Al₂O₃/TiO₂ stack layers for effective surface passivation of crystalline silicon

Dongchul Suh, Duk-Yong Choi, and Klaus J. Weber

Citation: [Journal of Applied Physics](#) **114**, 154107 (2013); doi: 10.1063/1.4825258

View online: <http://dx.doi.org/10.1063/1.4825258>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/114/15?ver=pdfcov>

Published by the [AIP Publishing](#)

Re-register for Table of Content Alerts

Create a profile.

Sign up today!

Al₂O₃/TiO₂ stack layers for effective surface passivation of crystalline silicon

Dongchul Suh,^{1,a)} Duk-Yong Choi,² and Klaus J. Weber¹

¹Center for Sustainable Energy Systems, College of Engineering and Computer Science,
The Australian National University, Canberra, Australian Capital Territory 0200, Australia

²Laser Physics Centre, Research School of Physics and Engineering, The Australian National University,
Canberra, Australian Capital Territory 0200, Australia

(Received 26 July 2013; accepted 30 September 2013; published online 16 October 2013)

For silicon surface passivation, we investigate stack layers consisting of a thin Al₂O₃ layer and a TiO₂ 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 Al₂O₃ single layers and Al₂O₃/TiO₂ stack layers. Our experiments show a substantial improvement of the passivation for the Al₂O₃/TiO₂ stack layers compared to a thin single Al₂O₃ layer. For the stacks, especially with less than 10 nm Al₂O₃, a TiO₂ capping layer results in a remarkably lower surface recombination. Effective fixed charge density of Al₂O₃/TiO₂ stack layers increases after TiO₂ deposition and O₂ annealing. It is also demonstrated that the enhanced surface passivation can be mainly related to a remarkably low interface defect density of $1.1 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$, whereas post-TiO₂ heat treatment in O₂ ambience is not beneficial for the passivation of silicon, which is attributed to increasing interface defect density of stack layers.

© 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4825258>]

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.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 SiO₂ has been used as effective passivation layer in high-efficiency solar cells.^{2,3} For low-temperature passivation of heterojunction solar cells, hydrogenated amorphous silicon deposited by plasma-enhanced chemical vapor deposition (PECVD) was introduced.⁴ Amorphous hydrogenated silicon nitride, a-SiN_x:H, is in common use for passivating the front n⁺ emitter of p-type silicon solar cells.^{5,6} There are two advantageous effects of a-SiN_x:H on passivation. Chemical passivation due to interfacial bonding occurs between the a-SiN_x:H layer and the silicon substrate, while field-effect passivation is caused by fixed positive charge near the silicon surface.⁷ Also a-SiN_x: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-SiN_x: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.⁸ Aluminum oxide (Al₂O₃)

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.^{9–11} Moreover, Al₂O₃ also provides excellent surface passivation on heavily doped p⁺ emitters.^{12,13} The passivation properties of Al₂O₃ are associated with the combination of a low interface defect density and an enhanced field-effect passivation.¹⁴

Al₂O₃ 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 Al₂O₃ and a thicker layer of a dielectric with suitable refractive index are the best solution. Recently, some results of Al₂O₃/a-SiN_x:H stacks have been reported for anti-reflection as well as surface passivation purposes.^{13,15} In the stacked Al₂O₃/a-SiN_x:H layers, stacks optimized for low surface reflection resulted in an improvement in the final photovoltaic characteristic of the solar cells. Compared to single Al₂O₃ layers, Al₂O₃/PECVD a-SiN_x:H stacks also showed a further reduction in the surface recombination velocity, which was attributed to the hydrogenation of Si/Al₂O₃ interface states, leading to a reduction in the interface state density.¹⁶ However, the extinction coefficient, especially below 600 nm, for a-SiN_x:H films increases greatly as the Si:N ratio is increased, which is undesirable for the application as an antireflection coating. In contrast, TiO₂ has a relatively high refractive index and moderate extinction coefficients for wavelengths down to 400 nm.¹⁷ TiO₂ is therefore also a good candidate as the top layer of Al₂O₃/dielectric stack due to its excellent optical properties. Another advantage of the use of TiO₂ is that the entire Al₂O₃/TiO₂ 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

^{a)}Electronic mail: dong-chul.suh@anu.edu.au

of materials with graded refractive index. Using Al_2O_3 and TiO_2 , it would be possible to grade the refractive index between the extremes given by the refractive indices of the two materials,¹⁸ allowing further reductions in optical reflectance.

