Influence of annealing temperature on passivation performance of thermal atomic layer deposition Al_2O_3 films*

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Chemical and field-effect passivation of atomic layer deposition (ALD) Al_2O_3 films are investigated, mainly by corona charging measurement. The interface structure and material properties are characterized by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), respectively. Passivation performance is improved remarkably by annealing at temperatures of 450 °C and 500 °C, while the improvement is quite weak at 600 °C, which can be attributed to the poor quality of chemical passivation. An increase of fixed negative charge density in the films during annealing can be explained by the Al_2O_3/Si interface structural change. The Al–OH groups play an important role in chemical passivation, and the Al–OH concentration in an as-deposited film subsequently determines the passivation quality of that film when it is annealed, to a certain degree.

Keywords: annealing, atomic layer deposition, Al_2O_3, passivation performance

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1. Introduction

Effective surface passivation is very important for the performance of high efficiency crystalline silicon solar cells, especially those with thinner wafers. Thermally grown SiO_2 (> 900 °C) is commonly used as the passivation material in high efficiency solar cells, while the high sensitivity of the silicon bulk lifetime to high temperature processes limits its application in industrial cell processes.[1] Atomic layer deposition (ALD) Al_2O_3 thin films are commonly used as high-k gate dielectrics in microelectronics devices.[2–4] Recently, such film has attracted much attention as a promising passivation layer for c-Si solar cell. In 2006, Hoex *et al.* demonstrated that the level of passivation for Al_2O_3 on lightly doped Si and p+ emitters was as good as that obtained by thermally grown SiO_2.[5,6] In addition to having comparable passivation results, ALD Al_2O_3 can be operated at low temperatures (< 300 °C) and integrated into high temperature industrial processes, which makes it superior to thermally grown SiO_2. Moreover, the excellent passivation measurements of p-type and n-type solar cells with ALD Al_2O_3 passivation have been reported as 21.4% and 23.2%, respectively.[7,8]

The high level of passivation provided by ALD Al_2O_3 is a combination of chemical passivation and field-effect passivation, which can be attributed to the reduction of interface defects and electrostatic shielding of minority charge carriers at the Si surface.[9] It is reported that the hydrogen released from the Al_2O_3 film passivates the Si interface defects to some degree.[10] The high fixed negative charge density (10^{12} cm^{-2}∼10^{13} cm^{-2}) located at the Al_2O_3/Si interface produces high quality field-effect passivation by shielding electrons from the interface.[11] Annealing at moderate temperatures enables the passivation of the silicon surface by ALD Al_2O_3 films.[12] In this article, we investigate the influence of annealing temperature on the passivation performance of ALD Al_2O_3. Also, the mechanism of passivation is studied by a series of characterization and measurement techniques from the two perspectives of field-effect and chemical passivation.

2. Experimental

The material used in this work was n-type Cz–Si, with a wafer thickness of 520 μm. The wafers were treated with diluted HF (1% in deionized H_2O) before deposition. We used a home-built KMT-200A Thermal ALD system, with trimethyl-aluminum (TMA) and H_2O as reaction precursors to prepare Al_2O_3 films on silicon substrate. The annealing was accomplished in a normal muffle furnace in nitrogen atmosphere.

The lifetime of the Al_2O_3 passivation and the corona charging were measured by a WT-2000 (Semilab) tester under 1-sun illumination. X-ray photoelectron spectroscopy (XPS) data were obtained using an ESCALab250 electron spectrometer. The samples were exposed to air and then transferred to

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the XPS spectrometer. The Al_2O_3/Si interface was examined by using a high-resolution transmission electron microscope (HRTEM), the TECNAI G2 S-TWIN F20.

3. Results and discussion

Al_2O_3 film is deposited at 250 °C for 100 growth cycles. The annealing temperatures are set as 350 °C, 450 °C, 500 °C, 600 °C, and 10 min is chosen as the annealing time based on our previous experiment results. Table 1 and figure 1 show the results of Al_2O_3 passivation. In Table 1, the lifetime, indicating the passivation performance, can be seen to have increased significantly after annealing at 350 °C, 450 °C or 500 °C, while annealing at 600 °C hardly changes the lifetime. This result is more visible in Fig. 1: the improvement percentage of passivation performance at 450 °C and 500 °C is more remarkable, while the improvement at 600 °C is quite weak, probably due to Si–H breaking apart during the high temperature process.

Table 1. Lifetime of as-deposited and annealed films for different annealing temperatures.

