2. High Efficiency Crystalline Si Solar Cells

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The target and timelines for this deliverable are shown in Fig. 2.1.

Fig. 2.1: Targets and timelines for high efficiency solar cells. Present status is 14.9% efficiency on p-type c-Si.

Achievements during the year under review (3rd year) in comparison to the status at the end of the previous year are shown in the table below.

<table>
<thead>
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<tbody>
<tr>
<td><strong>Cell fabrication</strong></td>
<td>Efficiency of 14.9% on p-type Si wafers - solid state diffusion with deadlayer removal – SiNx:H anti reflective coating - thermally evaporated metal contacts. Cell size 3.5 mm X 3.5 mm. Selective emitter cells with 13.2% on p-type Si wafers. Efficiency of 6.7% on n-type Si wafers with spin-on-dopant/boric acid sources for doping.</td>
<td>Efficiency of 13.3% on p-type wafers – <strong>POCl3 diffusion with deadlayer removal</strong> – SiNx:H anti reflective coating – Al BSF - screen printed contacts. Cell size 125 mm X 125 mm. Efficiency of 9.24% on n-type Si wafers (small area cells) with spin-on-dopant sources for doping.</td>
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<tr>
<td><strong>Texturization</strong></td>
<td>Texturization using SF6 based reaction ion etching; a novel lithography free inverted pyramid texturization process demonstrated.</td>
<td>Random pyramid texturization using KOH.</td>
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<tr>
<td><strong>Anti reflective coating</strong></td>
<td>A two layer SiNx:H layer was developed in ICP-CVD that is thermally stable and provides excellent surface passivation.</td>
<td>A two layer SiNx:H layer was developed in PECVD that provides excellent surface passivation.</td>
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<tr>
<td><strong>Phosphorous diffusion process</strong></td>
<td>Deadlayer removal confirmed by SIMS analysis. A process for diffusion without deadlayer formation developed. A selective emitter process was developed by combining a diffusion process with deadlayer and reactive ion etching.</td>
<td><strong>POCl3</strong> diffusion with deadlayer removal developed.</td>
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<tr>
<td><strong>Boron diffusion process</strong></td>
<td>Spin-on-dopant and boric acid based processes are developed with sheet resistance of 45 – 55 Ω/sq. and 70 – 95 Ω/sq.</td>
<td>Improved process with low concentration of boron precipitates in the boron rich layer.</td>
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<tr>
<td><strong>Surface passivation</strong></td>
<td>Al2O3 deposition and post deposition anneal processes optimized to obtain a surface recombination velocity of 42 cm/sec. SiNx:H film deposition process optimized to obtain a surface recombination velocity of 1.9 cm/sec.</td>
<td>Further optimization of Al2O3 sputtering to obtain a surface recombination velocity of 30 cm/sec. A Novel low temperature plasma oxidation process developed for surface passivation with SRV of 50cm/sec.</td>
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</table>
**Cell fabrication and results:**

In the previous year, we reported cells with 14.9% efficiency on 3.5 mm X 3.5 mm small area cells. These cells implemented phosphorus doped emitters by solid source diffusion, device separation by oxide grown in the wet ambient, Ti/Pd/Ag front contacts, thermally stable SiNx: H anti reflective coating and Al back contacts. The front surface was not textured. The progress during 2012 – 2013 are described below. A key highlight is that all the key processing and characterization tools are now being used process optimization and to gain a better understanding of the cells and processes.

Boron doped mono crystalline silicon wafers (p-type) of dimensions 125 mm X 125 mm and thickness 180±20 μm with bulk resistivity of 0.5-3 Ω cm and the carrier life time in the range of 0.75 - 0.85 μs were used for fabricating silicon solar cells. In order to keep track of electrical parameter’s progress and process optimization, process recipes of the conventional silicon solar cell were kept unchanged except the process recipe of phosphorous (P) doping. As per the conventional silicon solar cell process flow, first these wafers were subjected to the saw damage removal (SDR) and alkali texturization processes by using the required composition of potassium hydroxide (KOH) and isopropyl alcohol (IPA) with deionized water. The scanning electron microscope (SEM) and Zeta 3D microscope studies on these wafers reveal that the texture is uniform with average pyramid size of around 4μ. The images are shown in Fig. 2.2.

