Dual Function of Antireflectance and Surface Passivation of Atomic-Layer-Deposited Al_2O_3 Films

Li Qiang Zhu, Xiang Li, Zhong Hui Yan, Hong Liang Zhang, and Qing Wan

Abstract—**Surface antireflectance and passivation properties of the Al_2O_3 films deposited on Czochralski Si wafers by atomic layer deposition (ALD) are investigated. Textured Si with 100-nm Al_2O_3 shows a very low average reflectance of ∼2.8%. Both p- and n-type Si wafers are well passivated by Al_2O_3 films. The maximal minority carrier lifetimes are improved from ∼10 μs before Al_2O_3 passivation to above 3 ms for both p- and n-type Si after Al_2O_3 film deposition and annealing at an appropriate temperature. Hence, an ALD-deposited Al_2O_3 film shows the dual function of antireflectance and surface passivation for solar cell applications.**

Index Terms—**Antireflectance, atomic layer deposition (ALD)-deposited Al_2O_3 film, Si solar cells, surface passivation.**

I. INTRODUCTION

Al_2O_3 thin films provide excellent surface passivation on both lightly and highly doped p- and n-type crystalline silicon (c-Si) surfaces, resulting in the improved efficiency [1]–[5], which is attributed to a low density of interface defects D_{it} in the range of 10^{11} $\mathrm{cm}^{-2} \cdot \mathrm{eV}^{-1}$ and a field-effect passivation with a high density of fixed negative charges Q_{fix} above 10^{12} cm^{-2} [1], [6]. To activate the passivation, an annealing step at moderate temperatures after deposition was reported to be essential [7]. At the same time, effective antireflectance plays an important role for solar cells efficiency improvement. Conventionally, the textured Si surface coated with a SiN_x antireflective layer from the production line shows an average reflectance of below 5%. Although the strong passivation performance for Al_2O_3 films have been reported, the antireflective properties of Al_2O_3 films have not been reported yet [1]–[7]. In this letter, both antireflectance properties and passivation properties of the Al_2O_3 films deposited by atomic layer deposition (ALD) are studied. A minimal reflectance of ∼2.8% is obtained. A maximal minority carrier lifetime of above 3 ms was obtained for both p- and n-type Si passivated by Al_2O_3. Such results indicate that Al_2O_3 films have the dual function of antireflectance and surface passivation, which is favorable for c-Si solar cell applications.

II. EXPERIMENTAL DETAIL

The 400-μm-thick (100)-oriented p-type ($\rho = 30\ \Omega \cdot \mathrm{cm}$) and n-type ($\rho = 5.5\ \Omega \cdot \mathrm{cm}$) Czochralski (CZ) Si wafers were used as the substrates. For antireflectance investigation, some Si wafers were textured by ∼1.2% NaOH solution at ∼80 °C for ∼20 min. All substrates underwent an HCl solution dip for 5 min followed by a dilute HF dip. A deionized water rinse was adopted after each chemical dip step. Al_2O_3 films with different thicknesses were deposited on both sides of the Si wafers to obtain symmetric lifetime samples by a thermal NCD 200B ALD reactor at 200 °C with a 100-sccm background flow of N_2. A cycle in the reactor consisted of a 0.3-s injection of $Al(CH_3)_3$ vapors followed by 7-s N_2 purge and a 0.1-s injection of H_2O vapor followed by 7-s N_2 purge, resulting in a deposition rate of 1.25 Å/cycle. The lifetime samples were annealed at different temperatures in atmosphere ambient. SiN_x was deposited by plasma-enhanced chemical vapor deposition on the same textured Si at the production line for antireflectance comparison, which is noted as the standard (STD SiN_x) sample.

