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**Al$_2$O$_3$/TiO$_2$ stack layers for effective surface passivation of crystalline silicon**

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For silicon surface passivation, we investigate stack layers consisting of a thin Al$_2$O$_3$ layer and a TiO$_2$ capping layer deposited by means of thermal atomic layer deposition (ALD). In this work, we studied the influence of different thermal post-deposition treatments and film thickness for the activation of passivating ALD Al$_2$O$_3$ single layers and Al$_2$O$_3$/TiO$_2$ stack layers. Our experiments show a substantial improvement of the passivation for the Al$_2$O$_3$/TiO$_2$ stack layers compared to a thin single Al$_2$O$_3$ layer. For the stacks, especially with less than 10 nm Al$_2$O$_3$, a TiO$_2$ capping layer results in a remarkably lower surface recombination. Effective fixed charge density of Al$_2$O$_3$/TiO$_2$ stack layers increases after TiO$_2$ deposition and O$_2$ annealing. It is also demonstrated that the enhanced surface passivation can be mainly related to a remarkably low interface defect density of 1.1 $\times$ 10$^{10}$ eV$^{-1}$ cm$^{-2}$, whereas post-TiO$_2$ heat treatment in O$_2$ ambience is not beneficial for the passivation of silicon, which is attributed to increasing interface defect density of stack layers.

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I. INTRODUCTION

Charge carrier recombination in the silicon is one of the most significant loss mechanisms in conventional solar cells, and recombination losses must be decreased in order to obtain higher efficiency solar cells.\textsuperscript{1} Surface recombination losses are reduced by passivating the surfaces using dielectric films. Surface passivation is becoming more important as the wafer thickness is continuously being decreased in order to reduce material costs. Traditionally, thermally grown SiO$_x$ has been used as effective passivation layer in high-efficiency solar cells.\textsuperscript{2,3} For low-temperature passivation of heterojunction solar cells, hydrogenated amorphous silicon deposited by plasma-enhanced chemical vapor deposition (PECVD) was introduced.\textsuperscript{4} Amorphous hydrogenated silicon nitride, a-Si$_{x}$N$_{y}$, is in common use for passivating the front n$^+$ emitter of p-type silicon solar cells.\textsuperscript{5,6} There are two advantageous effects of a-Si$_{x}$N$_{y}$ on passivation. Chemical passivation due to interfacial bonding occurs between the a-Si$_{x}$N$_{y}$:H layer and the silicon substrate, while field-effect passivation is caused by fixed positive charge near the silicon surface.\textsuperscript{7} Also a-Si$_{x}$N$_{y}$:H layers often play the important role of the anti-reflection coating, in addition to providing good surface passivation.

However, in order to reduce surface recombination losses further for p$^-$ emitters of n-type silicon cells, a negatively charged dielectric is desirable, as the positive charge in a-Si$_{x}$N$_{y}$:H films results in a lowering of the majority carrier density at the surface and an increase in recombination. Further, for passivated emitter and rear cell (PERC) type solar cells on p-type silicon, parasitic shunting can occur when dielectrics with a fixed positive charge are used, due to the formation of an inversion layer.\textsuperscript{8} Aluminum oxide (Al$_2$O$_3$) has been shown to exhibit a high density of negative charge and provide a good level of surface passivation on both p- and n-type silicon.\textsuperscript{9-11} Moreover, Al$_2$O$_3$ also provides excellent surface passivation on heavily doped p$^+$ emitters.\textsuperscript{12,13} The passivation properties of Al$_2$O$_3$ are associated with the combination of a low interface defect density and an enhanced field-effect passivation.\textsuperscript{14}

