The influence of orientation and morphology on the passivation of crystalline silicon surfaces by Al₂O₃

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Abstract

We compare the passivation provided by Al₂O₃ deposited on planar <100> and <111>, and textured <100>, boron-diffused and undiffused crystalline silicon surfaces. The passivation of <111> surfaces is found to be somewhat worse than that of <100> surfaces for the as-deposited films, but improves to similar values after annealing. Higher recombination at textured surfaces compared to planar <111> surfaces can be largely, though not entirely, attributed to the difference in surface area. The passivation of both as-deposited and annealed films is found to improve over time when stored under ambient conditions. This helps give context to the myriad of results reported on planar <100> samples – we expect J₀ values measured for Al₂O₃ layers on such surfaces to increase by a factor of ~2 to 3 on textured surfaces.

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1. Context and previous work

Thin film amorphous aluminium oxide (Al₂O₃) has received a great deal of attention from the photovoltaic community in recent years due to its outstanding surface passivation properties when applied to crystalline silicon (c-Si) surfaces [1–7]. Its low interface defect density and large negative charge allow it to provide unsurpassed passivation of p-type c-Si surfaces, to the extent that measurements of Al₂O₃-passivated samples have necessitated a re-evaluation of the intrinsic limits to the bulk carrier lifetime of silicon [8]. It is therefore a prime candidate both to

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replace the Al-BSF for rear side passivation in conventional p-type cells, and to provide passivation for the boron-doped p⁺ region in new high-efficiency n-type cell structures.

In both of these applications, Al₂O₃ passivation layers are likely to be applied to surfaces that are far from planar. Particularly for p⁺ regions, which are typically located on the front surface of the cell, some surface structure, usually a random pyramid texture, is mandated by the need for effective light-trapping. However, even on the rear of the cell, the use of a textured surface can have optical benefits while reducing process complexity. It is well known that the presence of such a texture can exert a significant influence on the quality of a dielectric passivation, both through increased surface area, the exposure of <111> oriented crystalline facets, and potentially via other mechanisms such as the influence of mechanical stress at the edges and vertices of surface features [9]. Previous studies of the influence of such factors for other dielectrics such as SiO₂ and SiNx have revealed differences of up to five-fold in the passivation quality between <100> and <111> orientations, and even greater differences between planar and textured surfaces [9].

It is somewhat surprising, therefore, that relatively little systematic work has been performed to assess the impact of either crystalline orientation or surface morphology on the passivation performance of Al₂O₃. The great majority of reported passivation data are for planar <100> surfaces, and although some scattered results on <111> surfaces have been reported, there has generally been no effort to compare these directly to results on <100> surfaces. An exception is the recent work of [10], which examined the surface passivation of Al₂O₃ from atomic layer deposition (ALD), both thermal and plasma-assisted, on diffused and undiffused planar surfaces of <100> and <111> orientation, finding generally slightly worse passivation properties for <111> surfaces. However, no comparison to textured surfaces was made in that work.

Numerous examples of the application of Al₂O₃ to textured surfaces within device structures exist in the literature, but again there are relatively few direct comparisons to planar surfaces. Duttagupta et al. [11] measured the passivation quality of plasma-enhanced chemical vapour deposition (PECVD) Al₂O₃/SiNx stacks on boron-diffused textured and planar <100> samples, reporting a textured-to-planar J₀ ratio of 1.5–2. A similar experiment was performed by [12] with both Al₂O₃/SiNx stacks and Al₂O₃ by itself, where the Al₂O₃ was deposited by plasma-assisted ALD. They reported a textured-to-planar J₀ ratio between 1.7 and 2.5. However, neither [11] nor [12] included a comparison to planar <111> surfaces, which leaves the role played by the <111> surface orientation of the textured surface open to speculation.

In this work, we perform measurements of surface passivation quality for Al₂O₃-passivated boron-diffused and undiffused surfaces, both planar <100>, planar <111>, and with a random pyramid texture. This allows us to separate the influence of crystal orientation and surface area from any additional effects, on differences in the recombination rate between planar and textured silicon surfaces.

