Article

Wet Chemical Oxidation to Improve Interfacial Properties of Al₂O₃/Si and Interface Analysis of Al₂O₃/SiOₓ/Si Structure Using Surface Carrier Lifetime Simulation and Capacitance–Voltage Measurement

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Abstract: A thin silicon oxide (SiOₓ) layer (thickness: 1.5–2.0 nm) formed at an Al₂O₃/Si interface can enhance the interface properties. However, it is challenging to control the characteristics of thin SiOₓ layers because SiOₓ forms naturally during Al₂O₃ deposition on Si substrates. In this study, a ~1.5 nm-thick SiOₓ layer was inserted between Al₂O₃ and Si substrates by wet chemical oxidation to improve the passivation properties. The acidic solutions used for wet chemical oxidation were HCl:H₂O₂:H₂O, H₂SO₄:H₂O₂:H₂O, and HNO₃. The thicknesses of SiOₓ layers formed in the acidic solutions were ~1.48, ~1.32, and ~1.50 nm for SiOₓ-HCl, SiOₓ-H₂SO₄, and SiOₓ-HNO₃, respectively. The leakage current characteristics of SiOₓ-HNO₃ were better than those of the oxide layers formed in the other acidic solutions. After depositing a ~10 nm-thick Al₂O₃ on an SiOₓ-acidic/Si structure, we measured the effective carrier lifetime using quasi steady-state photoconductance and examined the interfacial properties of Al₂O₃/SiOₓ-acidic/Si using surface carrier lifetime simulation and capacitance–voltage measurement. The effective carrier lifetime of Al₂O₃/SiOₓ-HNO₃/Si was relatively high (~400 µs), resulting from the low surface defect density (2.35–2.88 × 10¹⁰ cm⁻²eV⁻¹). The oxide layer inserted between Al₂O₃ and Si substrates by wet chemical oxidation helped improve the Al₂O₃/Si interface properties.

Keywords: aluminum oxide; silicon oxide; quasi steady-state photoconductance; surface passivation; crystalline silicon (c-Si) solar cell; plasma-assisted atomic layer deposition

1. Introduction

The surface passivation of crystalline silicon (c-Si) solar cells can be improved using various materials such as SiO₂ [1–6], SiNₓ [7–9], Al₂O₃ [10–13], TiOₓ [14–16], MoOₓ [17,18], and poly-Si [19–22]. In particular, Al₂O₃ thin films are most widely used for boron-doped Si surfaces (or p⁺ emitter surfaces) owing to the low surface recombination velocity (SRV) [10,11]. The interface of Al₂O₃ films can be characterized by a low interface trap density and a high negative charge density because of the ultrathin SiOₓ and negatively charged interstitial O ions present at the Al₂O₃/Si interface [23,24]. The passivation
properties of an Al$_2$O$_3$/Si structure can be improved by optimizing the Al$_2$O$_3$ thickness and annealing temperature [25,26]. In particular, a thin SiO$_x$ layer is formed at the Al$_2$O$_3$/Si interface during the deposition process and can be activated through annealing. However, it is difficult to control the quality of this layer because it forms spontaneously.

In this work, we considered a method to improve the interfacial properties of an Al$_2$O$_3$/Si structure by inserting a thin silicon oxide layer between Al$_2$O$_3$ and Si substrates. The widely used methods of growing thin silicon oxides are thermal and wet chemical oxidations. In thermal oxidation, although the quality of the silicon oxide formed is excellent, it is difficult to control the thickness (<1.5 nm) at temperatures above 800 °C. If the silicon oxide layer becomes thicker, the field effect passivation of the Al$_2$O$_3$/Si interface may deteriorate [27]. Therefore, a thickness of ~1.5 nm or less is required to improve the interfacial properties of the Al$_2$O$_3$/Si structure and ensure a good field effect passivation. Wet chemical oxidation is a promising method of growing thin SiO$_x$, and the quality of thin oxides grown using this method has been verified [28–32]. In this research, a thin oxide layer was utilized to improve the passivation property of an Al$_2$O$_3$/Si structure. We applied wet chemical oxidation to grow ~1.5 nm-thick SiO$_x$ and then deposited a ~10 nm-thick Al$_2$O$_3$ using plasma-assisted atomic layer deposition (PA-ALD). To analyze the passivation characteristics and interface properties of the Al$_2$O$_3$/SiO$_x$/Si structure, the effective carrier lifetime was measured using quasi steady state photoconductance (QSSPC), and surface carrier lifetime simulation and capacitance–voltage (C–V) measurements were performed.

