Surface Passivation Schemes for High-Efficiency c-Si Solar Cells - A Review

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To reduce the cost of solar electricity, the crystalline-silicon (c-Si) photovoltaic industry is moving toward the use of thinner wafers (100 μm to 200 μm) to achieve a high efficiency. In this field, it is imperative to achieve an effective passivation method to reduce the electronic losses at the c-Si interface. In this article, we review the most promising surface passivation schemes that are available for high-efficiency solar cells.

Keywords: Passivation, SiO₂, SiNx, Al₂O₃

1. INTRODUCTION

Over the past decade, the annual growth rate of solar photovoltaic (PV) technology is approximately 50%, whereby Si-wafer-based PV technology accounted for approximately 90% of the total production quantity. The material usage for c-Si solar cells has been reduced significantly during the last five years from approximately 16 g/Wp to 6 g/Wp due to an increased efficiency and thinner wafers.

The corresponding reduction of manufacturing costs can be primarily attributed to economy of scale effects and technological progress. The reduced wafer thickness and manufacturing costs mean that the new technologies are very simple, cost effective, and highly efficient. To achieve a high efficiency, it is necessary to reduce both the loss of photo-generated carriers and the loss of sunlight entering into the cell [1].

To improve the effective minority-carrier lifetime, a passivation layer is used to reduce the surface recombination of the photo-generated carriers. An anti-reflection coating (ARC) is used to reduce the optical loss caused by the reflection at the air/c-Si interface. Reducing the electrical losses at the c-Si surface is more challenging than reducing those of optical losses. In this paper, a surface-passivation scheme is reviewed for high-efficiency c-Si-based solar cells.

2. SURFACE PASSIVATION TECHNIQUES

While the application of thinner c-Si wafers as the base material for high-efficiency solar cells has become a trend, corresponding electrical losses at the c-Si surface have become an increasing concern (Fig. 1 depicts the predicted reduction in wafer thickness); consequently, the recombination losses at the semiconductor interface must be minimized. Recombination losses at the semiconductor interface can be reduced by the following two passivation methods: chemical passivation and field-effect passivation. The latter can be undertaken using the charge...
induction in the Si-surface regions by means of a built-in electric field, viz. the front-surface field and back-surface field (BSF). The two passivation methods are discussed in the subsequent section of this paper.

Chemical passivation is achieved by reducing the number of defect states (D\text{d}) that are present at the Si surface, either by the hydrogen passivation provided by plasma deposition or by forming gas annealing (FGA). Chemical passivation is effective for both n- and p-type c-Si, since it reduces the surface defects by saturating the Si dangling bonds; therefore, the conversion efficiencies of both the n- and p-type c-Si-based solar cells can be improved. This strategy is much more sensitive to the presence of defects at the surface, and is usually carried out by depositing or growing a passivation layer over the c-Si surface.

Apart from chemical passivation, surface recombination can also be reduced by field-effect passivation by depositing a charged layer (for example, SiNx) over the c-Si, or by forming an electric field in a way that pushes away the minority carriers (i.e. toward the bulk c-Si), thereby preventing them from reaching the c-Si surface; therefore, the surface recombination is reduced.

The SRV can be related to thermal velocity (ν\text{th}) and surface trap density, as follows:

\[ S = \frac{U_{\text{r}}}{\Delta n_{\text{r}}} \]  

(3)

where S is the SRV and Δn\text{r} is the excess carrier density at the surface.

