

7.1 Introduction

For the purpose of implementing AlO_x film on silicon solar cells as surface passivation layer, one of the important criteria is that the passivation should be stable when the solar cell goes through high temperature processing. The stability against high temperature exposure is required due to the process step called “firing” which is used to activate the contacts by processing the cells to temperatures above 800 °C for a few seconds, especially in industrial screen-printed silicon solar cells [82]. The reports suggest degradation in surface passivation quality for PA-ALD Al₂O₃ film after this step, due to the effusion of hydrogen from the film [72]. The effusion of large amount of hydrogen from the film cause blistering in ALD and PECVD Al₂O₃ film after high temperature firing step [67,83]. It was also reported that the blistering is the main cause of degradation in surface passivation quality, by causing shunting in the solar cells and hence overall performance of cells degrade [67]. The stability against UV exposure is required especially when the film is applied on front surface passivation layer, for n-type silicon solar cells with p⁺ emitter [164]. Hezel et al. reported that after UV exposure to the film, the τ_{eff} is improving as a result of an increase in value of negative Q_f [164]. The humidity exposure to the

PA-ALD Al_2O_3 film on the other hand cause degradation in surface passivation quality as studied by Liang et al. [165]. In this chapter, we address the issue of thermal stability as the main passivation mechanism in the case of pulsed-DC sputter deposited AlO_x is field-effect passivation. The passivation of p^+ emitter would require chemical passivation [12], hence the application of this film may be limited to passivation of low doped p -type silicon surface as in the case of PERC solar cell structures.

It was reported that the thermal stability of the AlO_x film can be improved by the application of a capping layer, typically $\text{SiN}_x\text{:H}$ film [82,83,165-167]. Dingemans et al. reported excellent surface passivation quality with S_{eff} of $3 \text{ cm}\cdot\text{s}^{-1}$ (measured τ_{eff} of 4.6 ms) for the stack structure of Al_2O_3 (30 nm) capped with $\text{SiN}_x\text{:H}$ (70 nm) [82]. The Al_2O_3 film was deposited on $2 \Omega\cdot\text{cm}$ n -type c -Si using remote plasma ALD process and the $\text{SiN}_x\text{:H}$ was deposited by PECVD technique at a temperature of $400 \text{ }^\circ\text{C}$. The improvement in surface passivation quality after $\text{SiN}_x\text{:H}$ film capping layer was due to diffusion of hydrogen from the $\text{SiN}_x\text{:H}$ film to the PA-ALD Al_2O_3 film upon exposure to high temperature during the firing step [82]. Kania et al. reported that the improvement in surface passivation for stack structure was related to the reduction in the density of D_{it} by one order of magnitude [67]. Richter et al. reported practical application of $\text{AlO}_x/\text{SiN}_x\text{:H}$ stack structure on p^+nn^+ solar cells fabricated using $1 \Omega\cdot\text{cm}$ FZ silicon wafer and demonstrated an efficiency η of 20.8 %. In this case thickness of $\text{SiN}_x\text{:H}$ film was 70 nm, as the same thickness was optimized for ARC in cells [39,83].

In this chapter we will discuss the thermal stability of single layer pulsed-DC RS AlO_x film and later the stack structure with inductively coupled plasma CVD (ICP-CVD) $\text{SiN}_x\text{:H}$ film as capping layer.

7.2 Experimental details

The details of sample preparation and process for the two experiments viz.: single layer AlO_x and stack structure of $\text{AlO}_x/\text{SiN}_x\text{:H}$ are shown in Figure 7.1 (a) and (b), respectively.