Al$_2$O$_3$ films have been demonstrated to provide excellent surface passivation; however, they cannot be used by themselves as effective anti-reflection coatings due to the low refractive index (~1.6). Hence, for use on the front side of solar cells, dielectric stacks consisting of a thin layer of Al$_2$O$_3$ and a thicker layer of a dielectric with suitable refractive index are the best solution. Recently, some results of Al$_2$O$_3$/a-Si$_{x}$N$_{y}$:H stacks have been reported for anti-reflection as well as surface passivation purposes.\textsuperscript{15,16} In the stacked Al$_2$O$_3$/a-Si$_{x}$N$_{y}$:H layers, stacks optimized for low surface reflection resulted in an improvement in the final photovoltaic characteristic of the solar cells. Compared to single Al$_2$O$_3$ layers, Al$_2$O$_3$/PECVD a-Si$_{x}$N$_{y}$:H stacks also showed a further reduction in the surface recombination velocity, which was attributed to the hydrogenation of Si/Al$_2$O$_3$ interface states, leading to a reduction in the interface state density.\textsuperscript{16} However, the extinction coefficient, especially below 600 nm, for a-Si$_{x}$N$_{y}$:H films increases greatly as the Si:N ratio is increased, which is undesirable for the application as an antireflection coating. In contrast, TiO$_2$ has a relatively high refractive index and moderate extinction coefficients for wavelengths down to 400 nm.\textsuperscript{17} TiO$_2$ is therefore also a good candidate as the top layer of Al$_2$O$_3$/dielectric stack due to its excellent optical properties. Another advantage of the use of TiO$_2$ is that the entire Al$_2$O$_3$/TiO$_2$ stack can be deposited by atomic layer deposition (ALD) in the same chamber with excellent layer thickness control and efficient use of chemical precursors. Further, the use of ALD allows the creation of...
of materials with graded refractive index. Using Al₂O₃ and TiO₂, it would be possible to grade the refractive index between the extremes given by the refractive indices of the two materials, allowing further reductions in optical reflectance.

Recently, improved surface passivation has been reported when Al₂O₃ is combined with TiO₂ in a type of alternating layer compared to passivation obtained by Al₂O₃ only. However, the origin of this enhanced passivation is still under investigation. In this paper, we investigate the surface passivation of Al₂O₃/TiO₂ stacks. Of particular interest are stacks where the Al₂O₃ layer is sufficiently thin (generally in the order of 10 nm or less) that it has minimal impact on the optical properties of the stack. The focus is on investigating the underlying mechanisms of c-Si surface passivation as obtained by Al₂O₃/TiO₂ stacks.

II. EXPERIMENTAL DETAILS

Symmetrical p+/n/p⁺ structures on (100) damage-etched n-type float-zoned Si wafers were used for the measurement of the emitter saturation current density J₀e. The wafers had a resistivity of 100 Ω.cm and a thickness 500 μm. They were exposed to BBr₃ at a temperature of 910 °C in a diffusion furnace. The sheet resistance of the p⁺ diffusion was 100 Ω/□. Un-diffused and polished p-type Czochralski Si wafers with a resistivity of 1–10 Ω.cm were used for capacitance-voltage and Kelvin probe measurements. Before deposition, the samples were treated with a conventional RCA clean followed by a dip in diluted HF. Deposition of thin Al₂O₃ and TiO₂ layers was carried out in a commercial hot-wall flow-type ALD reactor (TFS200, Beneq). Trimethylaluminum and titanium chloride were used as aluminum and titanium precursors, respectively. H₂O were used as the oxidant for both TiO₂ and Al₂O₃ films in order to keep the process simple by using the same standard oxidant. The films were prepared by alternating metal precursor and oxidant exposure at a deposition temperature of 200 °C. The Al₂O₃ films were deposited first, followed by a forming gas anneal (FGA) at 400 °C. Subsequently, TiO₂ was deposited and annealed in O₂ at 300–400 °C. Post-TiO₂ deposition annealing was carried out in an O₂ ambient in order to minimize the concentration of oxygen vacancies and obtain stoichiometric films.

The passivation quality of the films was determined by the emitter saturation current density J₀e of the p⁺ emitters, which was measured using the inductively coupled photovoltaic decay technique. For the samples used for capacitance-voltage (C-V) and conductance measurements, Al₂O₃/TiO₂ stack layers were deposited onto the front of the samples followed by a very thin (~2 nm) Al₂O₃ capping layer. The deposition of a capping layer in top of the TiO₂ was found to be necessary to obtain reliable C-V measurement curves. Without a capping layer, the accumulation capacitance of Al₂O₃/TiO₂ samples was generally found to be greater than the accumulation capacitance of samples with Al₂O₃ only, which is attributed to non-negligible conductivity of the TiO₂ film or a diffusion of the evaporated aluminum contacts into the TiO₂. GaN contacts were formed on the rear of the samples. The interface characteristics of the MOS capacitors were evaluated by capacitance-voltage and conductance via small ac signal admittance measurement at frequencies ranging from 1 KHz to 1 MHz using a HP4284A Precision LCR meter.

