Further Studies on the Effect of SiNx Refractive Index and Emitter Sheet Resistance on Potential-Induced Degradation

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Further Studies on the Effect of SiN$_x$ Refractive Index and Emitter Sheet Resistance on Potential-Induced Degradation

Jaewon Oh, Bill Dauksher, Stuart Bowden, Govindasamy Tamizhmani, Peter Hacke, and John D’Amico

Abstract—We present the impacts of silicon nitride (SiN$_x$) antireflection coating refractive index and emitter sheet resistance on potential-induced degradation of the shunting type (PID-s). Previously, it has been shown that the cell becomes more PID-s-susceptible as the refractive index decreases or the emitter sheet resistance increases. To verify the effect of refractive index on PID-s, we fabricated cells with varying SiN$_x$ refractive index (1.87, 1.94, 2.05) on typical p-type base solar cells with $\sim$60 $\Omega$/sq emitters. However, none of these cells showed output power degradation, regardless of the refractive index. Further investigation of the emitter showed that the PID-s was suppressed at $\sim$60 $\Omega$/sq due to the extremely high surface phosphorus concentration ($6 \times 10^{21}$ cm$^{-3}$), as measured by secondary ion mass spectrometry. Furthermore, PID-s was observed on cells possessing a high emitter sheet resistance ($\sim$80 $\Omega$/sq). The emitter surface phosphorus concentration plays an important role in determining PID-s susceptibility.

Index Terms—Durability, high voltage, potential-induced degradation (PID), reliability, sheet resistance, silicon nitride (SiN$_x$).

I. INTRODUCTION

POTENTIAL-INDUCED degradation (PID) has become a hot issue in the photovoltaic (PV) industry due to the likelihood of rapid power degradation. The term PID was first used by Solon in 2005 [1]. Since its main failure mechanism manifests itself in cell shunting, the PID is specifically referred to as PID of the shunting type (PID-s) [2], [3]. There are also other types of PID, such as polarization [4] or PID of the surface passivation [5], [6], and further, PID may have different effects on thin film modules [7], [8]. In this paper, we will only discuss PID-s since it is observed on conventional p-type base solar cell modules, which are dominant in the PV market [9], [10]. PID-s is observed on p-type base solar cells when the cells are operated as a PV system which is accompanied by high voltage with severe environmental conditions, such as high temperature and humidity. Several studies indicate that PID-s is caused by the migration of sodium ions, and the source of sodium could be from the PV module glass (typically, soda-lime glass) [11]–[14] or contaminants at the cell surface [15]. A more recent study showed that a root cause of PID-s is the presence of a sodium-decorated stacking fault penetrating the n-p junction [2]. The shunting path by the sodium-decorated stacking faults leads to a decrease of shunt resistance [2], which causes a significant power loss by providing an alternate current path for light-generated current [16]. The effect of low shunt resistance on solar cell/module performance is more severe at low irradiance (LI) levels [17]. It has been observed that areas affected by PID-s in cells had an increase of the depletion region recombination current ($J_{02}$) and the ideality factor ($n_I$) [3]. It also has been reported that sodium out-diffusion from the stacking fault is observed as the PID-s-affected cell is recovered by exposure to high temperature [18].

There are multiple factors that contribute to PID-s susceptibility in a cell process. What we would like to clarify among them are the roles of the refractive index (RI) of the silicon nitride (SiN$_x$) antireflection coating (ARC), and the emitter sheet resistance. Many publications have shown that PID-s is suppressed by increasing the RI to a value greater than 2.1 [1], [19], [20]. Pingel et al. showed the general trend of increasing PID-s susceptibility with respect to increasing emitter sheet resistance [1]. In this study, we verify the effect of SiN$_x$ RI and emitter sheet resistance on PID-s.