Recently, improved surface passivation has been reported when Al_2O_3 is combined with TiO_2 in a type of alternating layer¹⁹ and bilayer,²⁰ compared to passivation obtained by Al_2O_3 only. However, the origin of this enhanced passivation is still under investigation. In this paper, we investigate the surface passivation of $\text{Al}_2\text{O}_3/\text{TiO}_2$ stacks. Of particular interest are stacks where the Al_2O_3 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 $\text{Al}_2\text{O}_3/\text{TiO}_2$ 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 J_{0e} . The wafers had a resistivity of $100\ \Omega\text{cm}$ and a thickness $500\ \mu\text{m}$. They were exposed to BBr_3 at a temperature of 910°C in a diffusion furnace. The sheet resistance of the p^+ diffusion was $100\ \Omega/\square$. Un-diffused and polished p-type Czochralski Si wafers with a resistivity of $1\text{--}10\ \Omega\text{cm}$ 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 Al_2O_3 and TiO_2 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. H_2O were used as the oxidant for both TiO_2 and Al_2O_3 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 Al_2O_3 films were deposited first, followed by a forming gas anneal (FGA) at 400°C . Subsequently, TiO_2 was deposited and annealed in O_2 at $300\text{--}400^\circ\text{C}$. Post- TiO_2 deposition annealing was carried out in an O_2 ambient in order to minimize the concentration of oxygen vacancies and obtain stoichiometric films.²¹

The passivation quality of the films was determined by the emitter saturation current density J_{0e} of the p^+ emitters, which was measured using the inductively coupled photoconductive decay technique.²² For the samples used for capacitance-voltage (C-V) and conductance measurements, $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layers were deposited onto the front of the samples followed by a very thin ($\sim 2\text{ nm}$) Al_2O_3 capping layer. The deposition of a capping layer in top of the TiO_2 was found to be necessary to obtain reliable C-V measurement curves. Without a capping layer, the accumulation capacitance of $\text{Al}_2\text{O}_3/\text{TiO}_2$ samples was generally found to be greater than the accumulation capacitance of samples with Al_2O_3 only, which is attributed to non-negligible conductivity of the TiO_2 film or a diffusion of the evaporated aluminium contacts into the TiO_2 .²³ GaIn 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 J_{0e} measured on samples after FGA (Al_2O_3 only) or immediately after the subsequent TiO_2 deposition. For the single layer Al_2O_3 films, a considerable increase in J_{0e} is observed for an Al_2O_3 thickness below 10 nm. This result is consistent with those of Dingemans *et al.*²⁴ J_{0e} 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 J_{0e} are attributed to changes in the contribution to J_{0e} from recombination at the sample surfaces J_{0eS} . J_{0eS} 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 Al_2O_3 and the negative charge density is thus not significantly affected even for films with a thickness of 5 nm.^{25,26} The increase in J_{0e} for thin Al_2O_3 films is therefore attributed to a degradation of the chemical passivation for very thin films. Following TiO_2 deposition, the same trend of higher J_{0e} for thin Al_2O_3 films is still observed, but the J_{0e} values are substantially lower, especially for thin Al_2O_3 below 10 nm. As the Al_2O_3 thickness increases, the effect of the TiO_2 film on passivation becomes weaker.

FIG. 1. Emitter saturation current density J_{0e} at a fixed injection level of 10^{16} cm^{-3} for $p^+/n/p^+$ symmetric lifetime samples passivated with Al_2O_3 films following various treatments: annealed at 400°C in forming gas (black squares); subsequent deposition of 50 nm TiO_2 (red circles); subsequent anneal in O_2 for 30 min at 300°C (blue triangle) and at 400°C (green inverted triangles), respectively.

FIG. 2. Emitter saturation current density J_{0e} at a fixed injection level of 10^{16} cm^{-3} for $p^+/n/p^+$ symmetric lifetime samples passivated with $\text{Al}_2\text{O}_3/\text{TiO}_2$ stacks with various TiO_2 film thicknesses. Samples received a 400°C , 30 min anneal in forming gas prior to TiO_2 deposition, and a 300°C 30 min anneal in O_2 after TiO_2 deposition.