![Texture uniformity, assessed using 3D optical microscopy (left) and the cross sectional SEM of texture (right).](image)

The textured wafers were exposed to RCA cleaning processes to remove the organic and metallic contaminants. After removing the organic and metallic contaminations, these wafers were doped with phosphorous in such a way to get the sheet resistance in the range of 30-35 Ω/sq. and 45-55 Ω/sq. by carrying out two trials. The phospho silicate glass (PSG) formed at the edges and also at the surface of the silicon wafers, were removed by plasma edge isolation (PEI) and with 2% HF wash respectively. In order to make use of the maximum incident light and for the hydrogen passivation, SiNx was coated of thickness ~ 78 nm and refractive index ~ 1.96 by employing plasma enhanced chemical vapour deposition (PECVD) technique. The back aluminum of about 850 mgm was deposited using conventional screen printing technique followed by the drying of printed aluminum at 250 °C around 7 minutes. Consequently the front silver contacts were made with paste lay down of 105 mgms. The FC printed cells were again dried at 250 °C around 7 minutes. The completed cells were cured by employing the rapid thermal annealing process (RTA) to realize the contacts. The temperature profile of rapid thermal annealing process was designed in such a way that the burn out and firing processes happened in a single route. The burn out process was done in the temperature range of 300-400 °C to drive out the organic binders and it was carried out in the nitrogen and oxygen ambient. The firing process was carried out in the temperature range of 800-860 °C so that the front silver contacts diffused the silicon nitride layer and adheres to the underlying silicon. The images of the completed cell are as shown in Fig. 2.3. The IV characteristics of the fabricated cells are shown Fig. 2.4 and the electrical data are tabulated in Table 2.2.
Fig. 2.3: Images of the completed cells.

Fig. 2.4: IV Characteristics of the cells.

Table 2.3: Electrical data of the cells.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Sample No</th>
<th>Sheet Resist. (Ω/sq.)</th>
<th>Rs (mΩ)</th>
<th>Rsh (Ω)</th>
<th>Jsc (mA/cm²)</th>
<th>Isc (A)</th>
<th>Voc (mV)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
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<tr>
<td>1</td>
<td>1</td>
<td>30</td>
<td>15.36</td>
<td>3.71</td>
<td>31.36</td>
<td>4.89</td>
<td>601.7</td>
<td>66.2</td>
<td>12.5</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>32.5</td>
<td>8.96</td>
<td>10.87</td>
<td>30.97</td>
<td>4.83</td>
<td>600.2</td>
<td>71.4</td>
<td>13.3</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>38</td>
<td>36.48</td>
<td>2.41</td>
<td>31.09</td>
<td>4.85</td>
<td>600.6</td>
<td>54.6</td>
<td>10.2</td>
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</table>
Characterization and its analysis were carried out to understand the process which helps to improve the electrical performance of the fabricated solar cells.

**Carrier Life Time measurement**

In order to understand the variation of carrier life time in each process, the carrier life time was measured after each and every process and are shown in Fig. 2.5.

From Fig. 2.5 it has been observed that the carrier life time is increasing with respect to the process and the increase in carrier life time is reasonably good after doping. However it is clearly showing that there is further scope for increasing efficiency by starting the process with higher carrier life time.

**Reflectivity**

Reflectivity of the textured wafer and the anti-reflective coated cell is as shown in Fig. 2.6. The average reflectivity calculated for the textured wafer and AR coated cell are 16% and 5% respectively. Normally the reflectivity of the textured wafer is in the range of 9-11% but in our case the reflectivity of the textured wafer is higher than the reported conventional process. This may be due to the IPA evaporation during the process, which yields poor texturization. This will be optimized by controlling the IPA evaporation and the action on controlling the evaporation is underway.

