Crystalline silicon surface passivation investigated by thermal atomic-layer-deposited aluminum oxide*

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Atomic-layer-deposited (ALD) aluminum oxide (Al_2O_3) has demonstrated an excellent surface passivation for crystalline silicon (c-Si) surfaces, as well as for highly boron-doped c-Si surfaces. In this paper, water-based thermal atomic layer deposition of Al_2O_3 films are fabricated for c-Si surface passivation. The influence of deposition conditions on the passivation quality is investigated. The results show that the excellent passivation on n-type c-Si can be achieved at a low thermal budget of 250 °C given a gas pressure of 0.15 Torr. The thickness-dependence of surface passivation indicates that the effective minority carrier lifetime increases drastically when the thickness of Al_2O_3 is larger than 10 nm. The influence of thermal post annealing treatments is also studied. Comparable carrier lifetime is achieved when Al_2O_3 sample is annealed for 15 min in forming gas in a temperature range from 400 °C to 450 °C. In addition, the passivation quality can be further improved when a thin PECVD-SiN_x cap layer is prepared on Al_2O_3, and an effective minority carrier lifetime of 2.8 ms and implied V_{oc} of 721 mV are obtained. In addition, several novel methods are proposed to restrain blistering.

Keywords: atomic layer deposition, Al_2O_3, surface passivation, effective minority carrier lifetime

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1. Introduction

Surface passivation is an important factor for improving solar cell efficiency. According to surface passivation mechanism, surface passivation can be enhanced by chemical passivation to reduce the interface state density D_{it} and by field-effect passivation to reduce the surface concentration of minority carriers.[1–5] As is well known, the thermal silicon oxide (SiO_2) is a very good surface passivation material for crystalline Si (c-Si).[6–8] However, the formation of thermal SiO_2 requires a high-temperature process (>1000 °C), which not only increases the processing cost, but also degrades the quality of the silicon wafer. In recent years, atomic layer deposition of aluminum oxide (Al_2O_3), as a promising passivation material, is widely used in passivating the surfaces of electron transport layers in organic photovoltaics,[9] the surfaces of perovskites and dye-sensitized solar cells,[10,11] and especially p- and n-type c-Si surfaces as well as highly doped p-type emitters, owing to its low midgap defect density at the interface in a range of 1×10^{11} $cm^{-2}\cdot eV^{-1}$ and a high quantity of negative fixed charges up to $1\times10^{12}-1\times10^{13}$ cm^{-2}.[12,13] Additionally, Al_2O_3 provides a refractive index of 1.65 and a large bandgap which inhibits a significant absorption in the visible part of the solar spectrum. Actually, excellent results in terms of surface passivation quality and thermal stability have been obtained for Al_2O_3 deposited by plasma ALD,[2,3] and Al_2O_3 surface passivation films synthesized by thermal ALD, with H_2O used as oxidant, which has been a most popular process in recent years and it has also been implemented in industrial single-wafer and batch reactors due to the low cost and its good surface passivation.[14–16] Therefore, this work mainly focuses on the characterization of Al_2O_3 deposited via thermal ALD particularly for the applications in passivating n-type solar cells. The passivation quality and the layer blistering characteristic for Al_2O_3 capped by PECVD-SiN_x layers after post-annealing processes are investigated. In addition, new approaches are expected to develop to restrain blistering.

2. Experiment

To study the surface passivation quality of Al_2O_3, Al_2O_3 films were fabricated on two-inch n-type Czochralsky-grown (Cz) Si wafers with a (100) orientation and a thickness of 300 μm. Prior to Al_2O_3 deposition, a conventional RCA clean