Although not shown here, it was confirmed that the improved passivation following TiO_2 deposition is related to the TiO_2 layer itself and not a result of the thermal budget the samples are exposed to during TiO_2 deposition. Samples with Al_2O_3 films on which mock deposition were carried out (including simulation of the entire deposition process except of the pulsing of the TiCl_4) displayed no significant change in surface passivation. Figure 1 also shows that annealing of the TiO_2 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 J_{0e} values approaching those of the samples prior to TiO_2 deposition.

Figure 2 shows results for the thickness dependence of the J_{0e} for $\text{Al}_2\text{O}_3/\text{TiO}_2$ films. Regardless of TiO_2 film thickness, a significant increase in J_{0e} is observed for 5 nm thick Al_2O_3 films compared to thicker Al_2O_3 layers. In general, an

increase in TiO_2 thickness improves the surface passivation up to a TiO_2 thickness between 40 and 50 nm. Importantly, J_{0e} values as low as 20 fA cm^{-2} can be obtained for an Al_2O_3 thickness of 20 nm and a TiO_2 thickness of $\sim 50 \text{ nm}$. This TiO_2 layer thickness is very close to the optimal TiO_2 thickness for an antireflection coating for a planar encapsulated cell given typical values of the refractive indices of Al_2O_3 (1.6) and TiO_2 (2.4).

B. TiO_2 crystallinity

In order to understand the reasons behind the improvement in passivation following TiO_2 deposition, the material and interface properties were investigated in more detail. Figure 3 shows the results of X-ray diffractometry (XRD) measurements on $\text{Al}_2\text{O}_3/\text{TiO}_2$. It can be seen that TiO_2 layers in as-deposited $\text{Al}_2\text{O}_3/\text{TiO}_2$ stacks are amorphous, even for a TiO_2 thickness of 50 nm (not shown in the figure). This is in contrast to the results of Aarik *et al.*^{27,28} who found that TiO_2 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 TiO_2 on all used substrates. Figure 3 also shows that following annealing the TiO_2 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 Al_2O_3 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 TiO_2 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) TiO_2 films on 10 nm Al_2O_3 following a 300°C anneal; compared to thinner TiO_2 films. Since 50 nm TiO_2 is

FIG. 3. XRD patterns of TiO_2 films deposited on Si substrates covered with 10 nm Al_2O_3 which was annealed at 400°C in forming gas (a) 30 nm TiO_2 subsequently annealed at different temperatures up to 500°C for 30 min, and (b) TiO_2 films with different thicknesses annealed at 300°C for 30 min.

FIG. 4. High frequency (1 MHz) C-V characteristics of 10 nm Al_2O_3 /30 nm TiO_2 stack layers. The Al_2O_3 films were annealed at 400 °C for 30 min in forming gas prior to TiO_2 deposition or C-V measurement. Post TiO_2 deposition anneal conditions were for 30 min in O_2 at either 300 or 400 °C as indicated in the legend. A ~ 2 nm Al_2O_3 film was deposited on top of the TiO_2 film prior to C-V measurements.

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 TiO_2 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 Al_2O_3 and TiO_2 stack layers before and after TiO_2 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 Al_2O_3 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 TiO_2 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 TiO_2 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 (ΔV_{FB}) characterizing the hysteresis of the C-V curves of Fig. 4 was used to estimate the charge trapping density Q_{ot} of the Al_2O_3 films in the $\text{Al}_2\text{O}_3/\text{TiO}_2$ stacks, using the relation

$$Q_{\text{ot}} = C_{\text{ox}} \times \frac{\Delta V_{\text{FB}}}{q} \quad (1)$$

for the calculation of Q_{ot} ,²⁹ 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 $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layer without subsequent anneal has a significantly lower Q_{ot} than the Al_2O_3 single layer. However, Q_{ot} values of $\text{Al}_2\text{O}_3/\text{TiO}_2$ increase up to that of Al_2O_3 single layer as anneal temperature increases.