III. RESULTS AND DISCUSSION

A. Emitter saturation current density

Figure 1 shows the emitter saturation current densities J₀e measured on samples after FGA (Al₂O₃ only) or immediately after the subsequent TiO₂ deposition. For the single layer Al₂O₃ films, a considerable increase in J₀e is observed for an Al₂O₃ thickness below 10 nm. This result is consistent with those of Dingemans et al. J₀e on diffused surfaces characterizes recombination within the emitter and at the surface. Since the emitter profile is the same for all the samples and the deposition and post deposition treatment are not expected to influence the emitter, the changes in J₀e are attributed to changes in the contribution to J₀e from recombination at the sample surfaces J₀es. J₀es is influenced by changes in the interface defect density as well as the net charge in the passivation film, which influences the degree of field-effect passivation. However, the field-effect passivation is expected to be virtually unaffected by the thickness because the negative charges reside at the interface between Si and Al₂O₃ and the negative charge density is thus not significantly affected even for films with a thickness of 5 nm. The increase in J₀e for thin Al₂O₃ films is therefore attributed to a degradation of the chemical passivation for very thin films. Following TiO₂ deposition, the same trend of higher J₀e for thin Al₂O₃ films is still observed, but the J₀e values are substantially lower, especially for thin Al₂O₃ below 10 nm. As the Al₂O₃ thickness increases, the effect of the TiO₂ film on passivation becomes weaker.

![Figure 1. Emitter saturation current density J₀e at a fixed injection level of 10¹⁶ cm⁻³ for p+/n/p⁺ symmetric lifetime samples passivated with Al₂O₃ films following various treatments: annealed at 400 °C in forming gas (black squares); subsequent deposition of 50 nm TiO₂ (red circles); subsequent anneal in O₂ for 30 min at 300 °C (blue triangle) and at 400 °C (green inverted triangles), respectively.](image-url)
Although not shown here, it was confirmed that the improved passivation following TiO₂ deposition is related to the TiO₂ layer itself and not a result of the thermal budget the samples are exposed to during TiO₂ deposition. Samples with Al₂O₃ films on which mock deposition were carried out (including simulation of the entire deposition process except of the pulsing of the TiCl₄) displayed no significant change in surface passivation. Figure 1 also shows that annealing of the TiO₂ film results in a degradation of the passivation; in the case of a 300°C anneal the degradation is slight while after a 400°C anneal it is more significant and results in the J₀ₑ values approaching those of the samples prior to TiO₂ deposition.

Figure 2 shows results for the thickness dependence of the J₀ₑ for Al₂O₃/TiO₂ films. Regardless of TiO₂ film thickness, a significant increase in J₀ₑ is observed for 5 nm thick Al₂O₃ films compared to thicker Al₂O₃ layers. In general, an increase in TiO₂ thickness improves the surface passivation up to a TiO₂ thickness between 40 and 50 nm. Importantly, J₀ₑ values as low as 20 fA cm⁻² can be obtained for an Al₂O₃ thickness of 20 nm and a TiO₂ thickness of ~50 nm. This TiO₂ layer thickness is very close to the optimal TiO₂ thickness for an antireflection coating for a planar encapsulated cell given typical values of the refractive indices of Al₂O₃ (1.6) and TiO₂ (2.4).

B. TiO₂ Crystallinity

In order to understand the reasons behind the improvement in passivation following TiO₂ deposition, the material and interface properties were investigated in more detail. Figure 3 shows the results of X-ray diffractometry (XRD) measurements on Al₂O₃/TiO₂. It can be seen that TiO₂ layers in as-deposited Al₂O₃/TiO₂ stacks are amorphous, even for a TiO₂ thickness of 50 nm (not shown in the figure). This is in contrast to the results of Aarik et al. who found that TiO₂ films deposited at temperatures below 140°C were amorphous while those deposited over 165°C and having sufficient thickness from 15 nm showed diffraction patterns characteristic of polycrystalline TiO₂ on all used substrates. Figure 3 also shows that following annealing the TiO₂ film became polycrystalline (anatase phase), with the transition from amorphous to crystalline phases depending on both the anneal temperature and layer thickness. The comparatively high anneal temperature required for crystallization suggests that grain growth is suppressed by the Al₂O₃ interlayer not only during the deposition process but also during the annealing process.