T/°C	350	450	500	600
As-deposited/μs	63.1	53.6	51.9	45.4
Annealed/μs	235.0	276.5	263.6	49.3

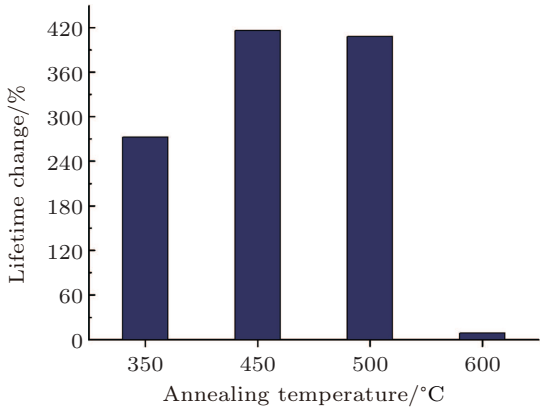


Fig. 1. (color online) Lifetime change of annealed films.

In order to understand this result, we investigated the passivation mechanism of ALD Al_2O_3 films, mainly by corona charging measurements. Being a contactless technique, corona charging is a very useful tool to investigate the passivation mechanism. For instance, there are fixed negative charges in ALD Al_2O_3 films. The effect of these charges can be counteracted by applying positive corona charges on the c-Si surface, as shown in Fig. 2. The change in c-Si lifetime is monitored. When the lifetime reaches its lowest value, the effect of fixed negative charges, which can be called field-effect passivation, is completely counteracted. The applied corona charge on the c-Si surface is a measure of the amount of fixed charge present in the film, and the current passivation performance is dominated by chemical passivation. Therefore, the amount of fixed negative charges in the Al_2O_3 film and the contribution of chemical passivation can be determined through corona charging measurement. And the field-effect and chemical passivation can be distinguished.

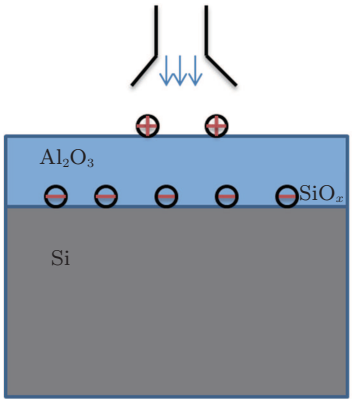


Fig. 2. (color online) The measurement mechanism of corona charging.

3.1. Field-effect passivation

Figure 3 and Table 2 show corona charging measurements at different annealing temperatures. In Fig. 3, the lowest value of each curve is the point at which the effect of fixed charges is completely counteracted, and the corresponding lifetime is the contribution of chemical passivation. In Table 2, the fixed negative charge density of as-deposited film is in the order of 10^{11}. After annealing above 450 °C, the charge density rises to the order of 10^{12}, which indicates good field-effect passivation.

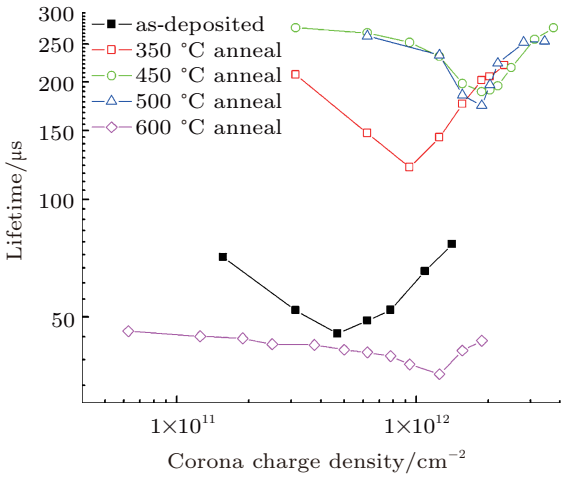


Fig. 3. (color online) Corona charging measurements of Al_2O_3 films.

Table 2. Fixed negative charge density (cm^{-2}) of Al_2O_3 films.

Annealing temperature/°C	350	450	500	600
As-deposited/10^{11}	–4.69	–4.69	–4.69	–4.69
Annealed/10^{12}	–0.938	–1.88	–1.88	–1.25

To understand this change, we investigated the Al_2O_3/Si interface of both the as-deposited and annealed films by TEM and XPS as shown in Fig. 4 and Fig. 5 respectively, based on the previous report's suggestion that the negative charge in Al_2O_3 is present at the interface.[13] Commonly, an interfacial SiO_x layer is formed between the Al_2O_3 film and the silicon substrate.[9] In Fig. 4, the thickness of the SiO_x interface layer increases obviously after annealing, indicating the atoms movement and the restructuring in the interfacial oxide during the annealing process. It can also be demonstrated in Fig. 5. In the as-deposited film, there is only a peak located at low binding energy (~98 eV) corresponding to Si–Si bonds,[14] while a small peak located at high binding energy (~103 eV), corresponding to Si–O bonds,[15] appears after annealing. This is also reported in our previous publication.[16]