D. Fixed charge density

Figure 5(a) shows high frequency C-V curves for $\text{Al}_2\text{O}_3/\text{TiO}_2$ stacks with different TiO_2 thicknesses, while Fig. 5(b) shows the values of the dielectric constant k_{TiO_2} of the TiO_2 films of the stacks. The values of k_{TiO_2} were determined by assuming that the $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layer behaves as two capacitors in series, so that the total oxide capacitance C_{ox} is given by

$$\frac{1}{C_{\text{ox}}} = \frac{1}{\epsilon_0 A} \left(\frac{d_{\text{Al}_2\text{O}_3}}{k_{\text{Al}_2\text{O}_3}} + \frac{d_{\text{TiO}_2}}{k_{\text{TiO}_2}} \right), \quad (2)$$

where ϵ_0 is the permittivity of free space and $k_{\text{Al}_2\text{O}_3}$, k_{TiO_2} , $d_{\text{Al}_2\text{O}_3}$, and d_{TiO_2} are the dielectric constants and thicknesses of the Al_2O_3 and TiO_2 films, respectively. The value of $k_{\text{Al}_2\text{O}_3}$ is assumed to be constant and was determined from the accumulation capacitance of the single Al_2O_3 film following 30 min forming gas anneal, which yielded $k_{\text{Al}_2\text{O}_3}$ of 7.3, in good agreement with published values.

The results of Fig. 5(a) indicate that as-deposited TiO_2 films thicker than ~ 10 nm have a relatively constant k_{TiO_2} in the range of 40 to 60. TiO_2 films annealed at 300 °C display a similar value of k_{TiO_2} except for the 50 nm thick film, for which k is substantially larger; corresponding to the onset of crystallization as shown in Fig. 3. TiO_2 films annealed at 400 °C experienced a dramatic increase in k_{TiO_2} (>100) with respect to the as-deposited film. The exact value of k_{TiO_2} 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_{TiO_2} are very large.

When all the charge is assumed to be located at the $\text{Si}/\text{Al}_2\text{O}_3$ interface, the effective fixed charge density (Q_{eff}) of the $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layers was determined from C-V measurements. Table II shows the Q_{eff} values measured on $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layers as a function of post-anneal temperature. The results are given for both Al_2O_3 single and $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layers. Compared to Al_2O_3 single layer, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layers show a higher density of

TABLE I. Charge trapping density Q_{ot} of 10 nm Al_2O_3 and 10 nm Al_2O_3 /30 nm TiO_2 stack layers.

	$\text{Al}_2\text{O}_3^{\text{a}}$	$\text{Al}_2\text{O}_3/\text{TiO}_2$ (as-deposited)	$\text{Al}_2\text{O}_3/\text{TiO}_2$ (annealed at 300 °C) ^b	$\text{Al}_2\text{O}_3/\text{TiO}_2$ (annealed at 400 °C) ^b
Q_{ot} (cm^{-2})	4.9×10^{11}	8.2×10^{10}	1.8×10^{11}	3.7×10^{11}

^aThe Al_2O_3 films were annealed at 400 °C for 30 min in forming gas prior to TiO_2 deposition.

^bPost TiO_2 deposition anneal conditions were for 30 min in O_2 at as indicated.

FIG. 5. High frequency (1 MHz) C-V characteristics of 10 nm $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layers. The Al_2O_3 films were annealed at 400°C for 30 min in forming gas prior to TiO_2 deposition. Post TiO_2 deposition anneal conditions were for 30 min in O_2 at 300°C . A ~ 2 nm Al_2O_3 capping layer was deposited on top of the TiO_2 film prior to C-V measurements. (b) Thickness dependencies of the relative dielectric constant of as-deposited and annealed TiO_2 films on Al_2O_3 .

negative fixed charge of $4.3 \times 10^{12} \text{ cm}^{-2}$. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layers show increasing Q_{eff} for higher anneal temperature.

To distinguish the contribution of Al_2O_3 and TiO_2 layers to effective fixed charge density, the variation in V_{FB} of the $\text{Al}_2\text{O}_3/\text{TiO}_2$ 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 $V_{\text{FB}} - (d_{\text{TiO}_2}/k_{\text{TiO}_2})$ data have been fitted with a straight line consistent with the solution to Poisson's equation using the following equation:³⁰

$$V_{\text{FB}} = \Phi_{\text{MS}} - \frac{q}{\epsilon_0} \left[Q_{\text{Al}_2\text{O}_3} \frac{d_{\text{Al}_2\text{O}_3}}{k_{\text{Al}_2\text{O}_3}} + (Q_{\text{Al}_2\text{O}_3} + Q_{\text{TiO}_2}) \frac{d_{\text{TiO}_2}}{k_{\text{TiO}_2}} \right], \quad (3)$$

TABLE II. Effective fixed charge density Q_{eff} of 10 nm Al_2O_3 and 10 nm $\text{Al}_2\text{O}_3/30$ nm TiO_2 stack layers.