A question that immediately arises from these observations is to what extent the crystallization of the TiO₂ films may impact the stack passivation properties or correlate with observed changes in the passivation. At present, the data are insufficient for a conclusive answer; however, in Fig. 2, no degradation in surface passivation was observed for thick (50 nm) TiO₂ films on 10 nm Al₂O₃ following a 300°C anneal; compared to thinner TiO₂ films. Since 50 nm TiO₂ is

![FIG. 2. Emitter saturation current density J₀ₑ at a fixed injection level of 10¹⁶ cm⁻³ for p⁺/n/p⁺ symmetric lifetime samples passivated with Al₂O₃/TiO₂ stacks with various TiO₂ film thicknesses. Samples received a 400°C, 30 min anneal in forming gas prior to TiO₂ deposition, and a 300°C 30 min anneal in O₂ after TiO₂ deposition.](image)

![FIG. 3. XRD patterns of TiO₂ films deposited on Si substrates covered with 10 nm Al₂O₃ which was annealed at 400°C in forming gas (a) 30 nm TiO₂ subsequently annealed at different temperatures up to 500°C for 30 min, and (b) TiO₂ films with different thicknesses annealed at 300°C for 30 min.](image)
observed to result in the formation of the crystalline phase in Fig. 3(b), there does not seem to be a direct correlation between the two; in other words, crystallization of the TiO2 films does not of itself appear to cause degradation in surface passivation.

C. Charge trapping density

Figure 4 shows the high frequency C-V characteristics of Al2O3 and TiO2 stack layers before and after TiO2 deposition and annealing. Capacitance was measured at 1 MHz as a function of gate voltage and the capacitor was swept from inversion to accumulation and back to determine the amount of hysteresis. A small amount of hysteresis can be observed in the C-V curve of the Al2O3 single layer, indicating that application of a positive gate voltage caused electron injection into the oxide from the substrate while during a sweep from positive to negative voltages the trapped electrons can be ejected from the oxide back into the substrate. Following TiO2 deposition, there is a decrease in the C-V hysteresis, indicating a reduction of the density of carrier-trapping defect sites that are responsible for the hysteresis. After annealing, there is increase in the hysteresis as crystallization of the initially amorphous TiO2 films occurs. This suggests that introduction of grain boundaries or crystal/amorphous boundaries may increase the density of such carrier-trapping defect sites.

The flatband voltage shift ($\Delta V_{FB}$) characterizing the hysteresis of the C-V curves of Fig. 4 was used to estimate the charge trapping density $Q_{ot}$ of the Al2O3 films in the Al2O3/TiO2 stacks, using the relation

$$Q_{ot} = C_{ox} \times \frac{\Delta V_{FB}}{q}$$

for the calculation of $Q_{ot}$, where $q$ is the electronic charge and $C_{ox}$ is the flatband capacitance. In spite of the limitation that $Q_{ot}$ is influenced by the measurement parameters, such as the magnitude and direction of the sweep gate voltage and sweep time, the extracted values allow comparison of the film defect density following various treatments. As can be seen in Table I, the Al2O3/TiO2 stack layer without subsequent anneal has a significantly lower $Q_{ot}$ than the Al2O3 single layer. However, $Q_{ot}$ values of Al2O3/TiO2 increase up to that of Al2O3 single layer as anneal temperature increases.