2. Experimental

After the Radio Corporation of America (RCA) cleaning developed by Werner Kern to remove ionic and organic impurities in the polished 4–5 Ω·cm p-type Si(100) substrate [33], we performed wet chemical oxidation using three acidic solutions: (i) HCl:H$_2$O$_2$:H$_2$O = 1:1.5, (ii) H$_2$SO$_4$:H$_2$O$_2$:H$_2$O = 1:1:5, and (iii) HNO$_3$ (68%) [28–30]. The wet chemical oxide layers formed in the acidic solutions are hereinafter abbreviated as SiO$_x$-HCl, SiO$_x$-H$_2$SO$_4$, and SiO$_x$-HNO$_3$, respectively. The process temperature was 85 °C for SiO$_x$-HCl and SiO$_x$-H$_2$SO$_4$ and 121 °C for SiO$_x$-HNO$_3$. The immersion time was varied from 10 to 60 min. The thickness and refractive index of the silicon oxide (SiO$_x$-acidic) layers formed on Si surface was measured using spectroscopy ellipsometry (SE) and transmission electron microscopy (TEM). The quality of SiO$_x$-acidic was evaluated in terms of the leakage current density, which was measured by conducting a current–voltage (I–V) analysis with mercury probe and Keithley 238 current source meter under dark conditions. To measure the surface passivation characteristics, an approximately 10 nm-thick Al$_2$O$_3$ film was deposited on a SiO$_x$-acidic/Si substrate using PA-ALD. The reaction sources for Al$_2$O$_3$ deposition were trimethylaluminum (Al(CH$_3$)$_3$), TMA, and O$_2$ (purity 99.999%) gas; the purge gas was Ar (purity 99.999%). The deposition process was performed at a substrate temperature of 250 °C, a process pressure of 1.0 torr, a plasma power of 200 W, an O$_2$ exposure time of 0.5 s, and a distance of 20 mm between the showerhead and the substrate. Annealing was then conducted in an electric furnace at 425 °C for 15 min to activate the Al$_2$O$_3$ layer. After annealing, the carrier lifetimes of the samples were measured using QSSPC to evaluate the surface passivation characteristics. For a detailed analysis of the interface properties of Al$_2$O$_3$/SiO$_x$-acidic/Si, a surface carrier lifetime simulation and C–V measurement were performed by mercury probe with Agilent E4980A LCR meter.

3. Results and Discussions

Figure 1 shows the thickness of the silicon oxide (SiO$_x$-acidic) formed in the acidic solutions with various immersion times. The film thickness was measured by SE. The measured wavelength range was 300–100 nm and the incident beam angle was 75° in the SE measurement. With the increase in the immersion time, the thickness increased, saturating in the range of 1.32–1.50 nm. The thicknesses of SiO$_x$ are ~1.48 nm for SiO$_x$-HCl, ~1.32 nm for SiO$_x$-H$_2$SO$_4$, and ~1.50 nm for SiO$_x$-HNO$_3$. These results are similar to those reported previously [28–30]. The thickness of SiO$_x$-HNO$_3$ was also confirmed by TEM.
measurement, as shown in Figure 2. In the TEM measurements, silicon nitride (SiNₓ) was used as the capping layer to avoid additional thin oxide growth in the Al₂O₃ deposition process. The SiOₓ-HNO₃ thickness was in the range of 1.43–1.54 nm, consistent with SE measurements. As the thicknesses of SiOₓ formed in each acidic solution saturated after approximately 15 min, the immersion time was fixed at 15 min (Table 1). To evaluate the characteristics of the SiOₓ-acidic layer, the leakage current densities were measured by I–V curves under dark conditions. As shown in Figure 3, the leakage current density of SiOₓ-HNO₃ was the lowest (~9.1 × 10⁻³ A/cm² at 1 V forward-bias and ~0.92 × 10⁻³ A/cm² at −1 V reverse-bias), indicating that the quality of SiOₓ-HNO₃ is relatively better than the other oxides. The leakage current density results are similar to those reported by Kobayashi Asuha et al. [30].

![Figure 1](image1.png)

**Figure 1.** Measured thicknesses of wet chemical oxide (SiOₓ) layers prepared in different acid solutions as a function of the immersion time. The optical model is shown in the insert (right bottom) for ellipsometry analysis.