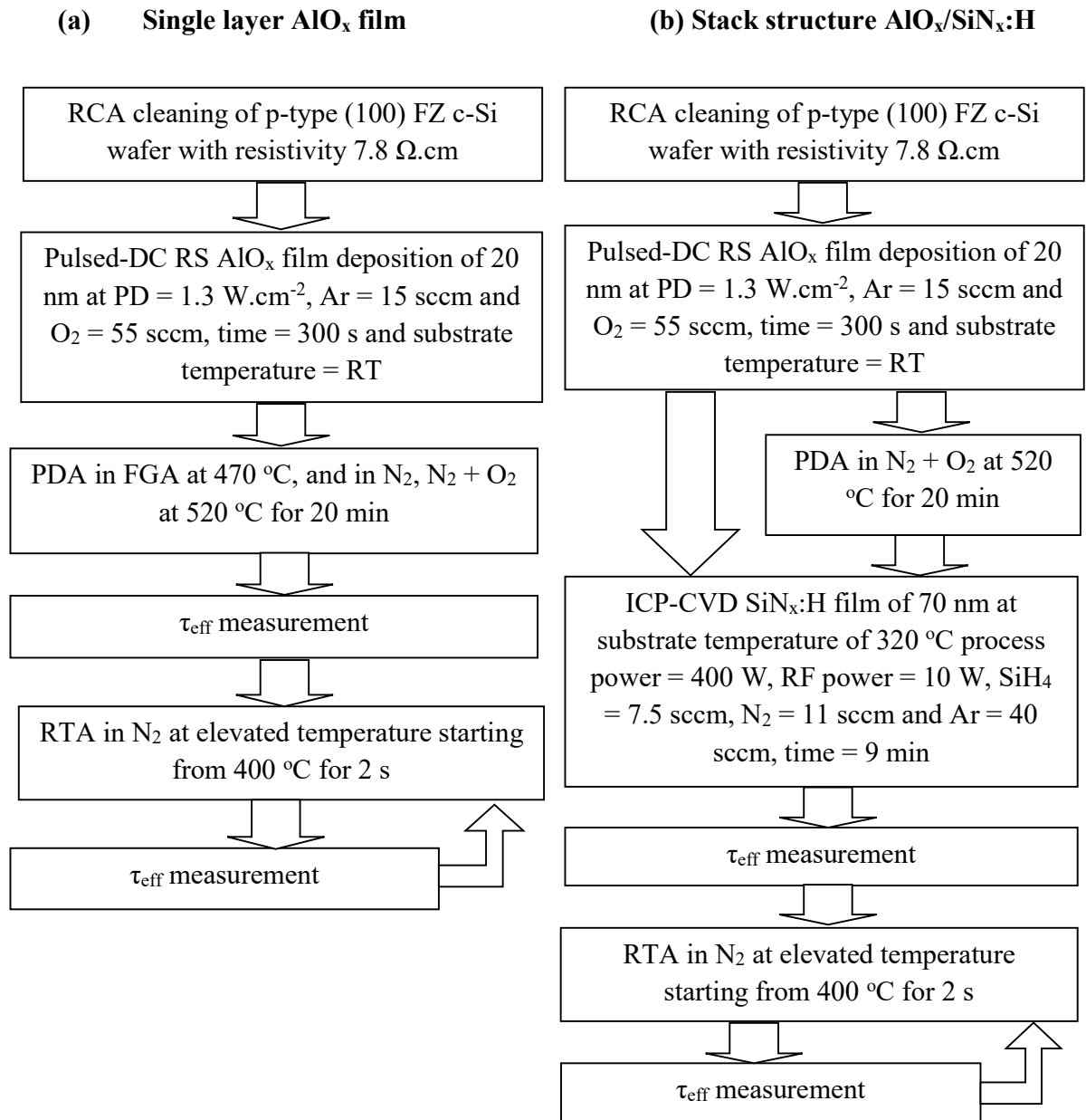


Figure 7.1 Sample preparation for τ_{eff} measurement of (a) single layer AlO_x film and (b) stack structure of $\text{AlO}_x/\text{SiN}_x:\text{H}$ layer for thermal stability study.

For these experiments the optimized process condition with $\text{PD} = 1.3 \text{ W}\cdot\text{cm}^{-2}$, Ar flow = 15 sccm and O_2 flow = 55 sccm, deposition time of 300 s were used for AlO_x film deposition at room temperature on RCA cleaned p-type (100) c-Si wafer. The p-type CZ wafer with resistivity of $5 \Omega\cdot\text{cm}$ was used for electrical characterization and p-type FZ wafer with resistivity of $7.8 \Omega\cdot\text{cm}$ was used for life-time measurements of the film. First experiment includes the study

of single layer pulsed-DC RS AlO_x film stability which was annealed in different PDA conditions. As shown in Figure 7.1 (a), for thermal study of single layer AlO_x film, the different films under study were annealed with PDA conditions as discussed in chapter 4, i.e., FGA at 470 °C, and N_2 , $\text{N}_2 + \text{O}_2$ PDA at 520 °C for 20 min. As shown in Figure 7.1 (b), second experiment includes the study of $\text{AlO}_x/\text{SiN}_x\text{:H}$ stack structure for two sets of samples (i) with $\text{SiN}_x\text{:H}$ film deposited on as-deposited AlO_x film and (ii) with $\text{SiN}_x\text{:H}$ film deposited on annealed AlO_x film (i.e., PDA in $\text{N}_2 + \text{O}_2$ ambient at 520 °C for 20 min).

The 70 nm thick $\text{SiN}_x\text{:H}$ film with RI of 2 was deposited using ICP-CVD system. The deposition was carried out at substrate temperature of 320 °C, using process power of 400 W and RF power of 10 W. Deposition time of 9 min was used to achieve the required thickness and RI for the film. The SiH_4 gas of 7.5 sccm, N_2 gas of 11 sccm and Ar gas of 40 sccm flow rates were used for the $\text{SiN}_x\text{:H}$ film deposition, at the chamber pressure of 6 mTorr. More details on the ICP-CVD $\text{SiN}_x\text{:H}$ film deposition and property can be found in report by Sandeep S.S. et al. [168].

The electrical characterization of single layer AlO_x and $\text{AlO}_x/\text{SiN}_x\text{:H}$ stack were carried by MOS capacitors fabrication, the details are discussed in chapter 2, section 2.4.1. Keithley 4200 SCS was used for C-V and G-V measurements, at measurement frequency of 100 kHz. For lifetime measurements, a symmetrical structure was used with film deposited on both sides of p-type (100) FZ c-Si wafers (resistivity of 7.8 $\Omega\cdot\text{cm}$). For thermal stability study, the sample were exposed to high temperature by RTA process in AnnealSys As-One150 system, at elevated temperature starting from 400 °C to 700 °C for exposure time = 2 s, in N_2 ambient and subsequently the τ_{eff} was measured by Sinton Consulting WCT-120 life-time tester. The S_{eff} was calculated from τ_{eff} and τ_{bulk} using eq. (2.29). For the S_{eff} calculation, the upper limit of $\tau_{\text{bulk}} = 30$ ms was used by generalized parametrization reported by Kerr et al. [119]. Sentech SE-800 SE for thickness and RI measurement.

7.3 Thermal stability of single layer pulsed-DC RS AlO_x film

The value of S_{eff} evaluated from measured τ_{eff} at $\Delta n = 10^{15} \text{ cm}^{-3}$ for the AlO_x films after RTA treatments at various temperatures are shown in Figure 7.2.

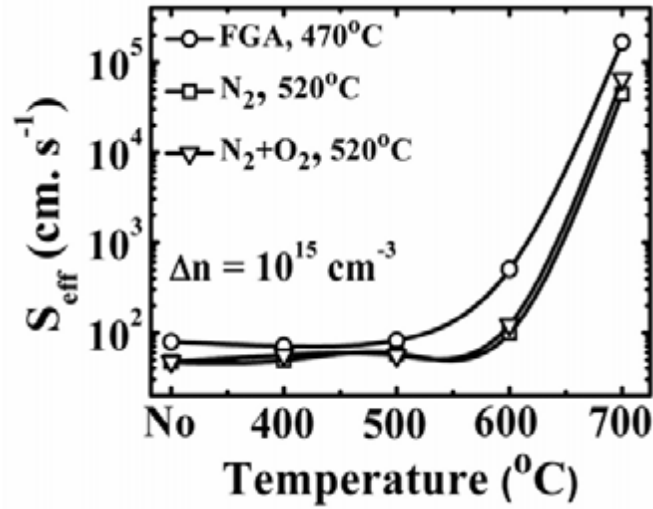


Figure 7.2 Thermal stability of AlO_x film subjected to high temperature exposure in RTA in N_2 . The films were subjected to various PDA conditions. The S_{eff} was measured at $\Delta n = 10^{15} \text{ cm}^{-3}$.