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was performed, then the wafer was rinsed in diluted HF. This step is for removing native oxide on the surface and providing hydrogen-terminated silicon substrates. Shortly after that, thermal ALD-Al_2O_3 film was deposited on both sides of the wafer to obtain a symmetrical structure and improve the reliability of the results. Trimethylaluminum (TMA) precursor was used as an aluminum source, the schematic representation of the ALD cycles employed is shown in Fig. 1(a).[17–19] To further improve the passivation property, a PECVD-SiN_x cap layer was deposited as shown in Fig. 1(b). The post annealing process was performed in a tube annealing furnace in forming gas (N_2:$H_2 = 9:1$) for the single Al_2O_3 and Al_2O_3/SiN_x layer stacks to activate the passivation. Optical microscopy was used to observe the surface morphologies of samples after annealing. The passivation quality was commonly quantified by the effective minority carrier lifetime ($\tau_{\rm eff}$), which depends on bulk lifetime and surface recombination. The effective lifetime can be analyzed by using the formula $1/\tau_{\rm eff} = 1/\tau_{\rm bulk} + 2{\rm SRV}/W$, where W is the thickness of the substrate and $1/\tau_{\rm bulk} = 1/\tau_{\rm Aug} + 1/\tau_{\rm rad} + 1/\tau_{\rm SRH}$ ($\tau_{\rm Aug}$, $\tau_{\rm rad}$, and $\tau_{\rm SRH}$ are the Auger, the radiative, and the Shockley–Read–Hall lifetimes within bulk Si, respectively).[20–23] The effective minority carrier lifetime ($\tau_{\rm eff}$) of the n-type Cz Si sample was determined from photoconductance decay (PCD) measurements by Sinton WCT-120. The surface recombination velocity (SRV) was measured by PV-2000A Solar Metrology System. The thickness of Al_2O_3 film was measured by spectroscopic ellipsometry.

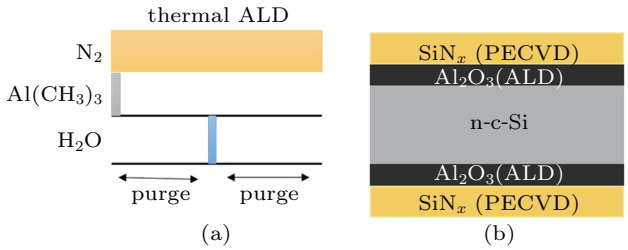


Fig. 1. (color online) (a) Schematic of thermal ALD cycles. $Al(CH_3)_3$ and H_2O dosing times in this study are in a ms range and the purge is of the order of seconds, N_2 was used as purge gas; (b) n-type c-Si sample with symmetrical passivation layers.

3. Results and discussion

3.1. Passivation effect of Al_2O_3 on n-c-Si

In order to obtain optimal passivation effect and fabricate high-efficiency silicon solar cells, the influences of Al_2O_3 deposition conditions, such as growth temperature and gas pressure, and Al_2O_3 film thickness on the passivation were investigated.

In Fig. 2(a), the deposition temperature is 200 °C, and 180 cycles ($\sim$ 20 nm) with a deposition rate of 1.1 Å/cycle are employed. All samples are annealed for 10 min at a preset temperature of 450 °C in forming gas. It is observed that the as-deposited passivation quality decreases slightly with gas pressure increasing. It is known that the gas pressure mainly affects the resident time of gas species in the chamber. For a long enough purge time, the growth of Al_2O_3 is only controlled by the absorption of gas species rather than the chemical reactions between the precursors. Whereas an obviously improved passivation quality with increasing substrate temperature and ALD-Al_2O_3 thickness is observed in Figs. 2(b) and 2(c), a similar trend is observed for the annealing films. For low ALD deposition temperatures, the H impurity concentration increases,[24] the poor passivation quality at low ALD deposition temperatures could be attributed to an excess of hydrogen and/or hydroxyl groups in the layer.[25] The passivation properties for as-deposited Al_2O_3 are improved with increasing substrate temperature, which is most probably ascribed to a more efficient surface oxidation by thermally activated oxidation by H_2O with increasing substrate temperature,[26,27] or it could be explained by an in situ annealing effect by which more charges are distributed within the layer for the Al_2O_3 film deposited at higher temperature, and the annealed Al_2O_3 film shows a highest lifetime at 250 °C. When deposition temperature is over 250 °C, lifetime decreases, which could be mainly attributed to a reducing density of OH surface groups due to dehydroxylation reactions.[2,28] In Fig. 2(c), samples with different Al_2O_3 thickness are grown at 250 °C and then annealed. The results indicate that a thin Al_2O_3 film (< 6 nm) leads to a poor passivation quality, whereas the passivation quality increases obviously when the thickness of Al_2O_3 is larger than 10 nm. Relatively good passivation with increasing the oxide thickness is attributed to the increasing of negative fixed charges distributed near the interface. It has been reported that the total oxide charge density is proportional to Al_2O_3 thickness.[29,30] For n-type substrate, the interface traps are due to the negative charge states between the Fermi level and the midgap. The interface charge and the fixed charge are both negative, so the charge is accumulative to form good field-effect passivation. In conclusion, effective surfaces passivation on n-type c-Si can be achieved at a low thermal budget of 250 °C for a given gas pressure of 0.15 Torr. An effective minority carrier lifetime ($\tau_{\rm eff}$) of over 1.8 ms is obtained with 20 nm Al_2O_3 single layer passivation. It can be improved to over 2 ms by Al_2O_3/SiN_x layer stack passivation, which is probably due to the very high hydrogen content in the PECVD-SiN_x film. During the deposition of SiN_x, hydrogen atoms diffuse from SiN_x through the thin Al_2O_3 to the interface where it effectively passivates dangling bonds.[31]