![Figure 2](image2.png)

**Figure 2.** Transmission electron microscopy (TEM) images of the wet chemical oxide (SiOₓ-HNO₃) layer in an SiNₓ/SiOₓ/Si structure.
Table 1. SiO$_x$ layer thickness and refractive index (n) at an immersion time of 15 min. The data are averaged with ten samples.

| Solution    | Thickness (nm) | Refractive Index (n) at 630 nm |
|-------------|----------------|-------------------------------|
| HCl         | 1.49           | 1.421                         |
| H$_2$SO$_4$ | 1.32           | 1.417                         |
| HNO$_3$     | 1.50           | 1.430                         |

To investigate the surface passivation properties of the SiO$_x$-acidic, a ~10 nm-thick Al$_2$O$_3$ layer was deposited on both sides of the SiO$_x$-acidic/Si substrate using PA-ALD, and the effective carrier lifetime was measured by QSSPC. The measured effective carrier lifetimes at 1.0 sun injection level [34] of Al$_2$O$_3$/SiO$_x$-HNO$_3$/Si, Al$_2$O$_3$/SiO$_x$-HCl/Si, and Al$_2$O$_3$/SiO$_x$-H$_2$SO$_4$/Si are ~400, ~317, and ~332 µs (Figure 4); notably, the passivation quality of SiO$_x$-HNO$_3$ is excellent. Moreover, the reference sample, which did not form an oxide film intentionally, exhibited a significantly lower effective carrier lifetime (~220 µs) than the samples with wet chemical oxides. This indicates that the quality of the thin SiO$_x$ layer formed at the Al$_2$O$_3$/Si interface influences the effective carrier lifetime and that the oxides formed in acidic solutions exhibit better passivation properties than oxide films formed naturally during the deposition process. To investigate the interfacial properties of Al$_2$O$_3$/SiO$_x$-acidic/Si, the surface carrier lifetime simulation and C–V measurement were performed. The surface carrier lifetime simulation is based on the extended Shockley–Read–Hall (SRH) recombination equation. This equation was derived from the SRV, expressed in Equations (1) and (2) [35,36].

\[
S \equiv \frac{U_s}{\Delta n_s} \tag{1}
\]

\[
U_s = \frac{n_s p_s - n_i^2}{n_i + n_i + p_i + p_i} \text{ with } S_{\rho \theta} = \sigma_p V_{th} D_\theta, \quad S_{n0} = \sigma_n V_{th} D_\theta \tag{2}
\]

where $S$ is the surface recombination velocity, $U_s$ is the surface recombination rate, and $\Delta n_s$ is the excess carrier density at the surface. $S_{n0}$ and $S_{\rho \theta}$ are the surface recombination velocities of electrons and holes, $n_s$ and $p_s$ are the electron and hole concentrations at the surface, $\sigma_n$ and $\sigma_p$ are the capture
cross-sections for electrons and holes, $n_1$ and $p_1$ are parameter in the SRH recombination equation and $D_{it}$ is the number of surface states per unit area. However, if band bending exists on the Si surface by fixed charges (such as negative or positive charges), it is difficult to evaluate $\Delta n_s$ because the carrier lifetime is determined by the carrier density in the bulk. To this end, we considered the surface of the semiconductor region ($z = 0$) and the space charge region ($z < d_{sc}$), as shown in Figure 5.

**Figure 4.** Effective carrier lifetime curves as a function of the excess carrier density ($\Delta n$) for Al$_2$O$_3$/SiO$_x$-acidic/Si structures and Al$_2$O$_3$/Si reference sample. The Al$_2$O$_3$ thickness is 10 nm and the SiO$_x$ thicknesses are 1.49 nm for SiO$_x$-HCl, 1.32 nm for SiO$_x$-H$_2$SO$_4$, and 1.50 nm for SiO$_x$-HNO$_3$, respectively.

**Figure 5.** Energy band diagram for a semiconductor–insulator interface under illumination, where the semiconductor is p-type and the insulator is negatively charged (i.e., Al$_2$O$_3$). The diagram shows the energy of the conduction band $E_c$, the valence band $E_v$, the intrinsic fermi level $E_i$, as well as the quasi-fermi energy of electrons $E_{Fn}$ and holes $E_{Fp}$. The distance $z = 0$ represents the interface between the semiconductor and the negatively charged insulator, and $z = d_{sc}$ represents the distance of the space charge region. $\Psi_s$ is the surface potential.
Therefore, the effective surface recombination velocity \( S_{eff} \) is the sum of the interface recombination velocity and the space charge recombination velocity, as shown in Equations (3)–(9) \[35–39\].

\[
S_{eff} = \frac{1}{\Delta n_{dc}} \left[ U_s + \int_0^{d_{sc}} U(z) dz \right] = S_{it} + S_{sc} \tag{3}
\]

\( S_{it} \) can be expressed in Equation (4) based on Equations (1) and (2).