As shown in Figure 7.2, the single layer AlO_x annealed at different PDA conditions are degrading at the firing temperature higher than 600 °C. While comparing the different samples, the sample subjected to PDA in FGA is less robust to those subjected to PDA in N_2 and $\text{N}_2 + \text{O}_2$ ambients. The thermal stability obtained for the single layer AlO_x film annealed in N_2 and $\text{N}_2 + \text{O}_2$ ambient is also not adequate for the screen-printed solar cell applications, as the requirement is stability against temperature in the range of 800 °C. On the other hand, this film shows adequate stability to be applied as passivation layer on PERC solar cells with Ni/Cu contacts, since the firing temperature requirement are in the range of 500 °C or lower [83,166].

The ALD and PECVD Al_2O_3 films are reported to have relatively better thermal stability for single layer [37,82,83]. Dingemans et al., studied the thermal stability of PA-ALD Al_2O_3 film, 30 nm film was deposited on both sides of n-type FZ (100) c-Si wafer (2 $\Omega\cdot\text{cm}$) at 200 °C using TMA precursor and annealed at 425 °C for 30 min in N_2 ambient. The firing step was performed in standard industrial belt furnace at temperature > 800 °C for few seconds, the result shows $S_{\text{eff}} < 14 \text{ cm}\cdot\text{s}^{-1}$ on this film, which concludes that the film was stable for application in screen-printed solar cells [82]. Kania et al., studied the thermal stability of PECVD Al_2O_3 film deposited on both sides of p-type FZ (100) c-Si wafer (1 $\Omega\cdot\text{cm}$) using industrial PECVD SiNA-system by Roth & Rau [67]. The 50 nm thick Al_2O_3 film was deposited using TMA precursor, with N_2O and Ar gases. The deposition temperature in range of 300-400 °C. The result showed $\tau_{\text{eff}} = 2 \text{ ms}$ for film

annealed in FGA at temperature of 400 °C for 25 min, and thermal stability was tested at firing temperature of 900 °C in fast firing chain belt oven, which results in decrease in τ_{eff} to 0.85 ms [67]. The study also showed that the film is stable till 750 °C, with $\tau_{\text{eff}} = 2$ ms [67]. In this case thermal stability for single layer pulsed-DC RS AlO_x film after PDA in N_2 and $\text{N}_2 + \text{O}_2$ ambient at 520 °C results in similar behaviour.

7.4 Thermal stability of $\text{AlO}_x/\text{SiN}_x:\text{H}$ stack structure

As reported in the literature, the thermal stability of AlO_x surface passivation layer can be improved by incorporating $\text{SiN}_x:\text{H}$ capping layer on top of the oxide. Dingemans et al. reported, an excellent quality of surface passivation with τ_{eff} of 4.6 ms for the stack structure of 70 nm PECVD $\text{SiN}_x:\text{H}$ film deposited on 30 nm PA-ALD AlO_x film [82]. The cause for degradation in surface passivation quality after high temperature exposure was assessed using thermal effusion transient measurements, which shows that the film loses both hydrogen as well as oxygen during the firing process. By applying a capping layer of PECVD $\text{SiN}_x:\text{H}$ film, the loss of hydrogen was prevented with diffusion of hydrogen into the AlO_x layer. The report also shows that the post firing degradation of surface passivation can be prevented by annealing the stack structure again. Kania et al. reported that the improvement in surface passivation for stack structure was related to an improvement in chemical passivation with decrease in the value of D_{it} [67]. The $\text{AlO}_x/\text{SiN}_x:\text{H}$ stack structure was also reported as the best choice for passivation of p^+ boron doped emitter layer on n-type silicon solar cell [39,83,169,170]. The ALD or PECVD deposited AlO_x films shows the formation of blisters were due to effusion of hydrogen from film for thickness > 10 nm after firing [82], while another report suggests the blister formation in ALD Al_2O_3 film were due to tensile residual stress for thickness > 10 nm [170]. The issue of blistering seems to be resolved for earlier case with $J_{0\text{e}}$ of 25 $\text{fA}\cdot\text{cm}^{-2}$ observed for the stack structure [39,82], since the high hydrogen content in the $\text{SiN}_x:\text{H}$ film reduces the gradient of hydrogen concentration and thus reducing the diffusion of the same from AlO_x layer [67,72]. Also, with capping layer the AlO_x layer may be protected from the tensile residual stress, hence resolving the issue of blister formation during firing process [171]. Similar result was observed by Dattagupta et al., for PECVD deposited $\text{AlO}_x/\text{SiN}_x:\text{H}$ stack structure with low $J_{0\text{e}}$ of 6 and 45 $\text{fA}\cdot\text{cm}^{-2}$ on 220 and 30 $\Omega\cdot\text{sq}^{-1}$ p^+ boron doped emitter [169]. The implementation of stack structure on the rear-surface

passivation of ion implanted p-type PERC solar cell was investigated by Wu et al., and they reported a cell η of 20.14 % for champion cell with $V_{oc} = 661$ mV and $J_{sc} = 38.88$ mA.cm⁻² [170].

7.4.1 Electrical characterization

The high-frequency C-V and G-V characteristic plots for single layer and stack structure measured at $f = 100$ kHz, are shown in Figure 7.3 (a) and (b), respectively. Two sets of samples were prepared, (i) as-deposited and annealed AlO_x film and (ii) stack structure with SiN_x:H deposited on as-deposited and annealed AlO_x film. The process flow is shown in Figure 7.1 (a) and (b).