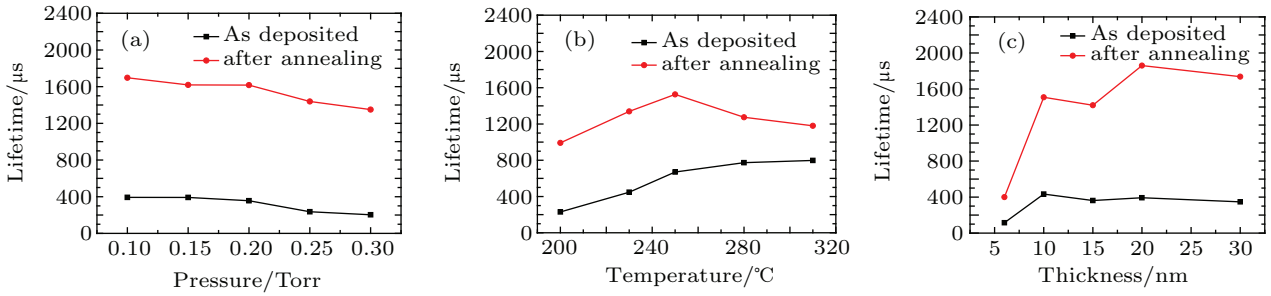


Fig. 2. (color online) Maximum effective minority carrier lifetime as a function of (a) pressure, (b) deposition temperature, and (c) Al_2O_3 thickness.

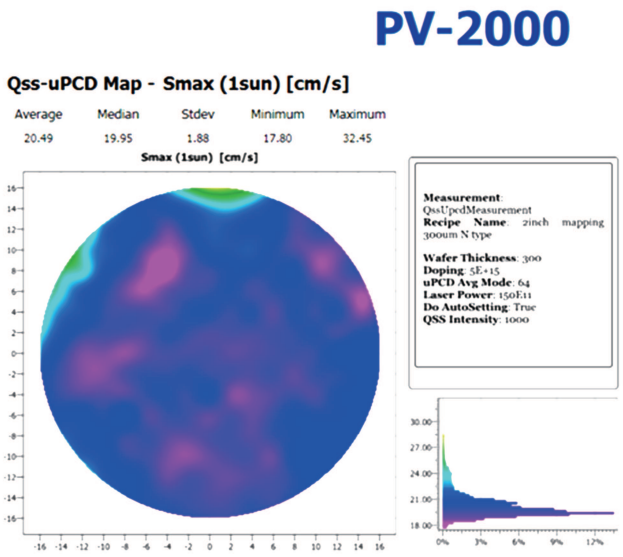


Fig. 3. (color online) Smax (1sun) images measured by PV-2000A Solar Metrology System.