II. EXPERIMENTS

Typical industrial size (156 mm $\times$ 156 mm) monocristalline silicon solar cells with a p-type base and an n-type emitter created by a POCl$_3$ diffusion were fabricated in the Solar Power Laboratory (SPL) pilot line located at the Arizona State University. The SPL standard p-type cell process flow is shown schematically in Fig. 1. For this study, three different SiN$_x$ ARC films were deposited onto wafers by adjusting the SiH$_4$ and NH$_3$ gas flow rates in the plasma-enhanced chemical vapor deposition (PECVD) equipment. All of the ARC film thicknesses are around 78 nm. First considering groups A–C
in Table I, an identical cell manufacturing flow was used except for the PECVD processes to vary the SiNx RI. Variable angle spectroscopic ellipsometry (VASE) characterized the RI and thickness of the ARC films deposited onto 6-in round single-side polished wafers. Quoted values for RI are given at a wavelength of 630 nm. Both a corona charging technique and time-resolved surface voltage measurements [21] were used to determine the PID-s susceptibility of SiNx ARC films deposited on finished solar cells and polished wafers. The corona charging technique requires charging to a dielectric leakage condition which is typically above ~7 and -10 MV/cm. Thus, a dose of about $2 \times 10^{13}$ q/cm² was used to ensure that a high field is reached. Noncontact ion drift (ID) spectrometry [22] was utilized to characterize mobile ions and verify the sodium contamination of test cells before PID testing.

For the study regarding the impact of emitter sheet resistance on PID-s, various emitter sample groups were prepared (shown as D–H in Table I). The identical cell process shown in Fig. 1 was used except for the diffusion process. These included the SPL standard diffused emitter with a sheet resistance of about 2 $\Omega$/sq (group D), and four emitters with higher sheet resistance (groups E–H) than the SPL standard emitter. The higher sheet resistance emitters were formed by decreasing the SPL standard diffusion temperature from 840 to 800 °C and lowering the bubbler temperature. A four-point probe measured the emitter sheet resistance after removal of phosphosilicate glass (PSG) created during the diffusion process. An SiNx ARC at RI of 1.94 was deposited onto these samples using identical PECVD deposition conditions and all of the samples in groups D–H have identical index of refraction and extinction coefficient spectra.

The phosphorus concentration in the SPL standard emitter was profiled by secondary ion mass spectrometry (SIMS) after diffusion and oxide strip using 6-in round, single-side polished wafers. SIMS was also carried out to determine sodium concentration in PID-s stressed cells and to verify the effect of phosphorus concentration on sodium gettering. Solar cell samples using groups D (PID-s-resistant) and F (PID-s-susceptible) conditions were prepared for this SIMS analysis. Wafers which were 6-in round single-side polished were used as substrates in fabricating these solar cells for the SIMS measurement. Texturing and front metallization was omitted for simplicity, but the SiNx ARC and aluminum back surface field (Al-BSF) were processed for PID-s characterization since they are necessary in observing PID-s [23]. The cell was cut into several pieces to divide into PID testing samples and non-PID testing samples. Subsequently, PID stressing was applied to those PID testing samples using the stacked method shown in Fig. 2. Electrochemical capacitance–voltage (ECV) was also carried out on polished wafer samples from groups F and H to compare with the SPL standard emitter.

One-cell coupons laminated by using typical commercial PV module materials (soda-lime glass, EVA, TPE backsheet) were prepared to carry out the PID stress experiments. These coupons were PID stressed under conditions of 60 °C/85% relative humidity (RH) and -600 V in an Atlas Ci4000 weathering chamber. An alternate PID test setup that does not require coupon lamination was also used in this study to prepare samples for analysis (e.g., SIMS measurements) after stress testing. The cell and PV module materials are simply stacked up for PID stressing [3], [24], [25], and therefore, the PID-stressed cell is easily removed from the module materials without the need to employ a complicated delamination process. Fig. 2 graphically depicts the alternate test setup used in this study. We have previously shown that conventional laminated cells and ones unlaminated such as used in the present study result in a similar grade of PID-s when stressed [26]. PID stress was carried out for these cells under 60°C/0% RH and -600 V in a scientific oven.