As shown in Figure 7.3 (a), the difference in C_{acc} is due to the difference in effective dielectric thickness between the samples. Similar to result as observed earlier for single layer AlO_x film, a positive shift in V_{FB} after annealing is observed in this experiment also. In the case of AlO_x/SiN_x:H, a positive shift in V_{FB} value is observed for the sample with as-deposited AlO_x film capped with SiN_x:H. The difference between as-deposited and annealed V_{FB} values for single layer AlO_x film is $\Delta V_{FB} = 1.17$ V, which is higher compared to ΔV_{FB} of 0.26 V for stack structure with SiN_x:H film deposited on as-deposited and annealed AlO_x films.

As shown in Figure 7.3 (b), the G-V characteristic of different samples, the improvement in interface property is observed for annealed AlO_x film as discussed in earlier chapters. Again capping as-deposited AlO_x film with SiN_x:H film shows improvement in interfacial property which is similar to annealed AlO_x film.

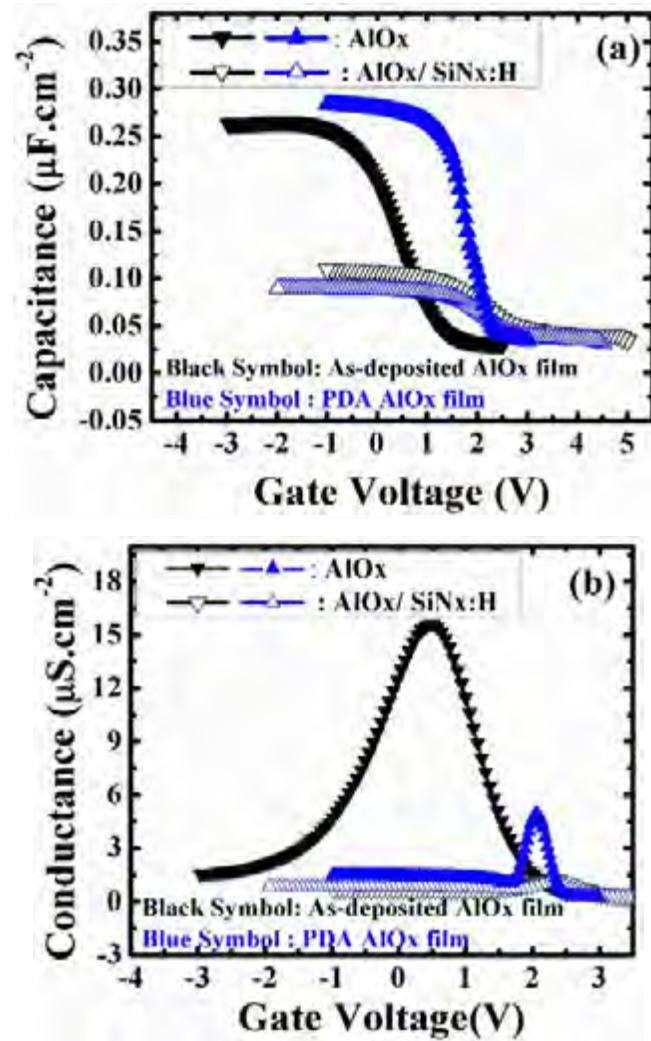


Figure 7.3 (a) The C-V and (b) G-V characteristics plot for AlO_x film (close symbol) and $\text{AlO}_x/\text{SiN}_x:\text{H}$ stack structure (open symbol). Black color: as-deposited AlO_x film and blue color: annealed AlO_x film.

Since the ICP-CVD $\text{SiN}_x:\text{H}$ capping layer was deposited at high temperature of 320°C and with SiH_4 gas, this may results in improvement of interfacial quality with saturating the dangling bonds by hydrogen present in the system during deposition at such temperature. The values of negative Q_f and D_{it} for both samples extracted using eq. (2.15) and eq. (2.20), from C-V and G-V characteristics plot are shown in Figure 7.4 (a) and (b), respectively.

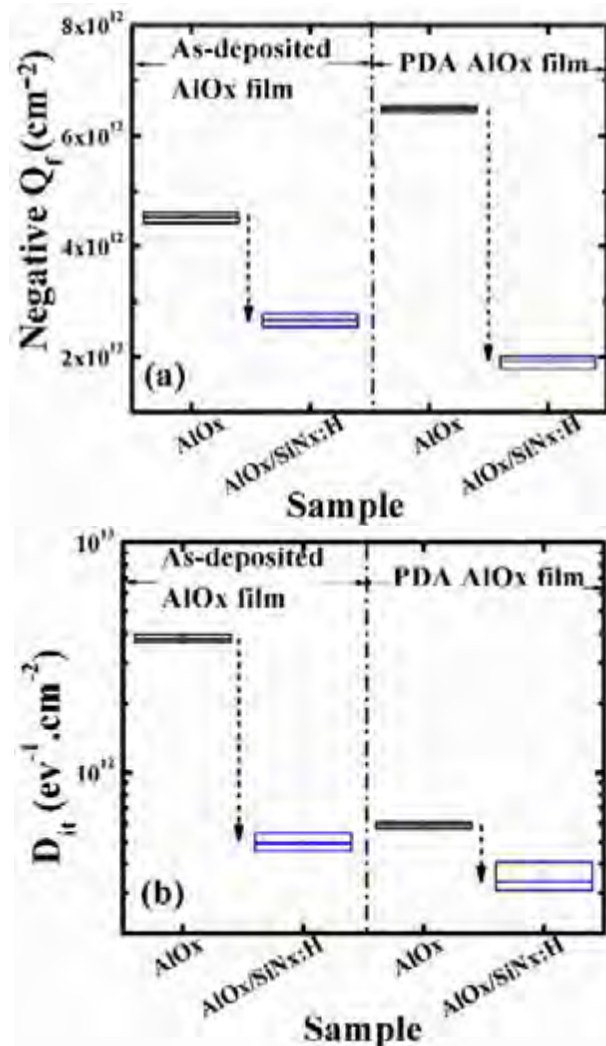


Figure 7.4 Extracted values of (a) negative Q_f and (b) D_{it} from C-V and G-V characteristics, respectively, for single layer AlO_x film (black color) and $AlO_x/SiN_x:H$ stack structure (blue color). The results are shown for as-deposited and annealed AlO_x film.