\[
S_{it} = \frac{1}{\Delta n_{dc}} \left[ \frac{\left( n_s p_b - n_i^2 \right) D_{it} V_{th} E_g}{n_i + n_i^2 + \Delta n_i^2} \right] \tag{4}
\]

\( S_{sc} \) can be described by Equation (5) as follows by using Equations (6)–(9) for surface potential \( \Psi_s \) and surface electron and hole concentrations by effective carrier density \( Q_f \) \[34,35\].

\[
S_{sc} = \frac{1}{\Delta n_{dc}} \int_0^{d_{sc}} \frac{\left( n_s(z) p_b(z) - n_i^2 \right) N_d V_{th} E_g}{n_i + n_i^2 + \Delta n_i^2 + p_i + p_i + \Delta n_i^2} dz \tag{5}
\]

\[
\int_0^{d_{sc}} n_s(z) dz = \beta \lambda_D \int_{\psi_s}^0 n(\psi) F d\psi, \int_0^{d_{sc}} p_b(z) dz = \beta \lambda_D \int_{\psi_s}^0 p(\psi) F d\psi \tag{6}
\]

\[
Q_f = \frac{F(\psi_s, \Phi_p, \Phi_n)}{\alpha \beta D} \tag{7}
\]

\[
F(\psi_s, \Phi_p, \Phi_n) = \sqrt{\frac{2}{p_i + n_i} \left[ p_i \left( e^{-\beta \psi_s} + \beta \psi_s - 1 \right) + n_i \left( e^{\beta \psi_s} - \beta \psi_s - 1 \right) \right]} \tag{8}
\]

\[
p_i = n_i \text{e}^{\beta \Phi_f}, n_i = n_i \text{e}^{\beta \Phi_f} \tag{9}
\]

Here, \( S_{it} \) is the interface recombination velocity between the Si surface and the dielectric layer \( (z = 0) \), \( S_{sc} \) is the recombination velocity in the space charge region \( (z < d_{sc}) \), \( d_{sc} \) is the distance of the space charge region, and \( z \) is the coordinate perpendicular to the semiconductor surface and increases toward the bulk of Si, \( V_{th} \) is the thermal carrier velocity, \( E_g \) is the energy band gap of Si, \( \Psi \) is the surface potential, \( Q_f \) is the fixed charge density, \( \Phi_i \) and \( \Phi_p \) are quasi-fermi level for electrons and holes, \( p_b \) and \( n_b \) are the carrier concentration for electrons and holes, \( n_i \) is intrinsic carrier concentration. With Equation (3), we can calculate the theoretical effective surface carrier lifetime using Equation (10).

\[
\frac{1}{\tau_{eff}} = \frac{1}{\tau_{it}} + \frac{1}{\tau_{sc}} = \frac{W}{2} \left( \frac{1}{\tau_{it}} + \frac{1}{\tau_{sc}} \right) \tag{10}
\]

where \( \tau_{eff} \) is the effective surface carrier lifetime, \( \tau_{it} \) is the carrier lifetime in the interface region between the Si surface and the dielectric layer, \( \tau_{sc} \) is the carrier lifetime in the space charge region, and \( W \) is the thickness of the wafer. The surface carrier lifetime simulation was performed by comparing the effective carrier lifetime \( (\tau_{measured}) \) measured using Equation (10). Assuming that the capture cross-section of the electron and hole is \( \sigma_n = \sigma_p = 1 \times 10^{15} \text{ cm}^2 \), we analyzed the interface trap density \( (D_{it}) \) and the fixed charge density \( (Q_f) \) as variable parameters so that the curves of \( \tau_{simulated} \) and \( \tau_{measured} \) matched well. Figure 6 shows the \( \tau_{simulated} \) and \( \tau_{measured} \) curves.
would be more influenced by the quality of SiO$_x$-HNO$_3$ values of $Q_f$ and $D_{it}$ extracted from the surface carrier lifetime analysis, the passivation properties would be more influenced by $D_{it}$ than $Q_f$. C–V measurements were also performed to compare the values of $D_{it}$ and $Q_f$ with those obtained from the surface carrier lifetime analysis. The C–V measurement results show that $V_{FB}$ (flat band voltage) of the silicon substrates with wet chemical oxide layers shifts by 1.77–2.08 V toward the positive bias, as shown in Figure 7.