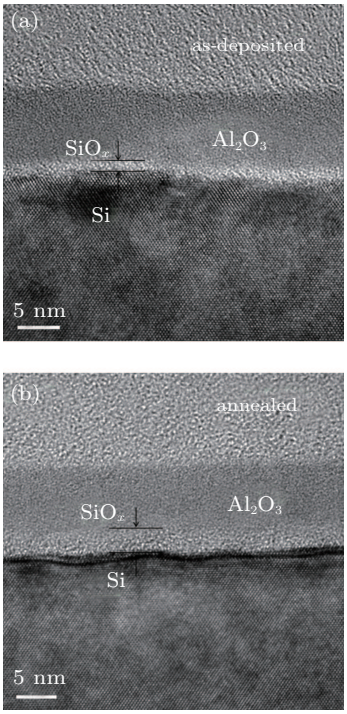


Fig. 4. TEM images of (a) as-deposited and (b) annealed films.

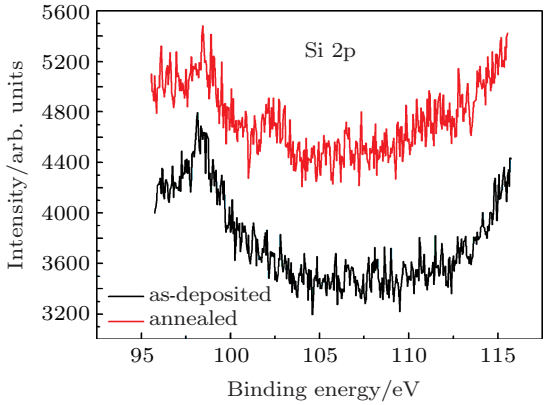


Fig. 5. (color online) The Si 2p XPS spectra of as-deposited and annealed films.

The high temperature annealing can enhance the atoms' movement to reconstruct the interface and bulk material, resulting in a change of lattice structure. It is well known that the origin of the charge traps are (ionized) point defects with candidates such as (oxygen or metal atom) vacancies and interstitials.[17] We infer that the structural change causes the change of electrical property after annealing, i.e. the density of fixed charge located at the interface is raised.

3.2. Chemical passivation

Figure 6 shows the contribution of chemical passivation at different annealing temperatures. The chemical passivation contributes much more at 450 °C (188.9 μs) and 500 °C (173.8 μs) while it is quite weak at 600 °C (35.6 μs). The improvement of passivation performance at 600 °C as shown in Fig. 1 is also weak although the fixed charge density of annealed film at 600 °C is as high as at 450 °C and 500 °C shown in Table 2. We can conclude that the poor passivation performance at 600 °C is not sensitive to field-effect passivation, but should instead be attributed to the decline of chemical passivation.

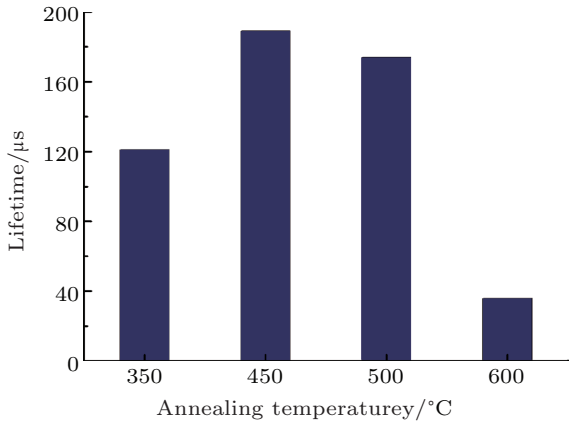


Fig. 6. (color online) The influence of annealing temperature on chemical passivation.

Figure 7 shows the O 1s XPS spectra of Al_2O_3 as-deposited and annealed films. The O 1s peak can be decomposed into two peaks located at 531.2 eV–531.4 eV and 532.5 eV–532.8 eV. So the binding energy related to the Al–O–H group is 1.3 eV–1.4 eV higher than that of the Al–O bonds.[15] After annealing, the Al–O–H concentration is reduced while the Al–O concentration increases, as shown in Table 3, indicating the breaking apart of O–H and the bonding of Al–O. Similar results were reported by B. Hoex and O. Renault.[9,15] Hydrogen is mostly incorporated as OH groups in Al_2O_3 films, and from the perspective of silicon surface passivation, the released hydrogen from O–H breaking up during annealing can passivate silicon's dangling bonds at the Al_2O_3/Si interface, reducing the interface's defect states. As a result, chemical passivation is improved.