For single layer AlO_x film, the value of negative Q_f increases significantly after PDA. For stack structure, after deposition of $SiN_x:H$, the Q_f is observed to decrease. The similar result was observed for FGA annealing of the AlO_x film at $520\text{ }^\circ\text{C}$, reported in chapter 4. The reason for this change can be twofold: (i) The diffusion of hydrogen from the $SiN_x:H$ during deposition to the $AlO_x/c\text{-Si}$ interface influencing the structural modifications responsible for the change in negative charges at this interface. A similar situation exist in the case of annealing in FGA ambient. (ii) The $AlO_x/c\text{-Si}$ interface contains negative Q_f , while the $SiN_x:H$ film consists of positive Q_f

charges, as reported by Aberle et al. [172]. Hence it is possible that the negative Q_f in AlO_x film are compensated by the positive Q_f in $\text{SiN}_x\text{:H}$ film and results in net reduction of negative Q_f in the stack structure. The reduction is more in case of sample with $\text{SiN}_x\text{:H}$ film deposited on annealed AlO_x film. Similar result was also reported by Kania et al., that shows a reduction in negative Q_f after deposition of $\text{SiN}_x\text{:H}$ on annealed PECVD AlO_x film [67].

Figure 7.4 (b) shows the values of D_{it} for these samples. An improvement in D_{it} values after annealing of single layer AlO_x film is observed, similar to the result as discussed in chapter 4. The value of D_{it} is observed to reduce after deposition of $\text{SiN}_x\text{:H}$ film on both as-deposited AlO_x film and annealed AlO_x film. This may suggest an improvement in interfacial quality could be possible without any PDA process, since the deposition of $\text{SiN}_x\text{:H}$ film on as-deposited AlO_x film results in reduction of D_{it} . For ICP-CVD $\text{SiN}_x\text{:H}$ film, the SiH_4 was used as process gas and deposition temperature was kept as 320°C , hence the atomic hydrogen in the film may be used to passivate the dangling bonds in this case [168]. The high temperature deposition of $\text{SiN}_x\text{:H}$ film, acts as annealing process of AlO_x film. Therefore the stack structure shows improved interfacial quality even with as-deposited AlO_x film.

7.4.2 Surface passivation

In Figures 7.5 (a) and (b), the τ_{eff} measured using life-time tester and corresponding S_{eff} calculated using eq. (2.29) are shown for single layer annealed AlO_x film (PDA AlO_x film) and stack structure with $\text{SiN}_x\text{:H}$ film deposited on annealed AlO_x film (PDA $\text{AlO}_x/\text{SiN}_x\text{:H}$ stack). The S_{eff} was calculated from τ_{eff} and upper limit of $\tau_{bulk} = 30$ ms by generalized parameterization on low-resistivity silicon wafer [119], as discussed in chapter 4.

Figure 7.5 (a) shows that the τ_{eff} decreases after the AlO_x film capped with $\text{SiN}_x\text{:H}$ film. This results in high value of S_{eff} for stack structure, i.e., $400\text{ cm}\cdot\text{s}^{-1}$ as compared to $S_{eff} = 40\text{ cm}\cdot\text{s}^{-1}$ for single layer AlO_x at $\Delta n = 10^{15}\text{ cm}^{-3}$, as shown in Figure 7.5 (b). The degradation in the surface passivation quality for stack structure, can be related to decrease in negative Q_f , i.e., reduction of effect of field-effect passivation mechanism. This was also discussed in previous chapters, that the field-effect passivation mechanism is dominating for pulsed-DC RS AlO_x film, with high density of negative Q_f on p-type c-Si surface.

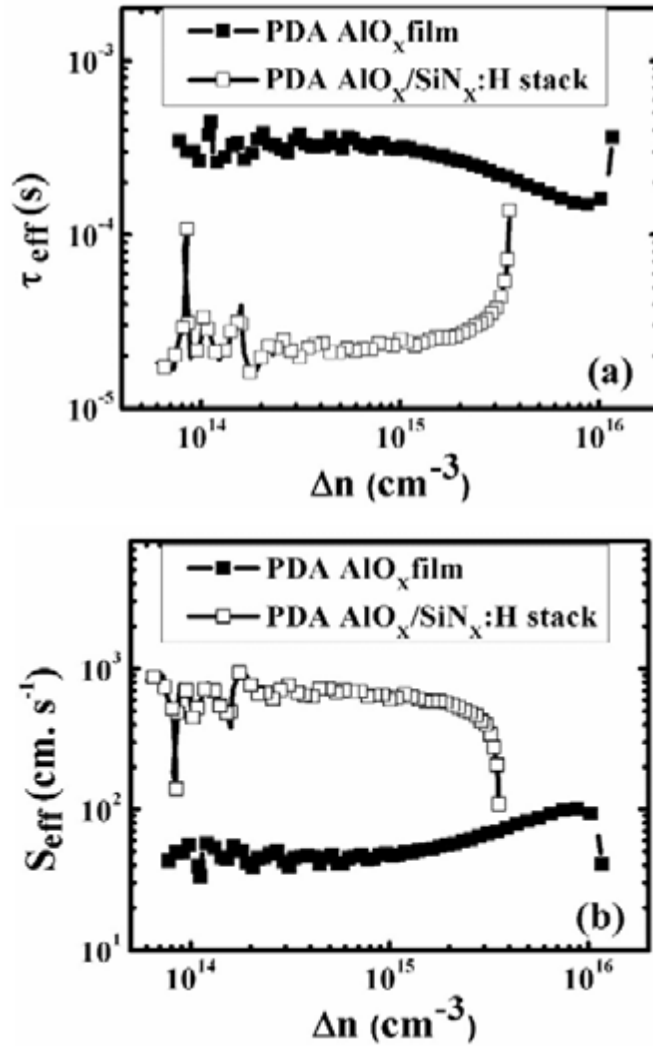


Figure 7.5 (a) Measured τ_{eff} and (b) corresponding S_{eff} value on p-type c-Si (FZ) wafer for single layer annealed AlO_x film (close symbols) and stack structure $\text{AlO}_x/\text{SiN}_x:\text{H}$ (open symbols) with the AlO_x film annealed before $\text{SiN}_x:\text{H}$ deposition.