	$\text{Al}_2\text{O}_3^{\text{a}}$	$\text{Al}_2\text{O}_3/\text{TiO}_2$ (as-deposited)	$\text{Al}_2\text{O}_3/\text{TiO}_2$ (annealed at 300°C) ^b	$\text{Al}_2\text{O}_3/\text{TiO}_2$ (annealed at 400°C) ^b
$Q_{\text{eff}} (\text{cm}^{-2})$	2.3×10^{12}	4.5×10^{12}	5.5×10^{12}	6.4×10^{12}

^aThe Al_2O_3 films were annealed at 400°C for 30 min in forming gas prior to TiO_2 deposition.

^bPost TiO_2 deposition anneal conditions were for 30 min in O_2 at as indicated.

FIG. 6. Flatband voltage of 10 nm $\text{Al}_2\text{O}_3/\text{TiO}_2$ stacks as a function of the $d_{\text{TiO}_2}/k_{\text{TiO}_2}$ in the as-deposited and post- TiO_2 annealed states, respectively.

where Φ_{MS} is the metal-semiconductor work function difference (0.87 eV), q is the electronic charge, assuming that $Q_{\text{Al}_2\text{O}_3}$ is the charge located at the $\text{Si}-\text{Al}_2\text{O}_3$ interface, and Q_{TiO_2} is the charge located at the internal dielectric interface between the Al_2O_3 and TiO_2 layers. From the y-intercept and slopes, $Q_{\text{Al}_2\text{O}_3}$ and Q_{TiO_2} can be estimated, respectively, by a least-squares linear fit. In case of Al_2O_3 single layer once annealed at 400°C , additional $300\text{--}400^\circ\text{C}$ anneal does not have an impact on Al_2O_3 passivation, so the V_{FB} of single Al_2O_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 $\text{Al}_2\text{O}_3/\text{Si}$ interface but also within the TiO_2 film or (more likely) at the $\text{Al}_2\text{O}_3/\text{TiO}_2$ interface. Figure 7 shows the charge densities extracted from the data of Fig. 6 assuming an additional sheet of charge located at the $\text{Al}_2\text{O}_3/\text{TiO}_2$ interface. As compared to these results, the anneal exhibits mostly changes in slope, indicating the fixed charge at $\text{Al}_2\text{O}_3/\text{TiO}_2$ interface changes. As a result, the fixed charge density of $\text{Al}_2\text{O}_3/\text{TiO}_2$ 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_2O_3 layer. As anneal temperature increases to 400°C , Q_{TiO_2} 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 $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack layer on the passivation is more limited than that of the charge at $\text{Si}/\text{Al}_2\text{O}_3$ 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.

FIG. 7. Relationship between the negative fixed charge density of Al₂O₃ and TiO₂ layer and the negative charge in the TiO₂ on 10 nm Al₂O₃.

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,³¹ it becomes less sensitive with increasing capacitance since the voltage shift is inversely proportional to the insulator capacitance.³⁰ 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 D_{it} , the insulator capacitance and series resistance effects are removed from the measured conductance G_m peak using the following relation:³²

$$G_p = \frac{\omega^2 C_{ox}^2 G_m}{G_m^2 + \omega^2 (C_{ox} - C_m)^2}, \quad (4)$$

where G_p is the corrected conductance, ω is the angular frequency and C_m is the measured capacitance. The D_{it} is calculated from³²

$$D_{it} = \left(\frac{G_p}{\omega} \right)_{f_p} \frac{1}{q f_D (\sigma_s) A}, \quad (5)$$

where G_p/ω is the corrected conductance loss, f_p 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 σ_s , and A is an area of electrode. The f_D value used for our samples is 0.402.³³ The D_{it} for the conductance loss values of 3.3 pF is found to be approximately $1.2 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$. It should be noted that the D_{it} at midgap determined by the high-frequency C-V method consisting of contributions from the oxide and interface traps shows much higher value of $10^{13} \text{ eV}^{-1} \text{ cm}^{-2}$, showing higher inaccuracies compared to the conductance method.