Light current–voltage (I–V) and dark I–V were measured before and after the PID tests. Shunt resistance was determined from the slope of the linear region of the dark I–V curve around zero volts. A steady-state solar simulator was used for the I–V measurements, and the light I–V was taken at both standard test condition (STC), which is 1000 W/m² irradiance and 25 °C cell temperature, and under LI (~250 W/m²) conditions. Electroluminescence (EL) image was acquired via a coolSamBa HR-830 Si camera with concomitant imaging software.
III. RESULTS AND DISCUSSION

A. Effect of SiN\textsubscript{x} Refractive Index

Pervasive in the literature, PID-s has been observed in cells that have a low RI (<2.1) SiN\textsubscript{x} ARC [1], [19], [20]. In this study, the three samples shown as groups A–C in Table I, including an SPL standard cell, all have lower refractive indices than 2.1. Fig. 3 shows the spectral $n$ and $k$ for samples used in this study and is typical for solar cell SiN\textsubscript{x} layers [27]. Thus, it was expected to observe PID-s on all the cells after PID stressing (60 °C/85% RH, −600 V, 96 h). Fig. 4 shows the PID-s results of those three samples. Contrary to the work cited above, none of the samples showed any maximum power point ($P_{\text{max}}$) degradation after PID 96 h, regardless of the RI. Even the cell that with a very low RI (group A, RI: 1.87) showed no $P_{\text{max}}$ decrease at all. The only change seen was a decrease in the shunt resistance ($R_{\text{sh}}$) of group A to 60% of its initial value as shown in Fig. 4(a). The SPL standard sample (group B) that has an RI of 1.94 showed a lower decrease of $R_{\text{sh}}$ after PID stressing than what was observed for the group A cell with RI 1.87. The highest RI cell (group C) showed no degradation in either $P_{\text{max}}$ or $R_{\text{sh}}$, as shown in Fig. 4(c). Note that the initial $R_{\text{sh}}$ for this cell is already very low as compared to groups A and B cells due to nonoptimization of the firing conditions for the RI 2.05 SiN\textsubscript{x} film. However, in terms of $R_{\text{sh}}$, this result is consistent with prior experimental observations showing stronger PID-s-resistant cells with increased RI [1], [19], [20]. In order to verify the PID-s susceptibility of those SiN\textsubscript{x} ARC films, a method employing high dose corona charging followed by time-resolved measurement of surface voltage [21] was carried out for both polished wafer samples and solar cell samples without lamination. The result is presented in Fig. 5. Wilson et al. [21] showed that PID-s susceptibility correlates with a higher surface voltage that is dependent on SiN\textsubscript{x} RI after corona charging. As shown in Fig. 5, the surface voltage after corona charging increases as RI decreases from both samples, and this trend is consistent with the result of Wilson et al. They also showed PID-s-susceptible cells for retained surface voltage >15 V after corona charging. On our completed cells, the retained surface voltage after corona charging of RI 1.87 and 1.94 SiN\textsubscript{x} films is very high (~30 V), as compared to that of the RI 2.05 (~5V) SiN\textsubscript{x} film. The results of Fig. 5 and the high retained surface voltage indicate that our RI 1.87 and 1.94 SiN\textsubscript{x} films would be expected to be PID-s-susceptible. However, Fig. 4 shows only a slow change in $R_{\text{sh}}$ and that all cells are PID-s-resistant regardless of the RI of the SiN\textsubscript{x} ARC film. The reason for the PID-s resistance could be attributed to the low emitter sheet resistance, which is about 60 Ω/sq. Pingel et al. reported that the emitter sheet resistance is one of the factors which influences PID-s susceptibility [1] and that PID-s susceptibility is decreased as emitter sheet resistance decreased. Therefore, a further study regarding the effect of emitter sheet resistance on PID-s was carried out, which is presented in Section III-B.