The above results shows, after application of ICP-CVD $\text{SiN}_x:\text{H}$ capping layer, the reduction of negative Q_f is leading to degradation of surface passivation quality.

The thermal stability of the single layer and stack structure, are tested for firing stability with exposure to high temperature for 2 s using RTA process as discussed in experimental details. Figure 7.6 shows the minimum values of S_{eff} at $\Delta n = 4 \times 10^{14} \text{ cm}^{-3}$ for samples fired at different temperatures upto 700 °C in steps of 100 °C for 2 s.

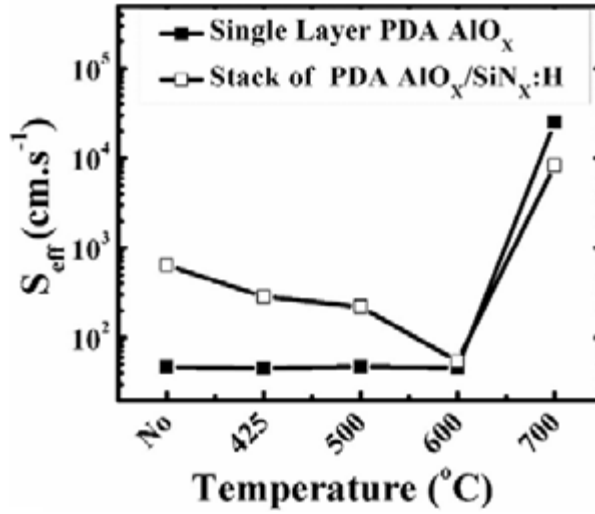


Figure 7.6 Thermal stability for single layer AlO_x film (close symbol) and AlO_x/SiN_x:H stack structure (open symbol) at different firing temperatures using RTA process. The AlO_x film was annealed in N₂ + O₂ ambient at 520 °C for 20 min for both the cases.

Figure 7.6 shows, the S_{eff} of the stack structure is higher than the single layer AlO_x film without any firing process. As the samples exposed to firing temperature, the S_{eff} for the single layer passivation remains unchanged between 420 °C to 600 °C and degrades further at higher temperature exposure. Whereas the stack structure shows improvement in passivation quality with firing temperature till 600 °C and degradation after exposure of any higher temperature. The result shows, the passivation using the stack is never better than the single layer AlO_x film at any firing temperature. Since the stack structure with high temperature may lead to dissociation of the Si–H bonds at the interface may and hence may lead to degradation of interface quality. While another possible explanation is based on the study of different PDA conditions on surface passivation of AlO_x film, as discussed in chapter 4, shows the significant degradation in passivation quality for film annealed in FGA ambient at high temperature was due to reduction of negative Q_f . In this case for stack structure, the hydrogen may be diffusing from SiN_x:H film into the AlO_x, hence may also cause reduction in the negative Q_f at such high temperature. The experiment shows even with application of SiN_x:H capping layer the high temperature degradation remains same for both single layer and stack structure for pulsed-DC RS AlO_x film.

7.5 Summary

In this chapter, we have discussed the thermal stability of pulsed-DC RS AlO_x film for firing temperature as required by industrial screen-printed solar cell fabrication process. The films subjected to PDA in N_2 and $\text{N}_2 + \text{O}_2$ ambients have shown better thermal stability as compared to films annealed in FGA. The film has shown degradation in passivation for firing at $700\text{ }^\circ\text{C}$, which is lower than the typical firing temperatures used for industrial screen-printed solar cell manufacturing. The film, however, may be used as passivation layer on PERC cells with Ni/Cu contact where the firing temperature in the range of $500\text{ }^\circ\text{C}$ or less. Further experiment on thermal stability of stack structure with AlO_x film capped by ICP-CVD $\text{SiN}_x\text{:H}$ was conducted, as various reports suggested an improvement in firing stability for such stack structure. The result from this experiments show a decrease in the net negative Q_f while marginal improvement in D_{it} values were observed for the stack structure assessed using electrical characterization. The stack structure is tested for stability at different firing temperature using RTA process. The result has shown improvement in S_{eff} value till firing temperature of $600\text{ }^\circ\text{C}$ and post that the passivation quality of stack degrades in similar manner as single layer AlO_x film. Hence with this experiment we can conclude the additional film does not improve the surface passivation quality of pulsed-DC RS AlO_x film on p-type c-Si, unlike the ALD and PECVD AlO_x films reported elsewhere.

Chapter 8. Conclusions and Future Work

In this work we have investigated the applicability of pulsed-DC RS AlO_x film for surface passivation of p-type c-Si. We have shown the process development of AlO_x film deposition using pulsed-DC RS technique in industrial PVD system of ENDURA by Applied Materials Inc. in chapter 3. While the film has shown electrical robustness with mean E_{BD} of 18.07 MV.cm^{-1} for film EOT of 8.59 nm and $\epsilon_{r-\text{AlO}_x}$ of 8.15. Using this characteristics of the film it was applied and tested as IPD layer in flash memory applications.