G_p/ω is plotted in Fig. 8(a) as a function of frequency. Figure 8(b) shows the D_{it} at midgap for the Al₂O₃/TiO₂ stack layers as obtained by the conductance method. With a value of $1.1 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$ at midgap, the D_{it} of the as-deposited TiO₂ on Al₂O₃ is very low, and an order of

FIG. 8. (a) The measured conductance loss with frequency plot of 10 nm Al₂O₃ (annealed at 400 °C in forming gas)/30 nm TiO₂ (as-deposited) as a function of gate voltage near the midgap, and (b) interface trap densities determined by the conductance method.

magnitude of lower than that of Al₂O₃ only passivated sample. However, as the post-TiO₂ annealing temperature increases, D_{it} increases again and reaches a value of $1.1 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ at midgap following a 400 °C anneal, which is the almost same as that of only Al₂O₃-passivated sample.

On the basis of the above results, we can consider the possible reasons for the improvement in J_{0e} following TiO₂ 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 TiO₂ deposition. Empirically, the degree of field effect passivation is generally found to saturate at a charge density of around $5 \times 10^{12} \text{ cm}^{-2}$.³⁴ Since the charge density in the Al₂O₃ 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 TiO₂ also results in a significant reduction in D_{it} , 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_{it} improves following TiO_2 deposition. One possible reason (and the reason most often cited for improvements in D_{it} 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_2O_3 films to passivate interface defects. For example, Veith *et al.* demonstrated that the passivation quality of thin thermal ALD- Al_2O_3 can be improved using a-SiN_x:H as a capping layer, which might be because of the hydrogenation of interface states.³⁵ 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 %),³⁶ 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 $TiCl_4$.^{35–37} 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.³⁸ Since atomic hydrogen is beneficial to the passivation of silicon by SiO_2 (as observed following a so-called anneal treatment),⁷ 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_2O_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_2O_3 films as a function of both Al_2O_3 deposition and anneal temperature. For films deposited around 200 °C, the onset of effusion did not occur until anneal temperatures of around 300 °C.³⁹ 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_2O_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_2O_3/TiO_2 stack layers as a function of TiO_2 layer thickness and for different post-deposition anneals. For the single Al_2O_3 layers, J_{0e} was found to increase strongly for an Al_2O_3 layer thickness below 10 nm. Significantly enhanced passivation was observed following deposition of TiO_2 on thin Al_2O_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_2O_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.

ACKNOWLEDGMENTS

This project has been supported by the Australian Government through the Australian Solar Institute, part of the Clean Energy Initiative. The authors would like to acknowledge the support of the project commercial partners, Transform Solar.