One of the fresh (non-PID stressed) bare cells from group A was chosen for ID spectrometry measurement to determine the source of sodium ions causing PID-s. Initially, no mobile ions, especially sodium ions, were observed from this sample since only a small monotonic decrease of the surface voltage with increasing temperature was observed, as shown in Fig. 6.
To verify the possibility for sodium drift through the ARC layer, the same sample was subsequently intentionally contaminated with an ionic sodium solution and the ID spectrometer measurement was repeated. In the intentionally contaminated state, a reduction of the surface voltage was observed with increasing temperature, with a transition at 110 °C and a peak temperature (T$_p$) of 150 °C and V/dT versus T spectra (not shown here); both characteristic of a drift of sodium ions in the nitride. The measurements indicate that the cell has no sodium contamination as a consequence of the cell manufacturing process and support the hypothesis that the source of the sodium is the module with the most likely candidate being the soda-lime glass. In addition, replacing the soda-lime glass with borosilicate glass shows no PID-s in a previous study [13].

B. Effect of Emitter Sheet Resistance

The cells in the previous section did not show PID-s, even after stressing for 96 h, despite being fabricated using SiN$_x$ ARC layers that would be expected to show PID-s degradation. Since the PID-s susceptibility is with respect to an increase of emitter sheet resistance [1], high emitter sheet resistance cells were prepared and stressed. Table II and Fig. 7 show PID-s test result of high emitter sheet resistance cells. The cells with 60 Ω/sq (group D) did not show PID-s, whereas PID-s was clearly observed in cells with possessing higher emitter sheet resistance >60 Ω/sq (groups E–H). Fig. 7 shows EL images of a group H cell and a group F cell before and after PID stressing. Interestingly, the group H cell has a darker shunted area than the group F cell in the EL images, although both cells showed nearly the same degree of degradation as shown in Table II. In addition, it was observed that the pattern of the shunted region as seen on the EL images in Fig. 7(b) and (d) is very similar. This phenomenon might be attributed to a difference of sheet resistance across the cell caused by the diffusion process. A total of 16 points were measured by a four-point probe after the diffusion process, and this was followed by the remainder of the standard SPL cell fabrication process. Overall emitter sheet resistance of, for example, one of the group F cells was ∼74 ± 2 Ω/sq. Such

<table>
<thead>
<tr>
<th>Group II</th>
<th>Group F</th>
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<tbody>
<tr>
<td>Before</td>
<td>After</td>
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<tr>
<td>I$_{sc}$ (A)</td>
<td>8.296</td>
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<tr>
<td>V$_{oc}$ (V)</td>
<td>0.613</td>
</tr>
<tr>
<td>P$_{max}$ (W)</td>
<td>3.889</td>
</tr>
<tr>
<td>FF (%)</td>
<td>76.5</td>
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<tr>
<td>R$_{sh}$ (Ω·cm$^2$)</td>
<td>21151.5</td>
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a cell was stressed at 60 °C/0% RH, −600 V, 23 h, and then, EL imaging was performed. Each point at which sheet resistance was measured was carefully investigated with EL imaging after PID-s; however, there was no clear correlation between PID-s susceptibility and sheet resistance within a cell. A more detailed study with high-resolution mapping of the sheet resistance using an automated tool might help to determine the relationship.

The uniformity might affect the PID-s susceptibility in addition to the value of the sheet resistance [1], so it was necessary to look into the sheet resistance uniformity of cells from all of the different diffusion processes. The emitter sheet resistance was measured on all the wafers from different groups of each batch (∼13 wafers) as shown in Fig. 8. The sheet resistance distribution of the SPL standard emitter (group D) that has shown no PID-s (cell #08) is shown in Fig. 8(a). It has quite a good uniformity within the wafer (about ±2 Ω/sq) and across the boat. The other diffusion processes that were used in making higher emitter sheet resistance than the SPL standard emitter (60 Ω/sq) result in a high nonuniformity of sheet resistance within the wafer, as shown in Fig. 8(b) and (c), but cell groups [e.g., cells #04 and #07 in Fig. 8(b) and cell #02 in Fig. 8(c)] with larger within-wafer nonuniformity than group D did not always exhibit pronounced PID-s. Group E showed very minimal PID-s (1.1% degradation in power at STC, see Fig. 9), although it has a similar range of emitter sheet resistance to group F as shown in Fig. 8(b). Therefore, the emitter sheet resistance uniformity cannot be the only criteria determining PID-s susceptibility.