The value of negative Q_f of $2.88 \times 10^{12} \text{ cm}^{-2}$ was obtained in as-deposited AlO_x film at high PD of 1.3 W.cm^{-2} on p-type c-Si wafer. With the application of optimized PDA process in $\text{N}_2 + \text{O}_2$ ambients at $520 \text{ }^\circ\text{C}$ for 20 min, the best value of $S_{\text{eff}} = 31 \text{ cm.s}^{-1}$ was observed on p-type FZ c-Si ($7.8 \text{ } \Omega\text{.cm}$) wafer. Through electrical measurements an improvement in surface passivation was related to an increase in negative Q_f to $6 \times 10^{12} \text{ cm}^{-2}$ and reduction in D_{it} values to $2.3 \times 10^{11} \text{ eV}^{-1}\text{.cm}^{-2}$. The film deposited at high PD of 1.3 W.cm^{-2} , resulted in high deposition rate of 5 nm.min^{-1} . Hence the high quality surface passivation may be realised using this deposition technique with high throughput.

Through material characterization presence of thick IL of 8.2 nm with the composition of aluminum silicate was observed using cross-sectional TEM and depth-resolved XPS measurements. The presence of both *T* and *O* coordinated Al, with *T* coordinated Al increasing near the IL after annealing was observed for this film using EELS measurement technique. The dominating *T* coordinated Al results in increase of negative Q_f in AlO_x film. From the FTIR measurement a symmetrical peak at 1090 cm^{-1} , corresponding to Si-O-Si

stretching mode, was observed on annealed films, resulting in improvement in interfacial quality.

The film annealed in optimized PDA condition has shown slow gradual degradation in passivation quality for firing temperature of upto 700 °C. Which is lower than typical firing temperature for industrial screen-printed solar cell, hence the film may be applicable as passivation layer on PERC cells with Ni/Cu contact where the firing temperature is in the range of 500 °C or less.

8.1 Future direction

With pulsed-DC RS AlO_x film, we have obtained the S_{eff} of 31 cm. s^{-1} on p-type FZ c-Si surface deposited using optimized process conditions and annealed in optimized PDA conditions. The thermal stability against firing temperature has shown that the film is stable upto 700 °C. Since the thermal stability of stack structure with AlO_x film capped using ICP-CVD $\text{SiN}_x\text{:H}$ does not seem to improve the firing stability, hence the proposal to test the hydrogen diffusion hypothesis could be pursued in further research.

The integration of pulsed-DC RS AlO_x film as rear surface passivation layer on c-Si solar cells is required to assess the cell performance. The film may be integrated as rear-surface passivation layer in advance cell structure known as “PERC” structure, as shown in Figure 8.1.

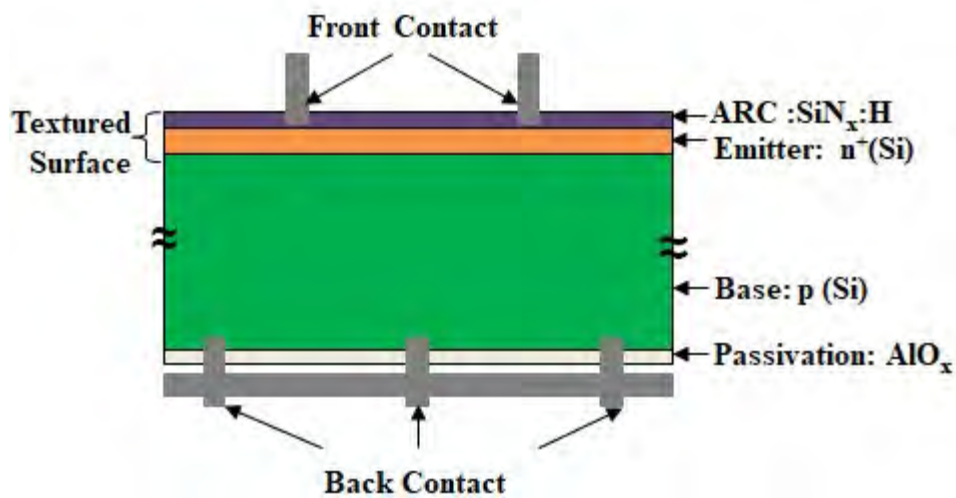


Figure 8.1 Typical p-type c-Si PERC solar cell with rear-surface passivated using AlO_x film.

In Figure 8.2, shows the proposed process flow for fabrication of advance PERC structure p-type c-Si solar cells with pulsed-DC RS AlO_x film integrated as rear-surface passivation layer.