D. Fixed charge density

Figure 5(a) shows high frequency C-V curves for Al2O3/TiO2 stacks with different TiO2 thicknesses, while Fig. 5(b) shows the values of the dielectric constant $k_{TiO2}$ of the TiO2 films of the stacks. The values of $k_{TiO2}$ were determined by assuming that the Al2O3/TiO2 stack layer behaves as two capacitors in series, so that the total oxide capacitance $C_{ox}$ is given by

$$\frac{1}{C_{ox}} = \frac{1}{\varepsilon_0 A} \left( \frac{d_{Al2O3}}{k_{Al2O3}} + \frac{d_{TiO2}}{k_{TiO2}} \right),$$

where $\varepsilon_0$ is the permittivity of free space and $k_{Al2O3}$, $k_{TiO2}$, $d_{Al2O3}$, and $d_{TiO2}$ are the dielectric constants and thicknesses of the Al2O3 and TiO2 films, respectively. The value of $k_{Al2O3}$ is assumed to be constant and was determined from the accumulation capacitance of the single Al2O3 film following 30 min forming gas anneal, which yielded $k_{Al2O3}$ of 7.3, in good agreement with published values.

The results of Fig. 5(a) indicate that as-deposited TiO2 films thicker than ~10 nm have a relatively constant $k_{TiO2}$ in the range of 40 to 60. TiO2 films annealed at 300 °C display a similar value of $k_{TiO2}$ except for the 50 nm thick film, for which $k$ is substantially larger; corresponding to the onset of crystallization as shown in Fig. 3. TiO2 films annealed at 400 °C experienced a dramatic increase in $k_{TiO2}$ (>100) with respect to the as-deposited film. The exact value of $k_{TiO2}$ in these films as determined from the C-V data is expected to be quite inaccurate; all that can be said with some certainty is that the value of $k_{TiO2}$ are very large.

When all the charge is assumed to be located at the Si/Al2O3 interface, the effective fixed charge density ($Q_{eff}$) of the Al2O3/TiO2 stack layers was determined from C-V measurements. Table II shows the $Q_{eff}$ values measured on Al2O3/TiO2 stack layers as a function of post-anneal temperature. The results are given for both Al2O3 single and Al2O3/TiO2 stack layers. Compared to Al2O3 single layer, the Al2O3/TiO2 stack layers show a higher density of

| TABLE I. Charge trapping density $Q_{ot}$ of 10 nm Al2O3 and 10 nm Al2O3/30 nm TiO2 stack layers. |
|----------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| $Q_{ot}$ (cm$^{-2}$)                     | $4.9 \times 10^{11}$           | $8.2 \times 10^{10}$           | $1.8 \times 10^{11}$           | $3.7 \times 10^{11}$           |

*The Al2O3 films were annealed at 400 °C for 30 min in forming gas prior to TiO2 deposition.

*Post TiO2 deposition anneal conditions were for 30 min in O2 at as indicated.
negative fixed charge of $4.3 \times 10^{12} \text{cm}^{-2}$. The Al$_2$O$_3$/TiO$_2$ stack layers show increasing $Q_{\text{eff}}$ for higher anneal temperature.

To distinguish the contribution of Al$_2$O$_3$ and TiO$_2$ layers to effective fixed charge density, the variation in $V_{\text{FB}}$ of the Al$_2$O$_3$/TiO$_2$ stack layers as a function of the film thickness and dielectric constant are shown in Fig. 6 in the as-deposited and annealed states. The $V_{\text{FB}} = (d_{\text{TiO2}}/k_{\text{TiO2}})$ data have been fitted with a straight line consistent with the solution to Poisson’s equation using the following equation:

$$V_{\text{FB}} = \Phi_{\text{MS}} - \frac{q}{\varepsilon_0} \left[ Q_{\text{Al2O3}} \frac{d_{\text{Al2O3}}}{k_{\text{Al2O3}}} + (Q_{\text{Al2O3}} + Q_{\text{TiO2}}) \frac{d_{\text{TiO2}}}{k_{\text{TiO2}}} \right],$$  

(3)

where $\Phi_{\text{MS}}$ is the metal-semiconductor work function difference (0.87 eV), $q$ is the electronic charge, assuming that $Q_{\text{Al2O3}}$ is the charge located at the Si-Al$_2$O$_3$ interface, and $Q_{\text{TiO2}}$ is the charge located at the internal dielectric interface between the Al$_2$O$_3$ and TiO$_2$ layers. From the y-intercept and slopes, $Q_{\text{Al2O3}}$ and $Q_{\text{TiO2}}$ can be estimated, respectively, by a least-squares linear fit. In case of Al$_2$O$_3$ single layer once annealed at 400°C, additional 300–400°C anneal does not have an impact on Al$_2$O$_3$ passivation, so the $V_{\text{FB}}$ of single Al$_2$O$_3$ layer annealed at 400°C is also included.