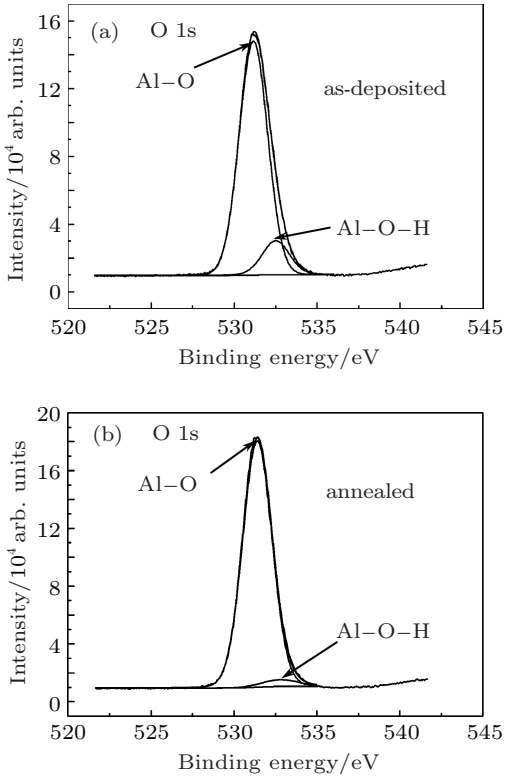


Fig. 7. Oxygen 1s XPS spectra of (a) as-deposited and (b) annealed films.

Table 3. Oxygen concentrations of as-deposited and annealed films.

	Al–O		Al–O–H	
	B.E.	at.%	B.E.	at.%
As-deposited	531.16	33.25	532.53	4.35
Annealed	531.41	40.31	532.8	1.33

Figure 7 and Table 3 both show that Al–OH groups play an important role in chemical passivation. Further, we investigated the influence of Al–OH concentration on the passivation performance of Al_2O_3 films. In order to obtain different Al–OH concentrations, Al_2O_3 films were prepared at different deposition temperatures (100, 150, 200, 250, 300 °C) in 60 growth cycles. The Al–OH concentration of as-deposited films and the passivation performance of annealed films as respective functions of the deposition temperature are shown in Fig. 8. Dramatically, the trend of lifetime with deposition temperature is quite similar to that of Al–OH concentration. According to the results in Fig. 7 and Table 3, the hydrogen atoms present in as-deposited films are released during annealing. Then they diffuse and passivate the defect states, both at the interface and in the c-Si bulk, resulting in a reduction of carrier recombination centers. Therefore, the passivation performance of annealed films can be improved significantly compared to that of as-deposited films. The interesting result in Fig. 8 indicates that the Al–OH concentration in as-deposited films determines the passivation quality of annealed films to a certain degree.

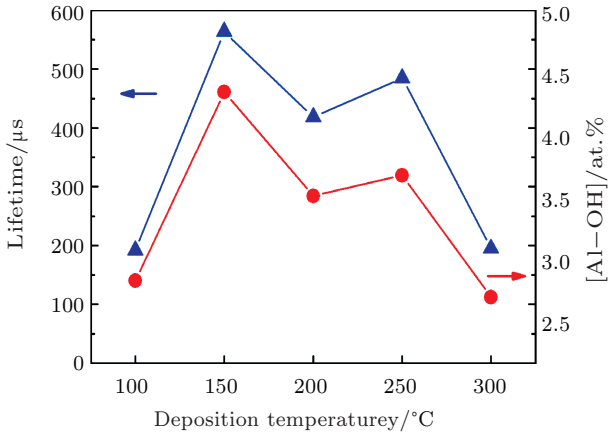


Fig. 8. (color online) The Al–OH concentration of as-deposited films and lifetime after annealing, as functions of depostion temperature.

4. Conclusion

In this paper, the influence of annealing temperature on the passivation performance of ALD Al_2O_3 is investigated. After annealing, the fixed negative charge density of ALD Al_2O_3 films, indicating the quality of field-effect passivation, increases from 10^{11} to 10^{12}, which can be explained by the interface's structural change during annealing. The poor passivation quality at the annealing temperature of 600 °C is not significantly dependent on field-effect passivation, but rather, it should be attributed to the chemical passivation. The chemical passivation takes effect due to the breaking of O–H bonds and the reaction of dangling bonds with released hydrogen atoms. Therefore, Al–OH groups play an important role in chemical passivation. Further, the Al–OH concentration of an as-deposited film subsequently determines the passivation quality of that film after it is annealed, to a certain degree.

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