When the semiconductor surface is in the flat-band condition, the excess concentrations of electrons (Δn\text{e}) and holes (Δn\text{h}) are equal under illumination; then, we can use Δn\text{e} to represent the excess carrier concentration at the surface. Note that Δn\text{e} is constant in the semiconductor from the bulk to the surface, as the energy bands are flat [5]. SRV can also be calculated from the following expression:

\[ S(\Delta n_{\text{e}}) = \frac{n_{\text{e}} + p_{\text{e}} + \Delta n_{\text{e}}}{S_{\text{e}}} \]  

(4)

where ne and ph are the electrons and holes of the equilibrium concentration, respectively. According to the above equation, SRV is a function of parameters, injection level (ratio between
The high-quality interface between thermally grown SiO2 and c-Si contributes significantly to a high efficiency [22,23]. Thermal SiO2 leads to a very low SRV after the annealing process [16,23-26]. The hydrogen that is introduced during annealing passivates electronically active defects with defect densities in the region of 10^{13} cm^{-2} eV^{-1} [23,27] and fixed charges (Qf) in the range of 10^{10} cm^{-2} to 10^{11} cm^{-2}. In addition, the SiO2/Al stack at the rear side of the cell acts as an excellent reflector for near-band-gap photons and significantly improves the light-trapping properties, thereby also improving the short-circuit current of the cell. A Seff of less than 3 cm/s was achieved by M. Kerr, et al. on FZ wafers [25], and a Seff of less than 20 cm/s was obtained on n-type CZ wafers [28]. The SRV increases with the doping density due to the higher presence of their defects at the interface, and this trend is represented in Fig. 3. Zhao, et al. obtained a high-efficiency of 25% with a SiO2-passivation scheme on their PERL cell concept [29-31]. Since oxidation usually takes place at very high temperatures and needs a considerably long time duration, it is not widely used in industrial solar cell mass production in the current time period.

4.3 Passivation materials

4.3.1 Thermal SiO2

The high-quality interface between thermally grown SiO2 and c-Si contributes significantly to a high efficiency [22,23]. Thermal SiO2 leads to a very low SRV after the annealing process [16,23-26]. The hydrogen that is introduced during annealing passivates electronically active defects with defect densities in the region of 10^{13} cm^{-2} eV^{-1} [23,27] and fixed charges (Qf) in the range of 10^{10} cm^{-2} to 10^{11} cm^{-2}. In addition, the SiO2/Al stack at the rear side of the cell acts as an excellent reflector for near-band-gap photons and significantly improves the light-trapping properties, thereby also improving the short-circuit current of the cell. A Seff of less than 3 cm/s was achieved by M. Kerr, et al. on FZ wafers [25], and a Seff of less than 20 cm/s was obtained on n-type CZ wafers [28]. The SRV increases with the doping density due to the higher presence of their defects at the interface, and this trend is represented in Fig. 3. Zhao, et al. obtained a high-efficiency of 25% with a SiO2-passivation scheme on their PERL cell concept [29-31]. Since oxidation usually takes place at very high temperatures and needs a considerably long time duration, it is not widely used in industrial solar cell mass production in the current time period.

4. SURFACE PASSIVATION

4.1 Front-Surface passivation

The thermal growth of silicon dioxide (SiO2) is the most effective surface passivation technique for c-Si solar cell. The SiO2 growth formed at a high temperature (>900 °C) possesses a low interface-state density (1 x 10^{11} cm^{-2} eV) [6,7]. A high temperature, however, degrades the bulk life time and stability of the passivated surface significantly; therefore, this technique is not suitable for low-cost industrial processes [8]. A record-low, effective surface-recombination velocity (Seff) of 4 cm/s was obtained on 1 Ω-cm p-type c-Si wafers by using PECVD SiN [9-12]. The field-effect passivation provided by the positive interface charges, the properties of the captured cross-sections of dominant defects, the adjustable ARC refractive index, and the hydrogen passivation of bulk defects made SiN a superior passivation layer over the other passivation materials [5,8,13,14].