The data in Fig. 6 clearly indicate the presence of negative charge not just at the Al$_2$O$_3$/Si interface but also within the TiO$_2$ film (more likely) at the Al$_2$O$_3$/TiO$_2$ interface. Figure 7 shows the charge densities extracted from the data of Fig. 6 assuming an additional sheet of charge located at the Al$_2$O$_3$/TiO$_2$ interface. As compared to these results, the anneal exhibits mostly changes in slope, indicating the fixed charge at Al$_2$O$_3$/TiO$_2$ interface changes. As a result, the fixed charge density of Al$_2$O$_3$/TiO$_2$ stack layers can be obtained as shown in Fig. 7. A higher negative charge density of $4.9 \times 10^{12} \text{cm}^{-2}$ is obtained for as-deposited TiO$_2$ layer, compared to single thin Al$_2$O$_3$ layer. As anneal temperature increases to 400°C, $Q_{\text{TiO2}}$ increases significantly. As a result, compared to the trend of the effective fixed charge density in Table II, the effect of charge distributed throughout the Al$_2$O$_3$/TiO$_2$ stack layer on the passivation is more limited than that of the charge at Si/Al$_2$O$_3$ interface.

### E. Interface trap density

It is difficult to measure quasi-static capacitance of high-k TiO$_2$ due to relatively high leakage current, resulting in the inaccurate interface trap density determination.

**TABLE II. Effective fixed charge density $Q_{\text{eff}}$ of 10 nm Al$_2$O$_3$ and 10 nm Al$_2$O$_3$/30 nm TiO$_2$ stack layers.**

<table>
<thead>
<tr>
<th></th>
<th>Al$_2$O$_3$ $^a$</th>
<th>Al$_2$O$_3$/TiO$_2$ (as-deposited)</th>
<th>Al$_2$O$_3$/TiO$_2$ (annealed at 300°C)$^b$</th>
<th>Al$_2$O$_3$/TiO$_2$ (annealed at 400°C)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{eff}}$ (cm$^{-2}$)</td>
<td>$2.3 \times 10^{12}$</td>
<td>$4.5 \times 10^{12}$</td>
<td>$5.5 \times 10^{12}$</td>
<td>$6.4 \times 10^{12}$</td>
</tr>
</tbody>
</table>

$^a$The Al$_2$O$_3$ films were annealed at 400°C for 30 min in forming gas prior to TiO$_2$ deposition.

$^b$Post TiO$_2$ deposition anneal conditions were for 30 min in O$_2$ at as indicated.
Although the high-frequency Terman method provides a rough evaluation of interface trap density, which is based on the extraction of the experimental surface potential versus gate voltage, it becomes less sensitive with increasing capacitance since the voltage shift is inversely proportional to the insulator capacitance. For the extraction of more reliable interface trap density, the conductance method is more suitable because the surface potential fluctuation is a function of energy in the depletion region of the band gap. To determine an accurate Dit, the insulator capacitance and series resistance effects are removed from the measured conductance $G_m$ peak using the following relation:

$$G_p = \frac{\omega^2 C_\alpha G_m}{G_m^2 + \omega^2 (C_\alpha - C_m)^2},$$  

where $G_p$ is the corrected conductance, $\omega$ is the angular frequency and $C_m$ is the measured capacitance. The Dit is calculated from

$$D_{it} = \left(\frac{G_p}{\omega}\right) \left(\frac{1}{\int f_D(\sigma) A}\right),$$  

where $G_p/\omega$ is the corrected conductance loss, $\omega$ is the frequency corresponding to the peak value of conductance loss, $q$ is the electronic charge, $f_D$ is the universal function of standard deviation of band bending $\sigma$, and $A$ is an area of electrode. The Dit value used for our samples is 0.402. The Dit for the conductance loss values of 3.3 pF is found to be magnitude of lower than that of Al$_2$O$_3$ only passivated sample. However, as the post-TiO$_2$ annealing temperature increases, Dit increases again and reaches a value of $1.1 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ at midgap following a 400 $^\circ$C anneal, which is the almost same as that of only Al$_2$O$_3$-passivated sample.