Another interesting result is that PID-s was also affected by the bubbler temperature in the emitter diffusion process. Regardless of the bubbler temperature, both groups E and F showed a sheet resistance of ∼70 Ω/sq., as shown in Table I. However, the cells from group E showed insignificant PID-s degradation while the group F cells showed pronounced PID-s degradation as shown in Fig. 9. By increasing the bubbler temperature, the depth of the electrically active phosphorus plateau as determined by ECV is increased [28]. It is speculated that PID-s is suppressed by increasing the electrically active phosphorus plateau near the surface in the emitter. A pair of groups E and F and a pair of groups G and H cells have similar emitter sheet resistance ranges, which are ∼70 and ∼80 Ω/sq, respectively. However, group F showed more pronounced PID-s than group E (33% degradation in power at STC versus 1.1%), and group H showed higher PID-s degradation than group G (38% degradation in power at STC versus 26%), as shown in Fig. 9. This result clearly shows an effect of bubbler temperature on PID-s susceptibility, as well as an effect of emitter sheet resistance. In addition, as measured by SIMS, the SPL standard cell (group D) has extremely high total surface phosphorus concentration.
phosphorus concentration emitter (group D), more of the sodium ions remain in the top of the emitter layer as shown in Fig. 11. This result shows that sodium transport could be slowed down or blocked by a layer with a high phosphorous concentration. It also has been reported that PID-s was suppressed by keeping the PSG layer (which has high phosphorous concentration) after POCl₃ diffusion in a cell process [33]. Therefore, PID-s could be suppressed by the presence of a high surface phosphorus concentration region/layer in the emitter, which might work as a sodium gettering layer. Moreover, Fig. 11 shows that the non-PID stressed sample has a very low sodium concentration while the PID-stressed sample has higher than $1 \times 10^{22}$ cm$^{-3}$ of surface sodium concentration. A further study focusing on a detailed emitter analysis is in progress to elucidate a more exact PID-s mechanism.

IV. CONCLUSION

Fabrication of p-type cells with Al-BSF and phosphorus emitters with various SiNx RI ARCs were PID stressed for 96 h. No sodium contamination was detected by ID spectrometry and SIMS before PID testing. Cells with 60 Ω/sq showed no $P_{\text{max}}$ degradation, as confirmed by I–V and EL. However, a slight decrease of shunt resistance, which does not affect $P_{\text{max}}$, was observed from low RI cells (RI: 1.87 and 1.94). The SiNx film of these low RI cells would be expected to show PID-s, but there was little evidence in the final cell results. The extremely high surface phosphorous concentration in the emitter (60 Ω/sq) of SPL-fabricated cells getters the sodium and prevents contamination of the junction. Increasing the sheet resistance to 70 and 80 Ω/sq by modifying diffusion temperature increased the PID-s degradation. This result is consistent with Pingel et al. [1]. However, cells with a diffusion process resulting in $\sim 70 \Omega$/sq emitters did not always demonstrate PID-s. Changing other process parameters such as the bubbler temperature also affected the PID-s susceptibility. SIMS results for a PID-s-resistant cells show high sodium concentrations near the emitter surface after PID stressing and support the theory of sodium gettering by emitters with a high phosphorous concentration. The emitter sheet resistance alone does not determine the PID-s susceptibility and it is suggested that the active/inactive phosphorus concentrations as well as the emitter sheet resistance should both be monitored to avoid PID-s. Further emitter analysis is in progress to identify PID-s susceptibility with a change of phosphorus concentration in the emitter.

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Authors’ photographs and biographies not available at the time of publication.