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<tr>
<td>2</td>
<td>4</td>
<td>44</td>
<td>42.24</td>
<td>2.28</td>
<td>31.3</td>
<td>4.88</td>
<td>593.7</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>47</td>
<td>58.88</td>
<td>3.06</td>
<td>31.86</td>
<td>4.97</td>
<td>598.7</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>49</td>
<td>66.56</td>
<td>1.58</td>
<td>30.62</td>
<td>4.78</td>
<td>601.6</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>57</td>
<td>80.64</td>
<td>0.75</td>
<td>30.77</td>
<td>4.8</td>
<td>594.8</td>
</tr>
</tbody>
</table>

Fig. 2.5: Carrier Life Time of the Processed Wafers.

From Fig. 2.5 it has been observed that the carrier life time is increasing with respect to the process and the increase in carrier life time is reasonably good after doping. However it is clearly showing that there is further scope for increasing efficiency by starting the process with higher carrier life time.

Fig. 2.6: Reflectivity of the textured wafer and the anti-reflective coated cell.
**SEM Analysis**

**Front Side of the Cell**

Elemental mapping and the cross sectional analysis on the front side of the completed cell has been carried out and is shown in Fig. 2.7 and Fig. 2.8.

From the figures it has been observed that the silver was diffused at the front side. But by seeing the elemental composition, further firing optimization is needed to increase the silver diffusion, which will give the low Rs. Also the optimized firing will give the better aspect ratio which will increase the current, fill factor and thus the efficiency. The present aspect ratio of the grid line is 15.96% and the cross section of the grid line is depicted in Fig. 2.9. The expected aspect ratio of the grid line for the current screen specifications and for the current paste should be greater than the 25%. Hence it is our target to optimize the printing by changing the snap off, squeegee pressure and speed.
SEM Analysis
Rear Side of the Cell
Cross sectional and elemental analysis on the completed cell has been carried out to know the diffusion of pastes, Si-Al eutectic and P+ layer. The morphology and the elemental analysis of the back side of a fired mono crystalline Si solar cell are as shown in Fig. 2.10 and Fig. 2.11.

From figures, it has been observed that Al has properly deposited/printed on the Si surface and the thickness of this region is around 28 µm. The interface waviness is due to texturing of the cell. Alloyed region (Si-Al eutectic) has grown which consists of Si-rich and Al-rich phases and is around 5-6 µm of thickness. Also in general the Si-Al eutectic is always around 9-10 µm. But in our case it is around 5 µm hence further firing is needed to make thicker Si-Al eutectic.

Light Beam Induced Current and Shunt Scan
Light beam induced current and shunt scan measurements were carried out on the poor performance cell to understand the reason for its poor performance so that the process window will be narrowed down to avoid these defects. LBIC scan and shunt scans are shown in Fig. 2.12. From LBIC it is observed that current generation is more or less uniform however at centre it is low compared to other areas. This may be due to the wafer defects which have been occurred during the ingot manufacturing. Instability in temperature during diffusion exposes these defects. The shunt scan has been carried out on the same cell and it is clearly observed that the cell has poor shunting. This gives us an alarm to relook the diffusion and metallization process.

Further Process Optimization to Enhance the Efficiency

- Starting the process with slightly higher carrier life time wafers
- Reducing the weighted reflectance by optimizing the texture process
- Optimizing the doping process with temperature profile
- Increasing the shunt resistance either by changing the plasma power or increasing the process time during edge isolation
- Printing optimization by adjusting the printer parameters
- Firing optimization with different peak temperatures

N-type c-Si solar cells

n-type c-Si has a lot of advantages over p-type c-Si due to gettering effect of phosphorus and higher minority carrier lifetime values for the same resistivity. However, there are problems in B- diffusion which results difficulties in emitter formation in n-type solar cells. Formation of boron precipitates is one of them. In this work, we have studied different B- diffusion phenomena with spin on dopant source (SOD), studied B-precipitates to reduce its concentration at the emitter surface and optimized different process steps to fabricate n-type c-Si solar cells. The work progress seen in the last year is mentioned below.