X-ray photoelectron spectroscopy and scanning electron microscopy (SEM) are used for structural characterization. Spectroscopic ellipsometry has been employed to investigate the optical characteristics and the thickness of Al_2O_3 films on shiny-etched Si with the incidence angle of 55°, 65°, and 75°. The reflectance spectrum was measured by an AudioDev Helios LAB-rc system. Reflected light from a broadband halogen light source is collected and detected by a special designed integrating sphere. The average reflectance was calculated between 380 and 1090 nm, without any weighting. Effective minority carrier lifetime τ_{eff} is measured after annealing on a Semilab WT-2000PVN lifetime tester. The maximum achieved τ_{eff} were investigated. Lifetime τ_{eff} depends on both bulk minority carrier lifetime τ_{bulk} and surface recombination velocity S_{eff} [8], i.e.,

$$\frac{1}{\tau_{\mathrm{eff}}} = \frac{1}{\tau_{\mathrm{bulk}}} + \frac{2S_{\mathrm{eff}}}{W} \tag{1}$$

where W is the wafer thickness. The bulk minority carrier lifetime was assumed to be infinite. Accordingly, the calculated S_{eff} value marks an upper limit to the effective surface recombination velocity.

III. RESULTS AND DISCUSSION

An SEM image of the textured Si surface shows typical pyramid structures. The thicknesses of Al_2O_3 films are determined to be ∼100, ∼70, and ∼30 nm for 800, 560, and 240 ALD cycles, respectively. X-ray photoelectron spectroscopy results indicate that Al_2O_3 is stoichiometric with an O/Al ratio

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Manuscript received August 23, 2012; revised September 10, 2012; accepted September 13, 2012. Date of publication October 26, 2012; date of current version November 22, 2012. This work was supported in part by the National Natural Science Foundation of China under Grant 11104288 and in part by the Ningbo Natural Science Foundation under Grant 2011A610202. The review of this letter was arranged by Editor S. J. Koester.

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Digital Object Identifier 10.1109/LED.2012.2219491

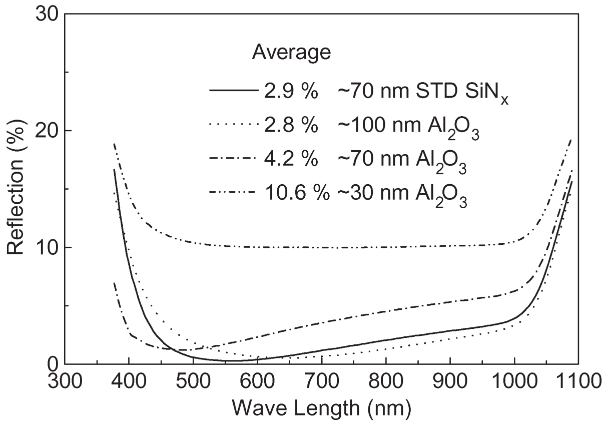

Fig. 1. Reflectance curves for the Al_2O_3-coated textured Si. Results for the standard SiN_x-coated textured Si (STD SiN_x) are included for comparison.

of ∼1.53. The refractive index is measured to be ∼1.65 at a wavelength of 630 nm, which is similar to the reported value [9]. Optical band gap E_g is extracted to be ∼6 eV, which means that the deposited Al_2O_3 layer is transparent for the wavelength above 200 nm. The obtained results are meaningful for antireflectance applications in solar cells.

Fig. 1 shows the reflectance spectrum of the Al_2O_3-coated textured Si wafers with different film thicknesses. The reflectance for the STD SiN_x sample is also included for comparison. The average reflectance is ∼10.6% and ∼4.2% when depositing ∼30-nm Al_2O_3 and ∼70-nm Al_2O_3 on textured Si, respectively. Meaningfully, the reflectance spectra for ∼100-nm Al_2O_3-coated textured Si are quite similar to that of the STD sample. At shorter wavelength, the reflectance for ∼100-nm Al_2O_3 is slightly higher than the STD sample, whereas at longer wavelength, the reflectance is slightly lower than the STD sample, which results in the best reflectance of ∼2.8% for ∼100-nm Al_2O_3 on the textured Si, close to 2.9% for the STD SiN_x sample. Such differences may be due to the different refractive index between SiN_x and Al_2O_3. The aforementioned results indicate the potential antireflectance applications of Al_2O_3 in c-Si solar cells.