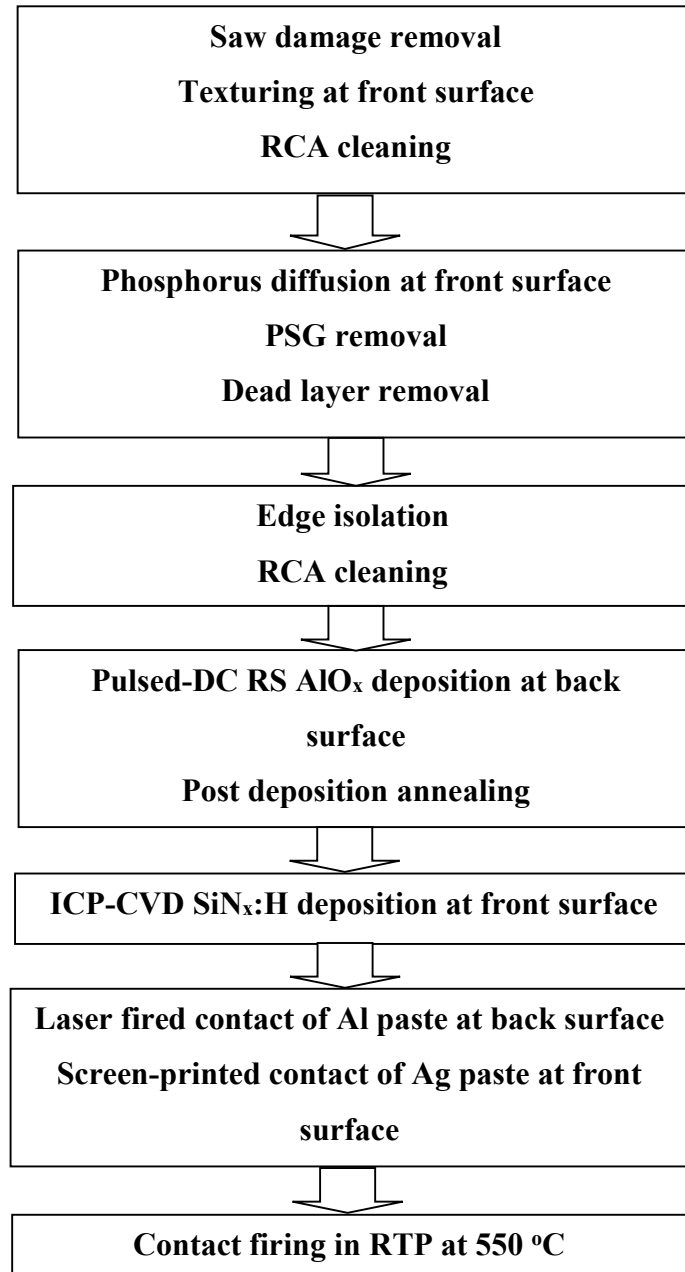


Figure 8.2 Proposed process flow for fabrication of PERC structure p-type c-Si solar cell using AlO_x film as rear-surface passivation layer.

The initial sample preparation involved, saw damage removal followed by texturing of the front surface of the wafer to reduce the reflection of light, followed by RCA cleaning of the wafer. The p-n junction can be formed by phosphorus doping in diffusion furnace to form

n^+ -emitter on p-type base. After formation of p-n junction, the phosphor silicate glass (PSG) and dead layer on the surface, should be removed before proceeding for edge isolation process. The wafer needs another RCA cleaning process to remove any metallic residue on the wafer before film deposition. The pulsed-DC RS AlO_x film deposited on the rear-surface and optimized PDA process applied after film deposition to activate the surface passivation of rear-surface. The ICP-CVD $SiN_x:H$ film is then deposited on front surface n^+ emitter to serve as ARC. Since the film contains positive fixed charges, it also act as emitter-surface passivation layer. The contacts formation process involves, the Al paste to be locally fired using laser at back surface and the Ag paste by screen printing technique at front surface. The contact firing process will be performed to activate the contacts.

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List of Publications

Journal publications

1. **M. Bhisare**, A. Misra, and A. Kottantharayil, "Aluminum oxide deposited by pulsed-DC reactive sputtering for crystalline silicon surface passivation," *IEEE J. Photovolt.*, vol. 3, no. 3, pp. 930-935, 2013.
2. **M. Bhisare**, A. Misra, M. Waikar, and A. Kottantharayil, "High quality Al₂O₃ dielectric films deposited by pulsed-DC reactive sputtering technique for high-k applications," *Nanosci. Nanotechnol. Lett.*, vol. 4, no. 6, pp. 645-650, 2012.

Conference publications

3. K. Midya, **M. Bhisare**, A. Kottantharayil, and S. Dhar, "Investigation of nature of UV induced negative charge in Al₂O₃ film," In Proc. of 3rd IEEE International Conference on Emerging Electronics, 2016, pp. 1-4.
4. **M. Bhisare**, S. S. Sandeep, and A. Kottantharayil, "Thermal stability of single layer pulsed-DC reactive sputtered AlO_x film and stack of ICP-CVD SiN_x on AlO_x for p-type c-Si surface passivation," In Proc. of 2nd IEEE International Conference on Emerging Electronics, 2014, pp. 1-4.
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6. **M. Bhisare**, G. Jeevanandam, and A. Kottantharayil, "Pulsed-DC reactive sputter deposited aluminum oxide for surface passivation of p-type silicon for solar cell applications," presented at 3rd International Conference on Advances in Energy Research, Mumbai, India, 2011.

7. **M. Bhisare**, A. Misra, M. Waikar, and A. Kottantharayil, "High quality Al₂O₃ dielectric films deposited by pulsed-DC reactive sputtering technique for high-k applications," presented at International Conference on Materials for Advance Technologies 2011, Singapore, 2011.
8. A. Mishra, H. Kalita, M. Waikar, A. Gour, **M. Bhisare**, M. Khare, M. Aslam, and A. Kottantharayil, "Multilayer graphene as charge storage layer in floating gate flash memory," In Proc. of 4th IEEE International Memory Workshop, Milano, 2012, pp. 1-4.
9. A. Misra, M. Waikar, A. Gour, **M. Bhisare**, S. Mane, P. Nyaupane, and A. Kottantharayil, "SiO₂/Al₂O₃ dielectric stack with low power pulsed-DC reactive sputtered high-k Al₂O₃ as blocking dielectric for NAND flash application," presented at International Workshop on Physics of Semiconductor Devices 2011, Kanpur, India, 2011.
10. M. A. Khaderbad, R. Pandharipande, A. Gautam, A. Mishra, **M. Bhisare**, A. Kottantharayil, Y. Meesala, R. Mangalampalli, and V. R. Rao, "Bottom-up Method for Work Function Tuning in High-k/Metal Gate Stacks in Advanced CMOS Technologies," In Proc. of 11th IEEE International Conference on Nanotechnology, Portland, Oregon, 2011, pp. 269-273.
11. A. Misra, S. Sadana, S. Suresh, **M. Bhisare**, S. Srinivasan, M. Waikar, A. Gaur, and A. Kottantharayil, "Effect of different substrate materials on the Pt nanocrystal formation statistics (size, density area coverage and circularity) for flash memory application," presented at MRS Fall Meeting 2010, Boston, 2010.

Manuscript under preparation

12. **M. Bhisare**, S. Kalaivani, K. Dileep, R. Datta, and A. Kottantharayil, "Study of origin and distribution of fixed oxide charges in pulsed-DC reactive sputtered aluminum oxide using electron energy loss spectroscopy,"