Optimization of B- diffusion process and minimization of boron precipitates on emitter surface

Boron diffusion was studied at different temperatures from 850°C to 950°C for time periods like 10min, 15min, 20min and 30min and sheet resistance values were measured after each process. Formation of boron precipitates, seen after deglazing the emitter surface with 2%HF were tried to reduce with three different processes. They are- reducing the dopant concentration before diffusion process, in-situ oxidation during ramping down of the diffusion process and HF: HNO₃ solution treatment after deglazing and they could together reduce the B- concentration (BRL) from 56% atomic percentage at the surface to 0% values as shown in the EDAX analysis of Table 2.4.

The process step for diffusion was optimized at temperature 850°C for time duration of 10mins. The three process steps used in this work to reduce boron precipitates (called boron rich layer, BRL) could give least boron precipitates at the emitter surface and with these process steps the emitter was optimized for sheet resistance values of 55±5 Ω/sq.
Table 2.4: EDAX elemental analysis comparing boron concentration at the emitter surface after deglazing and control process steps shows 0% of boron at the emitter surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(With no steps to reduce boron precipitates)</td>
<td>(With process control steps to reduce boron precipitates at the emitter surface)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boron</td>
<td>36.95</td>
<td>55.91</td>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>Carbon</td>
<td>7.65</td>
<td>10.42</td>
<td>4.61</td>
<td>10.16</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3.19</td>
<td>3.27</td>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>Silicon</td>
<td>52.20</td>
<td>30.40</td>
<td>95.39</td>
<td>89.84</td>
</tr>
</tbody>
</table>

The minority carrier lifetime values corresponding to with or without BRL are shown in Table 2.5. The carrier lifetime was found to be little reducing after removing BRL.

Table 2.5: Sheet resistance and minority carrier lifetime values after deglazing and removal of BRL.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sheet resistance values after deglazing with 2% HF (contains boron precipitates at the surface)</th>
<th>Minority carrier lifetime value after deglazing (in µsec, measured at carrier density $10^{14}$ carriers/cm$^3$)</th>
<th>Sheet resistance value after chemical (2% HF-HNO$_3$-2%HF) treatment to remove BRL (in Ω/sq) (contains almost zero boron precipitates at the emitter surface)</th>
<th>Minority carrier lifetime after 2%HF-HNO$_3$-2%HF treatment (in µsec, measured at carrier density $10^{14}$ carriers/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With diluted SOD source (8:1) prior to diffusion</td>
<td>45± 5</td>
<td>21.3</td>
<td>55± 5</td>
<td>20.7</td>
</tr>
<tr>
<td>Only SOD without any dilution</td>
<td>43± 5</td>
<td>20.3</td>
<td>49± 2</td>
<td>20.2</td>
</tr>
</tbody>
</table>

Solar cell efficiency without texturing, front passivation layer and ARC

Optimization of output characteristics of solar cells with boron spin on dopant (BSOD) diffusion at temperature 850°C for 10mins and in-situ oxidation at 700°C for 20mins was done for $V_{oc}$ values in between 470-490mV and $I_{sc}$ values in the range 37- 39.8mA/cm$^2$. The efficiency values of the cells were in the range 9-10%. The IV and PV characteristics of a typical cell is shown in Fig. 2.13.