2. Experimental procedure

Boron-diffused symmetrical lifetime structures were prepared on high resistivity (>100 Ω·cm) n-type <100> and <111> float-zone silicon wafers, approximately 450 and 325 μm thick respectively. The latter were supplied with a chemical polish by the manufacturer, and were used without additional etching, while the former received either a planar etch in HF:HNO₃ or TMAH solution, or a random pyramid texture in TMAH. All samples received an initial boron diffusion of ~110–120 Ω·cm, with some receiving additional drive-in anneals of 1, 3, or 6 hours at 1100 °C in N₂ in order to vary the surface dopant concentration and diffusion profile. Additional undiffused samples were prepared on various substrates (details in Table 1) in the same way. All samples were given an RCA clean and HF dip prior to Al₂O₃ deposition.

The Al₂O₃ films were deposited by atmospheric pressure chemical vapour deposition (APCVD) using an inline APCVD belt furnace tool developed by Schmid Thermal Systems [6, 13]. Triethylaluminium-tri-(sec-butoxide) (TEDA-TSB) and H₂O were used as precursors, with a substrate temperature of ~440°C. The films were deposited sequentially on the front and the rear of the samples. Characterisation was performed both before and after annealing in a quartz tube furnace at 425°C in N₂ for 30 minutes.

Measurements of the effective excess carrier lifetime τₑff vs excess carrier concentration Δn were performed using a Sinton Instruments WCT-120 photoconductance tool, generally under quasi-steady-state (QSS) illumination conditions. The optical constant required to determine the generation rate was determined by comparison of QSS
measurements with those performed under transient illumination conditions, over the range of $\Delta n$ in which both methods were valid, or by comparison with the transient lifetime tail present in the QSS measurement itself following the illumination cutoff. Values of the optical constant determined in this way ranged from 0.59 to 0.64 for the planar samples, with values of 0.80 and 0.90 for the undiffused and diffused textured samples respectively.

3. $J_0$ extraction

The recombination rate at both diffused and undiffused surfaces was characterised in terms of the saturation current density $J_0$, calculated according to:

$$J_0 = \frac{qWn_i^2}{2} \frac{d}{d\Delta n} \left( \frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk,intrinsic}} \right)$$

where $q$ is the fundamental charge, $W$ is the wafer thickness, $n_i = 9.7 \times 10^9$ cm$^{-3}$ is the intrinsic carrier concentration in silicon, calculated using the expression of [14] at 300 K, and $\tau_{bulk,intrinsic}$ is the Auger-limited intrinsic bulk lifetime, calculated using the empirical parameterization of [8].

Fig. 1 shows the $J_0$ extraction from the Auger-corrected inverse lifetime for the undiffused samples. In most cases $J_0$ was determined from the slope of the data around $\Delta n = 1.8 \times 10^{16}$ cm$^{-3}$. For the as-deposited textured sample, only a transient photoconductance measurement was performed immediately after deposition, which results in an apparent reduction in inverse lifetime at higher $\Delta n$ due to non-zero generation. Therefore for this sample the slope was extracted at $\Delta n = 5 \times 10^{15}$ cm$^{-3}$, and it was confirmed that this resulted in agreement with measurements at higher $\Delta n$ for the same sample when later remeasured using both transient and QSS illumination. Note that for the more lightly doped $<111>$ samples $\tau_{eff}^{-1}$ is artificially reduced at lower $\Delta n$ due to depletion region modulation. The resulting $J_0$ values are given in Table 1.

![Figure 1](image-url)  
**Fig. 1.** Auger-corrected inverse effective lifetime for the undiffused $n$-type samples. Lines show the linear fits used to extract $J_0$.  

Table 1: $J_0$ values for undiffused $n$-type samples.
Table 1. Parameters of the undiffused n-type samples.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Finish</th>
<th>Resistivity (Ω cm)</th>
<th>Dopant Concentration (cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
<th>Thickness (µm)</th>
<th>J&lt;sub&gt;0&lt;/sub&gt; as-deposited (fA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>J&lt;sub&gt;0&lt;/sub&gt; annealed (fA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar &lt;100&gt;</td>
<td>polished</td>
<td>1.5</td>
<td>3×10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>235</td>
<td>11.4</td>
<td>7.9</td>
</tr>
<tr>
<td>Planar &lt;111&gt;</td>
<td>HF:HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>15</td>
<td>3×10&lt;sup&gt;14&lt;/sup&gt;</td>
<td>223</td>
<td>16.6</td>
<td>10.9</td>
</tr>
<tr>
<td>Textured</td>
<td>TMAH</td>
<td>2.3</td>
<td>2×10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>234</td>
<td>31.1</td>
<td>18.4</td>
</tr>
</tbody>
</table>