4.2 Rear-Surface passivation

In 1972, Mandelkorn, et al., introduced the rear-surface passivation of Si solar cells, whereby a homojunction was used to suppress the minority carrier concentration across the full back surface, and this technique has since been referred to as “BSF” [15]. To further improve efficiency, enhanced rear-passivation techniques beyond the simple full area of Al-BSF is a prerequisite. In 1989, the first so-called “passivated-emitter and rear cell” (PERC) was fabricated by Blakers et al. [16]. These cells feature a dielectric passivation with locally defined contact openings and a full-area metallization on the rear. Shortly afterward, the same group introduced the “passivated emitter, rear locally diffused” (PERL) cell [17] with thermal SiO2, that gave the lowest SRV and a high-efficiency [18]. In addition to SiN:H [8,21], atomic-layer deposition (ALD) of Al2O3 gives an SRV at lower temperatures that is similar to that of SiO2 [19,20].
4.3.2 SiO$_x$

To overcome bulk lifetime degradation, a low-temperature SiO$_x$ deposition by PECVD has been studied by different groups [33-35] for surface passivation. Another option for the synthesis of SiO$_x$ is chemical oxidation of the Si surface using nitric acid (HNO$_3$). A drawback of this method is that it can only produce a SiO$_x$ with a thickness of a few nanometers. In general, the level of passivation induced by a single-layer SiO$_x$ synthesized at low temperatures is lower than that obtained by thermal oxidation processes. Mihailetchi et al. successfully fabricated a cell with an ultrathin SiO$_x$ layer by soaking the Si wafers in a solution of HNO$_3$ prior to the deposition of SiN$_x$ as an ARC for effective boron-emitter passivation, whereby the $V_{oc}$ is 627 mV and the efficiency is 18.3% [36].

4.3.3 a-SiN$_x$:H

Over the past decade, PECVD-deposited SiN$_x$ has been the dominant surface passivation method for the Si photovoltaic industry [19,37,38]. SiN$_x$ is deposited using a SiH$_4$ and NH$_3$ gas mixture at a temperature of approximately 200°C, with the process pressure varying between 0.1 and 1 mbar. In direct PECVD, the process gasses are excited by an alternating electromagnetic field where the wafers form the electrodes. In batch systems, the wafers are loaded into graphite boats acting as electrodes and the wafers are processed in a quartz tube. An alternative approach is the remote PECVD process; in this method, plasma excitation is spatially separated from the wafer. A linear plasma source is used wherein microwaves from an external source are coupled in the process chamber. The wafers are loaded onto carbon-fiber-composite carriers and are moved horizontally through the plasma chamber. Direct and remote PECVD systems have the highest market share in the photovoltaic industry because of their high throughput and low process temperatures. The films contain a relatively large amount of hydrogen (10 at.% to 15 at.%) that mainly originates from the SiH$_4$.

By varying the SiH$_4$ and NH$_3$ compositions, both built-in charges and the surface states can be varied. Here, field-effect passivation is achieved by producing a high concentration of charges in the dielectric that originates from a number of defect states that are formed either at the nitride/c-Si interface or in the bulk of the film. For textured and polished surfaces passivated with SiN$_x$, measured $S_{rec}$ as a function of the excess electron concentration is depicted in Fig. 4.

The SiN$_x$ film, with a refractive index (n) of 2, results in optimal antireflection properties. Nitrogen-rich SiN$_x$ films where n=2 provide a reasonable-to-high level of passivation. When the nitrogen content is relatively low (i.e., in SiN$_x$, x>y), the high level of passivation is mainly governed by chemical passivation. Alternatively, for a high nitrogen content, the films induce a significant amount of field-effect passivation with fixed charge densities in the region of 1.012 cm$^{-2}$. The presence of these fixed charges is due to the presence of Si and nitrogen dangling bonds, normally denoted as “K center” and “N center,” respectively [39]. In stoichiometric nitrides (i.e. SiN$_x$), the K centers (Si atom back-bonded with three N atoms) [40,41] can be charged positively [42-44]. This significant positive-charge density leads to a strong inversion layer on the p-type c-Si surfaces, known as the “parasitic” or “inversion-layer shunting effect,” leading to a reduction of the short-circuit current and cell efficiency [45]. SiO$_2$/SiN$_x$ stacks are expected to reduce or nullify this detrimental effect [46, 47].