![JV and PV characteristics of BSOD diffused sample](image)

Fig. 2.13: JV and PV plot of BSOD diffused samples for $V_{oc}$ = 480mV, $I_{sc}$ = 39.6mA/cm$^2$, FF= 0.48, $R_{shunt}$ = 90
Unit Process Development:

DOPING MODULE OPTIMISATION: POCl\textsubscript{3} diffusion Optimization

POCl\textsubscript{3} diffusion is being optimised for the fabrication of the emitters in the P type solar cells. Once the furnace has been commissioned the standard recipes gave huge variation in the doping [variation in the Phosphosilicate glass (PSG) thickness] across the wafer as well as across the multiple wafers of the boat as shown in Fig. 2.14 (left). The furnace hardware and the wafer placement has been modified to provide a more uniform doping. The thickness of the phosphosilicate glass is now more uniform as seen in Fig. 2.14 and Fig. 2.15.

Non Uniformity in PSG glass formation after POCl\textsubscript{3} diffusion issue greatly reduced

Before making the changes
Variation (Rsh) - 50 to 400 ohm/square

Some trial after making changes in the Exhaust*, wafer placement pattern.

Fig. 2.14 : Non uniform PSG layer formed across the 4 (5” pseudo square) process wafers indicative from the colour (left). After optimization of the tool and process (right).

Fig. 2.15: Sheet resistance distribution before and after the optimization of the doping tool and process.
Surface passivation:

A novel low temperature plasma oxidation process was developed during the last year for surface passivation of silicon. We have carried out further optimization of the Al₂O₃ suprtter deposition process reported last year.

**Low Temperature Plasma Grown Oxides for Surface Passivation of Silicon Solar Cells:**

RCA cleaned, p-type, CZ <100> Si wafers with resistivity of 4-7 Ω-cm was chosen as the substrate for the experiments. The thin oxy-nitride was grown in an ICP system using N₂O plasma at a temperature of 320°C. Plasma oxides growth was also carried out at other ambient such as O₂, O₂ + Ar, and O₂ + N₂. The plasma oxidation process was carried out at a power of 1000W for 10 minutes. The thickness of the films was measured using a spectroscopic ellipsometer, and FTIR studies were conducted on as grown oxy-nitride/oxide samples to check for chemical composition of the film, and its dependence on the gas flow. A silicon nitride film (SiNₓ:H) deposited using a silane (SiH₄) - nitrogen (N₂) mixture in an ICP-CVD was used as a capping layer. The interface state density and the fixed oxide charges were studied by using Metal Oxide Semiconductor (MOS) capacitors fabricated on p-type silicon wafers, with Aluminum as the front and back contacts. The lifetime studies were carried out on n-type FZ wafers with a resistivity of 1Ω-cm and thickness of 300µm using a WCT lifetime tester from Sinton instruments. For lifetime studies the stacks were deposited on both sides of the wafers. Annealing of the samples was carried out in N₂ ambient using a rapid thermal processing system. Usage of a plasma oxy-nitride film prior to the nitride deposition leads to an improvement in the surface passivation properties. The lifetime improved from 10.5µs for the silicon nitride passivation to 18.8µs when the oxy-nitride film was grown at 4mT chamber pressure and capped with the same silicon nitride. The lifetime improved further to 82.5µs for the oxy-nitride film grown at 25mT and capped with the same silicon nitride film. The usage of an interfacial oxy-nitride film thus improves the passivation of the silicon surface. Fig. 2.16 shows the variation of the lifetime with minority carrier density. Surface passivation of the stack was studied by progressively annealing the stack at various temperatures ranging from 400°C to 800°C in N₂ ambient for 2s. The film showed a minimum surface recombination velocity of 50cm/s at 400°C which degraded upon further annealing to 493cm/s at 800°C. The lifetime value remains less than 100cm/s for temperatures less than 550°C, as can be seen in fig 2.17. The stack exhibited improved thermal stability as compared to single layer silicon nitride film and thus opens new avenues in the area of low temperature plasma oxides/oxy-nitrides for the surface passivation of silicon solar cell.