A low lifetime of ∼6.0 μs is obtained for the original p-Si wafer. After a 100-nm-thick Al_2O_3 deposition, a moderate surface passivation level with effective minority carrier lifetimes τ_{eff} of ∼140 μs is obtained, which is similar to that observed for conventional thermal ALD [10]. Similarly, a 30-nm-thick Al_2O_3 deposition results in higher effective minority carrier lifetimes τ_{eff} of ∼910 μs. To study the full potential for the surface passivation and the thermal stability of the Al_2O_3 layers, the lifetime samples were exposed to postdeposition annealing in atmosphere ambient for 5 min with temperature ranging from 300 °C to 650 °C. Fig. 2(a) illustrates the effective minority carrier lifetime of Al_2O_3-passivated p-type Si wafers as a function of the applied thermal treatment temperature. Flash annealing was also performed at 900 °C for 3 s. For the 100-nm Al_2O_3-coated samples, annealing performed at 600 °C for 5 min yields a good passivation with a lifetime of ∼750 μs. While for the 30-nm Al_2O_3-coated samples, the best passivation is obtained at 350 °C with a lifetime of ∼4.7 ms. Annealing at higher temperature results in the deteriorated lifetime. The flash annealing at 900 °C for 3 s for the 30-nm Al_2O_3-coated lifetime samples yields a moderate level of surface passivation with a lifetime of 120 μs. The passivation stabilities have been studied for the annealed samples. After two months in air ambient, the lifetime is reduced from 4.7, 4, and 2.5 ms to 2.5, 2.4, and 1.5 ms, for 350 °C, 400 °C, and 450 °C annealed 30-nm Al_2O_3-passivated p-type Si, respectively. Such degradations might be due to the decreased negative charge densities.

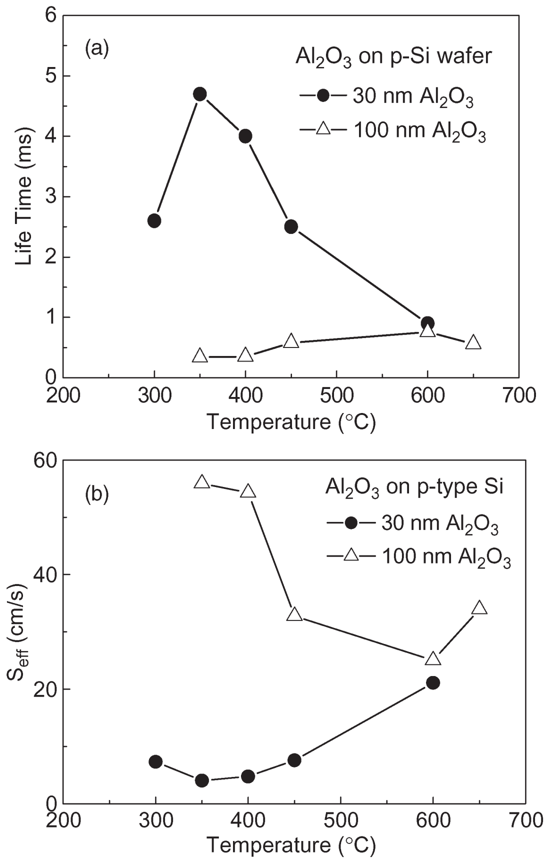

Fig. 2. (a) Lifetime values for p-type Si passivated by 100- and 30-nm Al_2O_3. (b) Effective surface recombination velocity S_{eff}.

The upper limit of the effective surface recombination velocity was also calculated. For the original Si wafer, a high S_{eff} value of ∼3200 cm/s is determined. Before annealing, the 100-nm Al_2O_3-passivated p-type Si wafer shows a moderate S_{eff} of ∼130 cm/s, whereas the 30-nm Al_2O_3-passivated p-type Si wafer shows a lower S_{eff} of ∼20 cm/s. The postdeposition annealing treatment results in the improved S_{eff} [as shown in Fig. 2(b)]. For 100-nm Al_2O_3-coated Si wafers, the best results are obtained at 600 °C, yielding the lowest S_{eff} of ∼25 cm/s. While for 30-nm Al_2O_3-coated Si wafers, a very low $S_{\mathrm{eff}} <$ 20 cm/s is obtained. The lowest S_{eff} of ∼4 cm/s is addressed at 350 °C. The flash annealing at 900 °C for 3 s yields a moderate level of surface passivation with an S_{eff} of ∼160 cm/s.