For the diffused samples, accurate extraction of J<sub>0</sub> is somewhat more complicated. Equation (1) is based on the assumption that Δn is spatially uniform throughout the thickness of the sample (i.e., Δn is the same at the surfaces and everywhere in the bulk of the wafer). This assumption is practically necessary, since only the average carrier concentration, Δn<sub>av</sub>, is generally accessible to experiment. However, it is never strictly true, even for spatially uniform carrier generation, because surface recombination is always non-zero, and carrier mobilities are finite [15]. When surface recombination is significant, Δn becomes significantly non-uniform due to the limited diffusion rate of carriers from the bulk to the surfaces, such that Δn<sub>av</sub> is significantly greater than Δn at the surfaces. Since the lifetime of carriers at the surface decreases with increasing Δn in high injection, this leads to an increasing overestimation of Δn at the surfaces with increasing Δn<sub>av</sub>, and a consequent underestimation of the apparent J<sub>0</sub> determined by (1). This will occur even for samples with low J<sub>0</sub> in sufficiently high injection, and the error will become significant at lower Δn as J<sub>0</sub> increases. Conversely, since τ<sub>bulk,par,insic</sub> in (1) is calculated from Δn<sub>av</sub>, and has approximately an inverse quadratic dependence on Δn, this value will be increasingly and systematically overestimated, which will tend to increase the apparent J<sub>0</sub>, especially as Auger recombination begins to dominate at very high Δn.

Fig. 2. (a) Auger-corrected inverse effective lifetime for selected boron-diffused and textured samples, showing the Δn-dependent slope resulting from non-uniformities in the carrier profile at high J<sub>0</sub> (b) apparent J<sub>0</sub> determined from (1) vs Δn for the same samples. Solid lines show the dependence predicted by numerical modeling due to nonuniformity in the excess carrier profile, while dashed lines show the dependence predicted under the assumption of a uniform carrier profile.

Fig. 2 shows that these predicted experimental dependencies of the apparent J<sub>0</sub> on Δn do in fact manifest in practice for the samples of this study, in good agreement with numerical simulations performed using the model described in [16]. The consequence is that the conventional practice of extracting J<sub>0</sub> for Δn = 10<sup>16</sup> cm<sup>-3</sup> or above will
result in significant underestimation for samples with higher \( J_0 \), such as those with a textured diffused surface. This is obviously a problem if we wish to compare samples with dissimilar values of \( J_0 \). For some samples, primarily those with planar <111> and (in some cases) textured surfaces and as-deposited \( \text{Al}_2\text{O}_3 \) layers, the dependence of the apparent \( J_0 \) on \( \Delta n \) was found to be even stronger than that predicted by modeling. It may be that in these samples additional mechanisms are present, for example lateral spatial non-uniformity of the surface passivation itself. This enhanced dependency is no longer seen for the same samples after annealing, which suggests that it is indeed most likely related to the properties of the passivation layer.

Given these additional factors, the extraction of \( J_0 \) by comparison to numerical modelling is not straightforward. However, it is clear that, as shown in Fig. 2, the error in \( J_0 \) is minimized by performing the extraction at lower values of \( \Delta n \). Consequently, for these samples we chose to determine \( J_0 \) by applying (1) to the data measured at lower \( \Delta n \), generally within the range \( 1.5 \times 10^{15} < \Delta n < 4 \times 10^{15} \) cm\(^{-3}\).

4. Results and discussion

Fig. 3 shows \( J_0 \) values measured on diffused surfaces for the \( \text{Al}_2\text{O}_3 \) films as-deposited and after annealing. Measurements of the as-deposited films were performed both immediately after deposition and immediately before annealing, approximately 18 hours later. It was found that the surface passivation of all samples, particularly the textured samples, improved significantly over this time under ambient conditions. A similar effect was observed for the annealed samples when remeasured 24 days after annealing. No significant difference in \( J_0 \) between planar <100> surfaces prepared by HF:HNO\(_3\) and TMAH etches was observed.