- ¹A. G. Aberle, *Prog. Photovoltaics* **8**, 473 (2000).
- ²J. H. Zhao, A. H. Wang, and M. A. Green, *Prog. Photovoltaics* **7**, 471 (1999).
- ³M. A. Green, *Prog. Photovoltaics* **17**, 183 (2009).
- ⁴Y. Tsunomura, Y. Yoshimine, M. Taguchi, T. Baba, T. Kinoshita, H. Kanno, H. Sakata, E. Maruyama, and M. Tanaka, *Sol. Energy Mater. Sol. Cells* **93**, 670 (2009).
- ⁵R. Hezel and R. Schorner, *J. Appl. Phys.* **52**, 3076 (1981).
- ⁶W. Soppe, H. Rieffe, and A. Weeber, *Prog. Photovoltaics* **13**, 551 (2005).
- ⁷A. G. Aberle, *Crystalline Silicon Solar Cells: Advanced Surface Passivation and Analysis* (University of New South Wales, Sydney, 1999).
- ⁸S. Dauwe, L. Mittelstadt, A. Metz, and R. Hezel, *Prog. Photovoltaics* **10**, 271 (2002).
- ⁹G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H. F. W. Dekkers, S. De Wolf, and G. Beaucarne, *Sol. Energy Mater. Sol. Cells* **90**, 3438 (2006).
- ¹⁰B. Hoex, S. B. S. Heil, E. Langereis, M. C. M. van de Sanden, and W. M. M. Kessels, *Appl. Phys. Lett.* **89**, 042112 (2006).
- ¹¹J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M. C. M. van de Sanden, and W. M. M. Kessels, *Prog. Photovoltaics* **16**, 461 (2008).
- ¹²B. Hoex, J. Schmidt, R. Bock, P. P. Altermatt, M. C. M. van de Sanden, and W. M. M. Kessels, *Appl. Phys. Lett.* **91**, 112107 (2007).
- ¹³J. Benick, B. Hoex, M. C. M. van de Sanden, W. M. M. Kessels, O. Schults, and S. W. Glunz, *Appl. Phys. Lett.* **92**, 253504 (2008).
- ¹⁴G. Dingemans, N. M. Terlinden, D. Pierreux, H. B. Profijt, M. C. M. van de Sanden, and W. M. M. Kessels, *Electrochem. Solid-State Lett.* **14**, H1 (2011).
- ¹⁵W. Dawei, J. Rui, D. Wuchang, C. Chen, W. Deqi, C. Wei, L. Haofeng, Y. Huihui, and L. Xinyu, *J. Semicond.* **32**, 094008 (2011).
- ¹⁶A. Richter, J. Benick, M. Hermle, and S. W. Glunz, *Phys. Status Solidi (RRL)* **5**, 202 (2011).
- ¹⁷H. Nagel, A. G. Aberle, and R. Hezel, *Prog. Photovoltaics* **7**, 245 (1999).
- ¹⁸S. Zaitso, T. Jitsuno, M. Nakatsuka, T. Yamanaka, and S. Motokoshi, *Appl. Phys. Lett.* **80**, 2442 (2002).
- ¹⁹P. Repo, H. Talvitie, S. Li, J. Skarp, and H. Savin, *Energy Procedia* **8**, 681 (2011).
- ²⁰B. G. Lee, J. Skarp, V. Malinen, S. Li, S. Choi, and H. M. Branz, in *38th IEEE Photovoltaic Specialists Conference*, Austin (2012), p. 1066.
- ²¹Y. Takahashi, A. Ogiso, R. Tomoda, K. Sugiyama, H. Minoura, and M. Tsuike, *J. Chem. Soc., Faraday Trans. 1* **78**, 2563 (1982).
- ²²D. E. Kane and R. M. Swanson, in *18th IEEE Photovoltaic Specialists Conference*, Las Vegas (1981), p. 578.
- ²³K. R. McIntosh, S. C. Baker-Finch, N. E. Grant, A. F. Thomson, S. Singh, and I. D. Baiki, *J. Electrochem. Soc.* **156**, G190 (2009).
- ²⁴G. Dingemans, R. Seguin, P. Engelhart, M. C. M. van de Sanden, and W. M. M. Kessels, *Phys. Status Solidi (RRL)* **4**, 10 (2010).
- ²⁵B. Hoex, J. J. H. Gielis, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **104**, 113703 (2008).
- ²⁶N. M. Terlinden, G. Dingemans, M. C. M. V. de Sanden, and W. M. M. Kessels, *Appl. Phys. Lett.* **96**, 112101 (2010).
- ²⁷J. Aarik, A. Aidla, T. Uustare, and V. Sammelselg, *J. Cryst. Growth* **148**, 268 (1995).
- ²⁸J. Aarik, A. Aidla, A. A. Kiisler, T. Uustare, and V. Sammelselg, *Thin Solid Films* **305**, 270 (1997).
- ²⁹R. S. Muller and T. I. Kamins, *Device Electronics for Integrated Circuits*, 2nd ed. (Wiley, New York, 1986).
- ³⁰D. K. Schroder, *Semiconductor Material and Device Characterization*, 2nd ed. (John Wiley & Sons, New York, 1998).
- ³¹L. M. Terman, *Solid-State Electron.* **5**, 285 (1962).
- ³²E. H. Nicollian and J. R. Brews, *MOS Physics and Technology* (Wiley, New York, 1982).
- ³³S. Chakraborty, M. K. Bera, P. K. Bose, and C. K. Maiti, *Semicond. Sci. Technol.* **21**, 335 (2006).

- ³⁴K. J. Weber, H. Jin, and C. Zhang, in *24th European Photovoltaic Solar Energy Conference*, Hamburg (2009), p. 534.
- ³⁵B. Veith, F. Werner, D. Zielke, R. Brendel, and J. Schmidt, *Energy Procedia* **8**, 307 (2011).
- ³⁶R. Matero, A. Rahtu, and M. Ritala, *Chem. Mater.* **13**, 4506 (2001).
- ³⁷J. D. Ferguson, A. R. Yoder, A. W. Weimer, and S. M. George, *Appl. Surf. Sci.* **226**, 393 (2004).
- ³⁸G. Dingemans and W. M. M. Kessels, *ECS Trans.* **41**, 293 (2011).
- ³⁹G. Dingemans, F. Einsele, W. Beyer, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **111**, 093713 (2012).