Figure 3 exhibits μW-PCD mapping measured on 5 Ω·cm n-type Cz sample passivated with 15 nm Al_2O_3 layer by PV-2000A Solar Metrology System, which is for analyzing the relative uniformity of Al_2O_3 passivation layer. In this work, the Al_2O_3 layer thickness of 15 nm (135 ALD cycles) is deposited first and then annealed for 10 min at a preset temperature of 400 °C in forming gas. After that, 70 nm PECVD-SiN_x layer is grown as anti-reflection coating (ARC), and then annealed for 15 min at a preset temperature of 450 °C in forming gas. The result shows a relatively good uniformity and passivation. The minimum surface recombination velocity is ∼ 17.8 cm/s.

3.2. Effect of post annealing process

In the oxide of an as-deposited sample, there are lots of defect traps, which is attributed to an excess of hydrogen atoms in the layer during the deposition or to oxygen vacancies in the oxide. With annealing, the oxide at the Al_2O_3/Si interface starts to be reconstructed, leading to negative charge evolution.[25,26] A previous work showed that the thermal ALD process provides very good chemical passivation due to the formation of an interfacial SiO_2 layer: this thin SiO_2 layer is responsible for reducing the interface states at SiO_2/Si interface, and its oxygen atoms can provide bonding to the negatively charged Al atoms, forming negative fixed charges.[28,29] Thus, optimal post-annealing condition is explored to increase the minority carrier lifetime of c-Si.

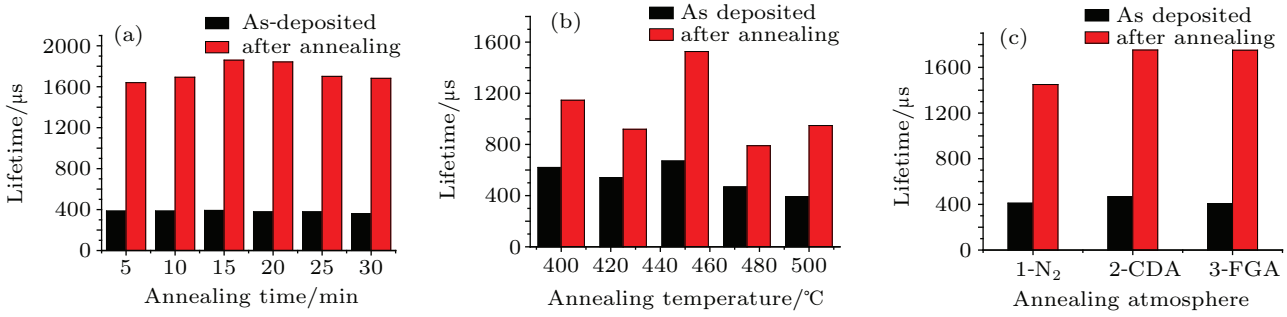


Fig. 4. (color online) Effects of (a) annealing time, (b) annealing temperature, and (c) annealing atmosphere on passivation.

As shown in Fig. 4(a), an appropriate increase of the annealing time indeed improves the passivation, and an annealing time of 15 min at 450 °C in forming gas optimizes the surface passivation. This is probably due to the fact that the oxide traps are annihilated as annealing time increases to 15 min. Figure 4(b) shows the effect of the annealing temperature with 15 min of annealing time. The measurements reveal that optimal annealing temperature is about 450 °C. However, the passivation effect begins to deteriorate at higher temperatures (above 450 °C). It is very likely to be due to the fact that Si:H