On the basis of the above results, we can consider the possible reasons for the improvement in $J_0$ following TiO$_2$ deposition as shown in Figs. 1 and 2. As already mentioned, surface passivation is determined by the degree of field effect passivation as well as chemical passivation. The results indicate that the negative charge in the film increases following TiO$_2$ deposition. Empirically, the degree of field effect passivation is generally found to saturate at a charge density of around $10^{12}$ cm$^{-2}$. Since the charge density in the Al$_2$O$_3$ film is well below this level, a significant improvement in field effect and surface passivation is expected as a result of the additional charge. The origin of the additional negative charge is not clear and requires further investigation.

As shown in Fig. 8(b), the deposition of TiO$_2$ also results in a significant reduction in Dit, which indicates an improvement in the chemical passivation of interface states and is very likely to also be a reason for the improved surface passivation.
An interesting question is why $D_{ht}$ improves following TiO$_2$ deposition. One possible reason (and the reason most often cited for improvements in $D_{ht}$ following treatments of dielectric layers) is the improved passivation of interface defects with atomic H. In other words, the deposition of TiO$_2$ may result in the release of atomic H which diffused through the TiO$_2$ and Al$_2$O$_3$ films to passivate interface defects. For example, Veith et al. demonstrated that the passivation quality of thin thermal ALD-Al$_2$O$_3$ can be improved using a-SiN$_x$H as a capping layer, which might be because of the hydrogenation of interface states. The deposition of a-SiN$_x$H at a temperature of 400°C for several minutes has an effect similar to a short anneal. The H content in the bulk of TiO$_2$ films deposited at around 200°C has been found to be relatively low (about 0.4 atom %), but it is possible that hydrogen is released during the layer-by-layer deposition of as a result of the reaction between surface hydroxyl groups and the titanium precursor TiCl$_4$. Dingemans et al. found that deposition of a TiO$_2$ capping layer did not lead to higher level of passivation for SiO$_2$ passivated silicon. Since atomic hydrogen is beneficial to the passivation of silicon by SiO$_2$ (as observed following a so-called anneal treatment), the release of significant quantities of atomic H during the deposition process would be expected to improve SiO$_2$ passivation. It must be noted that, however, Dingemans et al. used a different Ti precursor than used in our work, so the absence of improved passivation in their case is not conclusive evidence against the role of atomic H in the improved passivation observed in our work. However, defect passivation by atomic H does not seem to be a likely cause of the improved passivation for another reason, namely that the rate of diffusion of atomic H through Al$_2$O$_3$ at the deposition temperature of 200°C is likely to be too low to be effective. Dingemans et al. measured the rate of effusion of He atoms in Al$_2$O$_3$ films as a function of both Al$_2$O$_3$ deposition and anneal temperature. For films deposited at around 200°C, the onset of effusion did not occur until anneal temperatures of around 300°C. If atomic H is not the cause for the improvement in surface passivation, one may speculate that deposition of TiO$_2$ may result in some reconstruction of the Si/Al$_2$O$_3$ interface region, perhaps as a result of changed interface stress. However, at this stage, there is no evidence for such a hypothesis.

IV. CONCLUSIONS

We studied the surface passivation of Al$_2$O$_3$/TiO$_2$ stack layers as a function of TiO$_2$ layer thickness and for different post-deposition anneals. For the single Al$_2$O$_3$ layers, $J_{0e}$ was found to increase strongly for an Al$_2$O$_3$ layer thickness below 10 nm. Significantly enhanced passivation was observed following deposition of TiO$_2$ on thin Al$_2$O$_3$ passivated Si surfaces. Measurements of the effective fixed charge density in the stack revealed that TiO$_2$ deposition increases $Q_{eff}$. Further, the Al$_2$O$_3$/TiO$_2$ stack layers yield a high level of chemical passivation after TiO$_2$ deposition due to a low interface defect density, which increases with anneal temperature. Improved chemical surface passivation appears to be the main reason of the enhanced passivation quality.

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