![Fig. 3. \( J_0 \) of the boron-diffused planar <100>, planar <111>, and random textured samples with (a) as-deposited, and (b) annealed \( \text{Al}_2\text{O}_3 \) layers. Values are shown as measured immediately after deposition, immediately before annealing (~18 hours later), immediately after annealing, and 24 days after annealing.](image)

The ratio of \( J_0 \) for planar <111> surfaces relative to planar <100> (Fig. 4a) was generally in the range of 1.3–1.5 for the as-deposited films on both diffused and undiffused surfaces, decreasing to 1–1.2 after annealing for the diffused surfaces. This suggests either a higher interface defect density or lower fixed charge for the <111> interface compared to <100>, as well as a relative improvement in one or both properties following annealing. The ratio for undiffused surfaces was similar to that of diffused surfaces for the as-deposited films, but did not change
significantly after annealing. The reason for this difference is not clear. We note that while Auger recombination in the diffused region also contributes to $J_0$, and should be independent of surface orientation, its contribution is expected to be small relative to surface recombination for such lightly diffused surfaces.

The ratio of $J_0$ for textured surfaces relative to planar $\langle 111 \rangle$ (Fig. 4b) was found to be between 2.2 and 2.6 for most of the diffused samples. Since this value is higher than the geometric surface area ratio of 1.73 (or possibly 1.66 [17]), this implies the existence of an additional recombination enhancement factor due to the surface structure. A notable exception is the data for the unannealed films measured ~18 hours after deposition, where the $J_0$ ratio is very close to the geometric ratio. One tentative hypothesis might be that these unannealed films contain significantly more hydrogen, which allows for a greater degree of lattice relaxation in the vicinity of abrupt surface features, and hence less strain and consequent creation of unsatisfied (“dangling”) bonds. In contrast, $J_0$ ratios for the undiffused surfaces were found to be quite close to the geometric ratio, so that for these samples the increase in $J_0$ for textured surfaces over planar $\langle 111 \rangle$ can be explained solely by the difference in surface area.

The results presented in Fig. 4 are in broad agreement with the previous work of [11] and [12]. Their ranges of 1.5 to 2.0, and 1.7 to 2.5 for the ratio of $J_0$ at textured and planar $\langle 100 \rangle$ surfaces may be compared with the range of 2.0 to 3.3 measured here. The relatively limited influence of orientation and surface structure on recombination at Al$_2$O$_3$-passivated Si surfaces is in marked contrast to the case for SiO$_2$ and SiN$_x$. This points to fundamental differences in the structure of the Si–Al$_2$O$_3$ interface with respect to that of these other dielectrics.

![Graph](image)

Fig. 4. Ratio of $J_0$ for (a) planar $\langle 111 \rangle$ to planar $\langle 100 \rangle$ surfaces, and (b) textured to planar $\langle 111 \rangle$ surfaces. Data is shown for both boron-diffused surfaces and undiffused $n$-type surfaces. Values are shown as measured immediately after deposition, immediately before annealing (~18 hours later), immediately after annealing, and 24 days after annealing.

5. Conclusion

We have shown that the increase in $J_0$ at undiffused, randomly textured silicon surfaces passivated by Al$_2$O$_3$, with respect to planar $\langle 100 \rangle$ surfaces, may be entirely attributed to 1) the $\langle 111 \rangle$ surface orientation of the pyramid facets and 2) the increased surface area. For boron-diffused surfaces an additional factor due to surface features may be present, but is relatively small, in the range of 1.0 to 1.5. The increase of $J_0$ at $\langle 111 \rangle$ surfaces relative to $\langle 100 \rangle$ is also small, though the precise value will depend on the particular Al$_2$O$_3$ layer in question. In general one can expect $J_0$ values measured for Al$_2$O$_3$ on $\langle 100 \rangle$ Si surfaces to increase by a factor of ~2 to 3 when the same films are applied.
to textured surfaces. The relatively limited dependence of Si–Al₂O₃ interface recombination on orientation and surface structure is in marked contrast to the case for SiO₂ and SiNₓ, and makes Al₂O₃ a particularly attractive candidate to passivate non-planar surfaces.

References