bonds start to break and the hydrogen atoms at the interface start to diffuse out, leaving Si dangling bonds unsatisfied.[32] The choice of annealing atmosphere is also critical to passivation quality, this exploratory study proves that the presence of hydrogen or oxygen in the annealing atmosphere is conducive to improving the passivation quality, and a relatively satisfactory result is obtained when forming gas (FGA) or compressed air (CDA) annealing is performed instead of N_2. As Fig. 4(c) shows, comparable carrier lifetime is achieved when Al_2O_3 samples are annealed for 15 min in forming gas or in compressed air at 450 °C. Thermal energy produced by annealing process is believed to break O–/H bonds throughout the oxide and diffuse H atoms towards the interface, resulting in Si dangling bond passivation.[2,26] The O_2 rich gas environment (compressed air) contributes to forming a thicker oxide layer between the silicon substrate and Al_2O_3 layer, the diffusivity of the hydrogen in the SiO_2 at 400 °C is two orders higher than that in the Al_2O_3.[31,32] It is obvious that the sufficient hydrogen in Al_2O_3 layer will diffuse into the SiO_2 layer, which forms a hydrogen rich SiO_2 film, and further reduces the defect density at the interface between the Si and SiO_2. The N_2 rich gas environment (N_2) results in a thinner SiO_2 layer, which cannot form the hydrogen rich region. This probably leads to a degradation of the passivation properties.

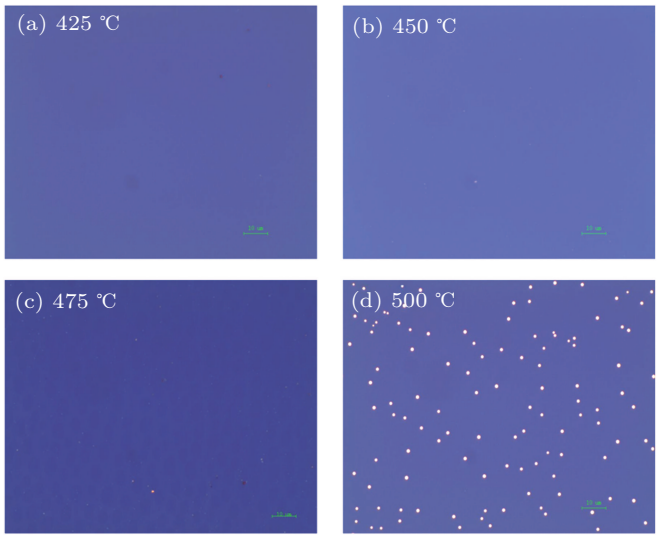


Fig. 5. (color online) Microscope images of n-type Cz Si samples passivated with 135 ALD cycles (∼ 15 nm) of Al_2O_3 annealed for 15 min at (a) 425 °C, (b) 450 °C, (c) 475 °C, and (d) 500 °C, respectively, then capped by 70 nm SiN_x.

Previous work has shown that both increasing layer thickness and low deposition temperature can increase the blister probability.[33–36] The above analysis shows that a high-quality surface passivation is achieved and meanwhile, the blister probability is increased, and changing annealing temperature is expected to be able to restrain blistering. From Fig. 5, we find that higher annealing temperature increases the blister probability. For sample annealed at 400 °C, no blistering is observed, while the sample annealed at above 450 °C shows a considerable blistering, which may be related to the relaxation of compressive thermal stress and partially caused by gaseous desorption.[35,36] Thus, the passivation stacks of ALD Al_2O_3 and SiN_x require annealing temperature below 450 °C to suppress blistering. In order to suppress blistering, other novel methods of post annealing are developed as well. Applying unique chemical treatment to the surface of the substrate has been proven to be effective. What is more, the temperature is set to be 300 °C when the sample is loaded into the tube, and then the temperature is increased linearly from 300 °C to 450 °C within 15 min. In order to ascertain more details, a further study is needed in the future.

4. Conclusions

Atomic-layer-deposited (ALD) aluminum oxide (Al_2O_3) is found to provide excellent surface passivation for n-type c-Si. Good surface passivation on n-type c-Si is achieved at a low thermal budget of 250 °C for a given gas pressure of 0.15 Torr. Thermal post annealing treatment enhances the passivation effect evidently, and the best result of passivation is obtained after annealing at 450 °C in forming gas environment, demonstrating a low SRV at 17 cm/s. In addition, novel methods are proposed to restrain blistering, and a blister-free sample is obtained by controlling post-annealing process or applying chemical treatment.

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