![Fig. 2.16 Variation in lifetime when an interfacial oxy-nitride is grown prior to deposition of SiNₓ.](image1)

![Fig. 2.17. Variation in SRV at a minority carrier density of 10¹⁵cm⁻³ during progressive anneal of 2secs each.](image2)

FTIR data for oxides/oxy-nitride grown in different plasmas are shown in Fig. 2.18 Si-O-Si stretching mode trough is seen to shift from 1100 cm⁻¹ to 1063 cm⁻¹ on addition of argon or nitrogen. For the samples grown in only oxygen ambient, a prominent peak at 515 cm⁻¹ can be seen, which corresponds to symmetric stretching mode vibrations of Si-O-Si defect molecule. It is reported that the trough is generated due to precipitation of oxygen within silicon. Upon adding argon, the intensity of the 515 cm⁻¹ trough comes down, while a trough indicating Si-Si unsaturated bonds at 615 cm⁻¹ is observed. For samples grown in N₂O ambient, the trough at 515 cm⁻¹ is absent, while a deeper trough at 610 cm⁻¹ is observed. However for samples grown in N₂O ambient, there are no troughs seen at 515 cm⁻¹ or 615 cm⁻¹. It is also reported that FTIR peaks at 1106 cm⁻¹ corresponds to interstitial oxygen in silicon. The same is manifested as troughs in case of films grown in O₂ and N₂O ambient. However for films grown in O₂+N₂ and O₂+Ar ambient, a sharp peak is seen in place of a trough. The reason for this anomaly is not clearly understood. In order to understand the role of various oxygen species towards the formation of the interstitial oxygen troughs, the plasma characteristics were investigated using optical emission spectroscopy. In order to assess how the ambient would influence the growth properties, plasma characteristics were studied using optical emission spectroscopy (OES). The results of the same are shown in
Fig. 2.19. OES revealed two major atomic lines of oxygen at 777 nm and 844 nm corresponding to the atomic transitions $3p^1P – 3s^1S$ and $3p^3P – 3s^3S$ respectively. When Argon was introduced, the intensity of the oxygen related peaks remained same. On adding nitrogen, the intensity of the peak at 777 nm remained same, while the intensity of the peak at 844 nm decreased. For nitrous oxide plasma, both the 777 nm, and 844 nm peaks came down in magnitude indicating lesser amount of oxygen radicals. From the FTIR and the OES spectrum, it could be seen that an increase in atomic oxygen intensity can result in an increase in the presence of interstitial oxygen.

SRV was calculated assuming infinite bulk lifetime, at a minority carrier density of $10^{15} \text{ cm}^{-3}$. It was seen that the films grown in $O_2$, $O_2 + Ar$, $O_2 + N_2$ ambient showed SRV $> 1000$ cm/s as can be seen in Fig. 2.20. On annealing the samples at 400°C, passivation was seen to improve, with the sample grown in $O_2 + N_2$ ambient showing a SRV of 582 cm/s. However for samples grown in $N_2O$ ambient, the SRV was found to be 148 cm/s which upon annealing at 400°C came down further to 50 cm/s indicating a well passivated surface. Lifetime study, reveal the role played by interstitial oxygen and Si-Si unsaturated bonds in degrading the surface passivation. Plasma oxide grown in $N_2O$ ambient resulted in the lowest SRV, and did not show any SiO$_4$ modes, and very low amount of Si-Si unsaturated bonds. The next best passivation was shown by film grown in $O_2 + N_2$ ambient. No interstitial oxygen signature at 515 cm$^{-1}$ was found from FTIR, but it showed a large amount of unsaturated Si-Si bonds. The improvement in passivation upon annealing can be attributed to the diffusion of hydrogen from the bulk of SiN$_x$:H towards the interface. However this effect is seen to be secondary to that due to the composition of the film. The firing stability of the film was investigated by annealing the stacks to 800°C and is shown in Fig. 2.21. It was observed that the passivation quality degraded significantly for all films grown in oxygen ambient. However, the film grown in nitrous oxide showed a much better passivation as compared to the films grown in oxygen ambient even after firing at 800°C.