4.3.4 Al$_2$O$_3$

Aluminum oxide (Al$_2$O$_3$) has recently emerged as a passivation layer for n-type c-Si solar cells owing to its excellent field-effect passivation that is associated with the negative fixed charges near the Al$_2$O$_3$/c-Si interface [19,48,49] that proved to be beneficial, especially for boron-emitter passivation, in comparison with SiN$_x$ and thermally grown SiO$_2$. An efficiency of 23.9% was obtained by applying Al$_2$O$_3$ layer on the boron emitter [50,51]. Al$_2$O$_3$ films are coated by a plasma-assisted method as well as a thermal-ALD method with a very low deposition rate of < 2 nm/min [19,48,52-55]. After annealing Al$_2$O$_3$ films at moderate temperatures, an outstanding $S_{rec}$ of <5 cm/s was obtained [49,53] on a low-resistive p-type wafer, and <1 cm/s was obtained on an n-type c-Si wafer (1 Ω-cm to 4 Ω-cm). After the annealing process, the SiO$_2$/Al$_2$O$_3$ stack yields a high level of chemical passivation due to a low interface defect density [56]. Using the SiO$_2$/Al$_2$O$_3$ stack, an excellent efficiency of 21.5% has been obtained; furthermore, the Al$_2$O$_3$ film overcomes the so-called “parasitic shunting” effects that are very common for SiN$_x$-passivated rear passivation [45]. The main disadvantage of ALD for photovoltaic applications is a low deposition rate; however, this disadvantage can be overcome by depositing ultrathin (2 nm to 30 nm) Al$_2$O$_3$ films using ALD and capping them with a thicker SiO$_x$ film deposited by PECVD. Another disadvantage is that ALD/Al$_2$O$_3$ film degrades substantially during the firing process; therefore, a capping layer such as SiN$_x$ [57] is required. A combination of ALD and PECVD may be a key technology for future industrial, high-efficiency solar cells. The passivation effects of different passivation materials and their industrial compatibilities are depicted in Table 1.

### Table 1. Passivation effects of different passivation materials and their industrial compatibilities.

<table>
<thead>
<tr>
<th>Passivation Material</th>
<th>Charge</th>
<th>H diffusion</th>
<th>ARC Layer</th>
<th>Industrial Compatibility</th>
</tr>
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<tbody>
<tr>
<td>Dry SiO$_x$</td>
<td>neutral</td>
<td>No</td>
<td>(FGA Process)</td>
<td>Yes</td>
</tr>
<tr>
<td>SiN$_x$ (N rich)</td>
<td>(+ve) charge</td>
<td>Yes, Low</td>
<td>Yes</td>
<td>PECVD</td>
</tr>
<tr>
<td>SiN$_x$ (Si rich)</td>
<td>(+ve) charge</td>
<td>Yes, High</td>
<td>Poor</td>
<td>PECVD</td>
</tr>
<tr>
<td>i-a-Si:H</td>
<td>Neutral</td>
<td>Yes, High</td>
<td>No</td>
<td>PECVD</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>(+ve) charge</td>
<td>No</td>
<td>...</td>
<td>No</td>
</tr>
</tbody>
</table>

Fig. 4. Measured surface recombination velocity as a function of the excess electron concentration for both textured and polished surfaces passivated with SiN$_x$. From [9], T. Lauinger et al. Record low surface recombination velocities on 1 Ω-cm p-silicon using remote plasma silicon nitride passivation. Appl. Phys. Lett. 68, (1996) 1232. Permission granted. License number 3674270659162. Copyright © 1996 American Institute of Physics.
4.3.5 PECVD-ONO

Thermally grown SiO₂ layers provide all of the following major characteristics that are required for a rear passivation for p-type c-Si based PERC solar cells: sound surface passivation, effective rear reflectance, and thermal stability. Unfortunately, thermally grown oxide growth requires a long (~90 min) high-temperature process that reduces the original carrier lifetime; also, the oxidation process produces a medium throughput. PECVD Si-oxide (SiOₓ) film may be a possible alternative to SiO₂ film due to the benefits of the PECVD process. Stacks of PECVD SiO₂/SiNₓ (or ON) and PECVD SiOₓ/SiNₓ/SiOₓ (or ONO) have been investigated. These stacks resulted in as-deposited Sₐ values of <700 cm/s (ON) and <30 cm/s (ONO) [58,59].