Capacitance–voltage (1.0 MHz) characterizations were measured by a Keithley 4200 SCS semiconductor parameter analyzer on MOS structures with Al_2O_3 films with different thicknesses, as shown in Fig. 3. High densities of negative fixed charges are obtained for both the 30- and 100-nm Al_2O_3 on the order of $\sim 10^{12}/\mathrm{cm}^2$ by using the following relation: $V_{\mathrm{fb}} = \Phi_{\mathrm{ms}} - Q_{\mathrm{fix}} T_{\mathrm{Al_2O_3}} / \varepsilon_{\mathrm{Al_2O_3}}$. The high densities of the negative fixed charges in the 30-nm films result in a strong field-effect passivation [6]. A big stretch-out in the C–V curves for the

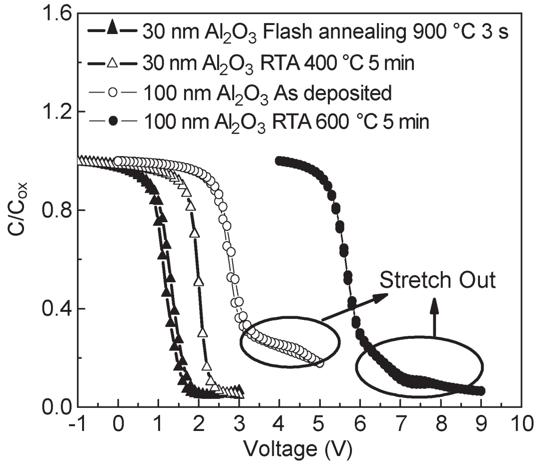

Fig. 3. Normalized C–V curves of MOS structures with Al_2O_3 films on p-type Si substrates measured at 1.0 MHz.

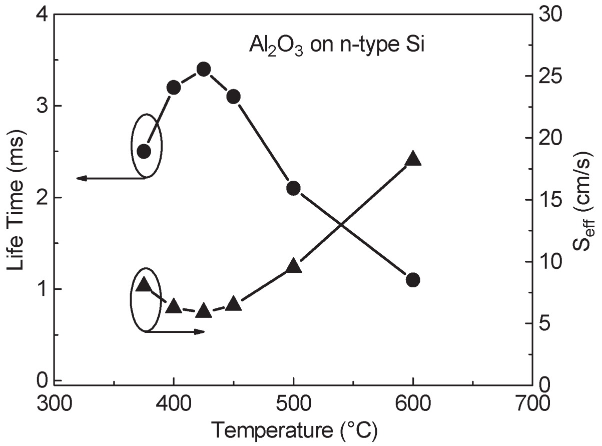

Fig. 4. Lifetime values for n-type Si passivated by 100-nm Al_2O_3 and the effective surface recombination velocity S_{eff}.

100-nm Al_2O_3 is observed, which is likely due to the high-density interfacial state D_{it} and defects. Hence, the 100-nm Al_2O_3 shows a relatively poorer passivation performance.

Similarly, n-type Si wafers are also passivated by 100-nm-thick Al_2O_3, as shown in Fig. 4. The original n-type Si wafer shows a low minority carrier lifetime of $\sim$13 μs. After passivated with 100-nm-thick Al_2O_3, the effective minority carrier lifetime increased to 1.2 and 3.4 ms for the as-deposited sample and the 425 °C annealed sample, respectively. The flash annealing at 900 °C for 3 s yields a moderate level of surface passivation with a lifetime of 450 μs. The upper limit of the effective surface recombination velocity is obtained. The n-type Si wafer passivated by a 100-nm Al_2O_3 layer shows a low S_{eff} of $\sim$16 cm/s before annealing. The lowest S_{eff} of $\sim$6 cm/s is obtained after annealing at 425 °C. The flash annealing at 900 °C for 3 s yields a moderate level of surface passivation with an S_{eff} of 44 cm/s.

IV. CONCLUSION

In summary, Al_2O_3 layers have been deposited by thermal ALD on both p- and n-type CZ Si wafers. The textured Si coated with 100-nm Al_2O_3 shows a low average reflectance of $\sim$2.8%. Both p- and n-type Si wafers can be well passivated by Al_2O_3 films. The maximal minority carrier lifetimes are improved from $\sim$10 μs to above 3.0 ms for both p- and n-type Si after Al_2O_3 passivation and annealing. Hence, the dual function of antireflectance and surface passivation of an ALD-deposited Al_2O_3 film was demonstrated, which has potential application in c-Si solar cells.

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