The role of ammonia addition on the plasma oxidation process was also investigated. OES studies had revealed the presence of atomic hydrogen in plasma composed of a mixture of NH$_3$ and $N_2O$. The aim of the study was to understand whether the atomic hydrogen can take part in improving the interface properties. For the plasma grown films, an interface state density in the order of $10^{12} \text{ ev}^{-1}\text{cm}^{-2}$ was observed, irrespective of the ambient used for the growth. However, it was observed that the films grown in $N_2O$ ambient showed lower $D_{it}$ and
higher $Q_{ox}$ value as compared to films grown in $N_2O + NH_3$ ambient. In order to improve the interface by potential hydrogen passivation, the plasma grown films were capped with hydrogenated silicon nitride films, and the C-V analysis was carried out. The interface state density came down by an order of magnitude to $\sim 4 \times 10^{10}$ ev$^{-1}$cm$^{-2}$ for the stack based on plasma oxide grown in nitrous oxide. However, for the stack based on $N_2O + NH_3$ ambient, the interface state density was found to be $\sim 1.7 \times 10^{11}$ ev$^{-1}$cm$^{-2}$ after annealing at 400$^\circ$C in $N_2$ ambient. The improvement in interface state density can be attributed to potential hydrogen based passivation of the interface upon annealing the films. It is reported that ammonia plasma exposure can lead to breakage of Si-O bonds within SiO$_2$ film. It is also reported that hydrogen plasma exposure at room temperature can also result in an increased interface state density. As was seen from the optical emission spectrum for NH$_3$ + N$_2$O ambient, the atomic hydrogen within the plasma may also have contributed in creating a defective interface. The fixed charge density for the stack based on N$_2$O was found to be $\sim 1.8 \times 10^{12}$ cm$^{-2}$, while for the stack based on N$_2O + NH_3$, it was found to be $\sim 2.5 \times 10^{12}$ cm$^{-2}$ for the stack based on N$_2$O, whereas it increased to $\sim 2 \times 10^{12}$ cm$^{-2}$ for the stack based on N$_2O + NH_3$, as seen in Fig. 2.22.

Fig. 2.22: Variation in $D_{it}$ and $Q_{ox}$ before and after anneal for the stack showing the impact of ammonia addition.

Al$_2$O$_3$ deposited by pulsed-DC sputtering for surface passivation

We present the effect of deposition power density (PD) on the quality of p-type silicon surface passivation by pulsed – DC (p – DC) reactive sputtered Aluminum oxide (AlO$_x$) films. The high quality surface passivation is related to the activation of both field - effect and chemical passivation i.e. high fixed oxide charges ($Q_f$) in the dielectric and low interface state density ($D_{it}$). The process is carried out at PD between 0.13 and 1.3 W. cm$^{-2}$. The films were subjected to post - deposition annealing (PDA) in N$_2$ + O$_2$ ambient in 79:21 ratios to mimic dry air at 520$^\circ$C.

Fig. 2.23 shows the deposition rate for different PD. The deposition rate increases with increase in PD. High deposition rate of $\sim 5$ nm. min$^{-1}$ is observed at PD of 1.3 W. cm$^{-2}$. A refractive index (RI) of 1.6 is measured for all the films after annealing. Film thickness ($t_{ox}$) of 16 nm and 20 nm were measured for PD of 0.13 W.cm$^{-2}$ and 1.3 W. cm$^{-2}$ respectively.