4.3.6 a-Si:H

The excellent material properties of the intrinsic hydrogenated amorphous silicon (i-a-Si:H) has attracted considerable attention in the field of heterojunction solar cells since it replaces the high-temperature dopant diffusion process of the intrinsic a-Si:H films at a low temperature.

Figure 5 represents the measured SRV of PECVD-deposited i-a-Si:H films as a function of the deposition temperature [60]. A-Si:H films are usually deposited by conventional PECVD at approximately 225 °C and contain a large amount of hydrogen (>10 at.%) [60]. This hydrogen content effectively passivates the c-Si/a-Si:H interface, resulting in a low interface-state density. The passivation principle of intrinsic a-Si:H is based on hydrogen-related chemical passivation. Using intrinsic a-Si:H, excellent passivation properties with Sₐ that are as low as 2 cm/s were obtained [61-64] with a high Vₚᵥ of >700 mV. Sano achieved a world-first high efficiency of 25.56% [65] on a-Si:H/c-Si heterojunction solar cells; using device modeling, the efficiency is reported to be 26.61% [66]. The parasitic absorption effects and the lack of thermal stability during a high-temperature process are the major limitations of applying a-Si:H film to be applied as a passivation layer; therefore, a-Si:H films cannot be applied in the production of standard, screen-printed solar cells. The variety of surface passivation methods that have been used in different kinds of c-Si solar cells are depicted in Table 2.

5. CONCLUSIONS

One way to achieve a high efficiency that is well above 20% at a reduced cost relies on the use of thinner wafers. Surface passivation is the most vital matter here, and passivation material is critical for the production of high-efficiency c-Si solar cells.

Due to the low growth rate or deposition rate of passivation, the extremely high-temperature process for the growth of SiO₂ has seldom been adopted as a passivation scheme for high-efficiency c-Si solar cells. Recently, even though low surface recombination velocities were achieved using SiNₓ that had been deposited by PECVD, the high density of the fixed positive charges within the SiNₓ layer induced parasitic shunting, thereby reducing the short-circuit current density; furthermore, it was also recently shown that, for boron emitters, ALD/Al₂O₃ (with a capping layer deposited by PECVD) provides an outstanding level of surface passivation, which can be attributed to its extremely high, negative fixed-charge density and low interface-state densities.

ACKNOWLEDGMENTS

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REFERENCES


Table 2. Surface passivation methods of c-Si solar cell.

<table>
<thead>
<tr>
<th>Solar Cell Type</th>
<th>Passivation Layer (s)</th>
<th>Cell Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PERL/LBSF</td>
<td>Thermal SiO₂</td>
<td>24.7</td>
<td>29-31</td>
</tr>
<tr>
<td>p-PERC</td>
<td>Al₂O₃ + SiNₓ</td>
<td>21.7</td>
<td>57</td>
</tr>
<tr>
<td>n-PERT</td>
<td>Al₂O₃ / SiNₓ</td>
<td>20.8</td>
<td>67</td>
</tr>
<tr>
<td>EWT</td>
<td>Al₂O₃ / SiNₓ</td>
<td>21.6</td>
<td>68</td>
</tr>
<tr>
<td>Bilacial</td>
<td>SiNₓ</td>
<td>20.4</td>
<td>69</td>
</tr>
<tr>
<td>MIS inversion</td>
<td>SiNₓ</td>
<td>18.5</td>
<td>70</td>
</tr>
<tr>
<td>HIT</td>
<td>a-Si</td>
<td>24.7</td>
<td>65</td>
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