**Table 2.** Results of capacitance–voltage (C–V) and surface carrier lifetime analyses.

| Sample (Average of Five Samples) | Capacitance–Voltage (C–V) Analysis | Surface Carrier Lifetime Analysis |
|----------------------------------|------------------------------------|----------------------------------|
|                                  | $Q_f$ (10$^{12}$ cm$^{-2}$) | $D_{it}$ (10$^{10}$ cm$^{-2}$eV$^{-1}$) | $V_{FB}$ (V) | $Q_f$ (10$^{12}$ cm$^{-2}$) | $D_{it}$ (10$^{10}$ cm$^{-2}$eV$^{-1}$) |
| Al$_2$O$_3$/Si                   | -1.53                             | 7.01                             | 1.20       | -1.00                     | 7.50                              |
| Al$_2$O$_3$/SiO$_x$-HCl/Si       | -3.03                             | 4.94                             | 2.97       | -3.30                     | 5.70                              |
| Al$_2$O$_3$/SiO$_x$-H$_2$SO$_4$/Si| -3.12                             | 4.60                             | 3.12       | -3.50                     | 3.90                              |
| Al$_2$O$_3$/SiO$_x$-HNO$_3$/Si   | -3.24                             | 2.88                             | 3.28       | -3.52                     | 2.30                              |

$Q_f$ was calculated using $V_{FB}$ extracted from the measured C–V graph, and $D_{it}$ was obtained using the Terman method (Table 2) [40,41]. The negative $Q_f$ values of the silicon oxides formed in the different acidic solutions did not change significantly in the range of 3.03–3.24 × 10$^{12}$ cm$^{-2}$. However, $D_{it}$ was markedly different depending on the acid solution used (Table 2). Therefore, we confirm that the quality of SiO$_x$ at the Al$_2$O$_3$/Si interface affects the passivation characteristics, and the insertion of a wet
chemical oxide layer improved the passivation quality, compared with the SiO\textsubscript{x} layer simultaneously formed during the deposition of Al\textsubscript{2}O\textsubscript{3}.

![Figure 7. Capacitance–voltage curves at 1 MHz of Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{x-acidic}/Si structures and Al\textsubscript{2}O\textsubscript{3}/Si reference sample for calculating the fixed charge density (Q\textsubscript{f}) and interface trap density (D\textsubscript{it}).](image)

4. Conclusions

In this study, we improved the interfacial properties of an Al\textsubscript{2}O\textsubscript{3}/Si structure by performing wet chemical oxidation on an Si substrate. The thickness of the wet chemical oxides grown on the Si surface in different acidic solutions was in the range of 1.32–1.5 nm, which was similar to that of SiO\textsubscript{x} naturally formed at the interface of the Al\textsubscript{2}O\textsubscript{3}/Si sample during PA-ALD deposition. In particular, SiO\textsubscript{x-HNO\textsubscript{3}} showed a relatively lower leakage current than SiO\textsubscript{x-HCl} and SiO\textsubscript{x-H\textsubscript{2}SO\textsubscript{4}}. The carrier lifetime of Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{x-HNO\textsubscript{3}}/Si measured by QSSPC to evaluate the passivation characteristics was ~ 400 \(\mu\)s, which was higher than those of the other SiO\textsubscript{x-acidic} layers (~317 \(\mu\)s for SiO\textsubscript{x-HCl} and ~332 \(\mu\)s for SiO\textsubscript{x-H\textsubscript{2}SO\textsubscript{4}}). C–V measurement and surface carrier lifetime analysis were performed to analyze the interface characteristics of the Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{x}/Si samples. The fixed charges showed little change with the oxides, and the D\textsubscript{it} values changed significantly. The wet chemical oxide formed in the HNO\textsubscript{3} solution showed better passivation characteristics than those formed in other acidic solutions, resulting from the low interface trap density of SiO\textsubscript{x-HNO\textsubscript{3}}. We confirmed the improvement in the passivation characteristics of the Al\textsubscript{2}O\textsubscript{3}/Si sample by inserting a wet chemical oxide between Al\textsubscript{2}O\textsubscript{3} and Si substrates. In addition, the values of the parameters associated with the interface properties, such as Q\textsubscript{f} and D\textsubscript{it}, obtained from the C–V measurement and surface carrier lifetime simulation were similar. Therefore, this simulation can be a useful tool to analyze interfacial characteristics. Moreover, this study lays a foundation for analyzing the interfacial properties of samples, such as poly-Si/SiO\textsubscript{x}/Si structures with ultra-thin SiO\textsubscript{x}, that cannot be analyzed by C–V measurements.

**Author Contributions:** K.H.M. designed experiments, performed the experiments and wrote manuscripts; H.-e.S. and H.-S.L. wrote manuscripts and interpreted experimental findings; S.P., M.G.K., J.I.L., Y.K., D.K. supervised the studies; S.C. and M.S.J. participated in discussion. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.
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