Fig. 2.23: Deposition rate for as - deposited films at different PD conditions.
Fig. 2.24 (a) and (b) shows the extracted negative $Q_f$ from capacitance – voltage (CV) and $D_{it}$ from conductance - voltage (GV) measured plot, respectively. A consistent increase in $Q_f$ is observed with increasing power for as - deposited films. The films show high negative $Q_f$ of $6 \times 10^{12}$ cm$^{-2}$ after annealing. Almost similar values of negative $Q_f$ is observed for all the PD conditions. The $D_{it}$ is independent of deposition power for both as - deposited and annealed samples. The $D_{it}$ decreases by an order of magnitude to about $2 \times 10^{11}$ cm$^{-2}\cdot eV^{-1}$ after annealing.

Fig. 2.24: (a) negative fixed oxide charges ($Q_f$) and (b) interface state density ($D_{it}$) for as - deposited and annealed films at different PD conditions.

Fig. 2.25 (a) shows the measured effective life-time ($\tau_{\text{eff}}$) and Fig. 2.25 (b) shows the calculated value of effective surface recombination velocity ($S_{\text{eff}}$) at the two extreme deposition powers of 0.13 and 1.3 W. cm$^{-2}$, measured on p - type FZ wafers. AlO$_x$ films are deposited on both sides of the FZ wafers.

Fig. 2.25: (a) $\tau_{\text{eff}}$ and (b) $S_{\text{eff}}$ for different excess minority carrier concentration ($\Delta n$) measured on as-deposited and annealed films for PD of 0.13 and 1.3 W.cm$^{-2}$.

A significant improvement in $S_{\text{eff}}$ is observed after annealing. Very low $S_{\text{eff}}$ of 30 cm. s$^{-1}$ is obtained for AlO$_x$ film deposited at high PD of 1.3 W. cm$^{-2}$, whereas at low PD of 0.13 W. cm$^{-2}$ the surface passivation degrades to $S_{\text{eff}}$ of 107 cm. s$^{-1}$. We have observed an increase in effective lifetime with increase in process power, while Zhang et al. (IEEE J. PV, 2012) reported a contrary trend in the case of RF sputtered AlO$_x$ films. The $S_{\text{eff}}$ values are different at two PD conditions, in spite similar negative $Q_f$ and $D_{it}$ values after PDA as shown using electrical characterization. The only difference is the large distribution of $D_{it}$ at low PD of 0.13 W. cm$^{-2}$. Thus from the electrical characterization we were not be able to draw any conclusion for difference in $S_{\text{eff}}$.

We have also analyzed an elemental composition of these films using X- ray photo - spectroscopy (XPS) measurement, as shown in Fig. 2.26 (a), (b), (c) and (d). The depth profile of different elements present in the film is plotted as atomic concentration versus etch time. As - deposited films are shown in Fig. 2.26 (a) and (c) for different PD deposition, the O/Al ratio is ~ 1 in AlO$_x$ region. However after PDA, an increase in O concentration of the films and hence the O/Al ratio approaches to the stoichiometry. An increase in O concentration is due to the re-oxidation of the film during annealing in N$_2$ + O$_2$ gas mixer. The stoichiometric AlO$_x$ film with O/Al ratio ~ 1.5 was obtained at high PD deposition of 1.3 W. cm$^{-2}$ after annealing. While at low PD deposition, the film is tends to be sub - stoichiometric after annealing. In all the conditions a peak at the
A binding energy of 103 eV is observed in the IL region, which is corresponding to SiO bond. Also the concentration of Al is seems to decrease gradually in IL region. This signifies the IL is in Al silicate form. Thus an improved surface passivation for high PD deposition can be related to the stoichiometric AlO\textsubscript{x} film, with the O/Al ratio \approx 1.5.

Fig. 2.26: XPS depth profile of (a) as-deposited, (b) annealed AlO\textsubscript{x} films deposited at PD of 0.13 W. cm\textsuperscript{-2} and (c) as-deposited, (d) annealed AlO\textsubscript{x} films deposited at PD of 1.3 W. cm\textsuperscript{-2}.