AlO_x prepared by atomic layer deposition for high efficiency-type crystalline silicon solar cell*

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The influence of atomic layer deposition parameters on the negative charge density in AlO_x film is investigated by the corona-charge measurement. Results show that the charge density can reach up to -1.56×10^{12} cm^{-2} when the thickness of the film is 2.4 nm. The influence of charge density on cell conversion efficiency is further simulated using solar cell analyzing software (PC1D). With AlO_x passivating the rear surface of the silicon, the cell efficiency of 20.66% can be obtained.

Keywords: AlO_x, atomic layer deposition, p-type, negative charge density, solar cell analyzing software

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1. Introduction

Recent research has shown that the high efficiency crystalline silicon (c-Si) solar cell can be realized by reducing the surface recombination velocity.[1–4] The silicon-based films, such as SiN_x, SiO_x, and a-Si films, are usually used as passivation layers to reduce the surface recombination for the silicon solar cells.[5] The AlO_x thin film, which has a large number of negative charges, has a good passivation effect on the silicon. With the AlO_x thin film serving as the passivation layer, high solar cell efficiency has been achieved on p-type[6] as well as n-type silicon wafers[7] due to the excellent field-effect passivation of AlO_x. So it is considered as another promising alternative passivated material for silicon-based photovoltaic applications. Plasma enhanced chemical vapour deposition (PECVD) and reactive sputtering are usually used to prepare the AlO_x films.[8,9] However, these films are often lacking in uniformity,[8] or their passivation quality cannot remain stable at a higher firing temperature.[10] Compared with the technology of atomic layer deposition (ALD), the preparing of ALD AlO_x is a special chemical vapor deposition process consisting of a series of self-limited surface saturation reactions, which can prepare the film with excellent conformity, uniformity and high- step-coverage. In additon, ALD Al_2O_3 provides a better passivation quality and firing stability than AlO_x deposited by PECVD and reactive sputtering.[10] Although certain types of ALD-AlO_x in the photovoltaic field have been studied systematically, to our knowledge the research focused on the influence of the ALD process on passivation performance. The effect of process parameters on the fixed charge density has not been well understood.

In this work, the AlO_x thin-film is prepared by ALD. The effect of ALD parameters on the negative charge density (Q_f) is investigated. The mechanism of the influence of fixed negative charge density on solar cell conversion efficiency is also analyzed by PC1D software.

2. Experiment

Home-made ALD equipment is used to grow the AlO_x films by using trimethyl-aluminium ($Al(CH_3)_3$, TMA) and deionized H_2O as precursors. P-type CZ silicon with a diameter of 100±0.4 mm, a thickness of 500±20 μm, and a resistivity of 10 Ω·cm–20 Ω·cm is used as the substrate. Before deposition, the substrate is subjected to a 30-second 0.2-wt% HF solution flush and followed by a deionized water rinse. High purity nitrogen (99.999% N_2) is used to carry the precursors and purge the by-products. The deposition parameters are shown in Table 1. During the deposition, the deposition pressure is kept constant at 0.3 Torr (1 Torr = 1.33322×10^2 Pa). The film thickness is controlled by the ALD cycles due to the linear film growth in the ALD process. The average growth rate of the process is 1.2 Å/cycle. After deposition, the sample is annealed in an anneal furnace at 400 °C for 10 min in N_2 ambient to activate the surface passivation.[11]

Table 1. Parameters of ALD Al_2O_3.

Precursor	Pulse time/s	Reaction time/s	Purge time/s
$Al(CH)_3$	0.01	5	30
H_2O	0.03	5	40

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UVSEL (Horiba) spectroscopy ellipsometer is used to determine the thickness values of the AlO_x films. The value of fixed charge density (Q_f) present in the film is measured from a Semilab lifetime tester WT2000.

3. Results and discussion

As a contactless technique, corona charging is a useful tool to investigate the presence of field-effect passivation and determine the quantity of fixed negative charges in AlO_x film.[12,13] The operation mechanism is used to counteract the negative charges by applying corona charges to the surface of the film. By applying positive corona charges to the sample surface, the effect of the fixed negative charges is counteracted, and electrons in *c*-Si are less shielded from the interface. As a result, the surface recombination increases. When the surface recombination reaches the top value, the density of fixed negative charges is counteracted completely by the corona charges and the quantity of negative charges can be determined. The schematic representation of the corona charging setup is shown in Fig. 1. The stainless steel mesh is used to improve the uniformity of the charge density deposited on the surface of the sample.

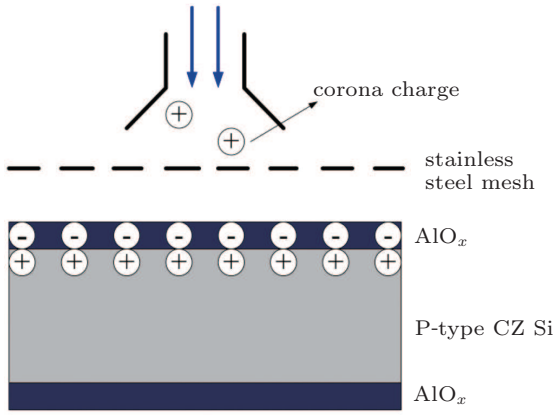


Fig. 1. (color online) Corona charging setup used for measuring the fixed negative charge density in AlO_x film.

The variation of fixed charge density with deposition temperature is shown in Fig. 2(a) for an annealed 7.2-nm AlO_x layer. It can be seen that a charge density of -4×10^{11} cm$^{-2}\sim-8\times10^{11}$ cm^{-2} is obtained at a deposited temperature between 150 °C and 300 °C. The charge densities in the AlO_x films achieved at the higher process temperatures are slightly lower than those of the films prepared at the lower process temperatures. These reduced values, Q_f as compared with those in the case of Al_2O_3 deposited at lower temperatures, could be attributed to the progressive loss of $AlOH^*$ and $AlCH_3^*$ surface species at higher temperatures,[14] which may reduce the negative charge quantities of the Al vacancies and O interstitials in the Al_2O_3 dielectric layers.

The variation of charge density with the thickness of AlO_x thin-film is given in Fig. 2(b). It is shown that the thickness of AlO_x thin-film has an important effect on the negative charge density. When the thickness of AlO_x thin-film is less than 12 nm, the charge density is higher than when the thickness of AlO_x is greater than 12 nm. Werner *et al.*[15] have reported that the ratio of oxygen to aluminum reduced with the increase of ALD cycles. They suggested that the high ratio of oxygen to aluminum resulting from the incomplete absorption of the TMA molecules is a possible source of the high negative charge density. This viewpoint can explain the phenomenon in our work. After an HF dip, the –OH functional surface groups on the surface of the silicon are inadequate for the absorption of the TMA molecules, which leads to an incomplete reaction of the TMA, and the oxygen concentration at the interface is relatively high. The AlO_x thin film is less dense due to the incomplete formation of the nucleation islands, causing parts of the surface of silicon to be unpassivated. This results in a higher ratio of oxygen to aluminum, and a large number of negative charge defects in the film. So the charge density is very high. With the thin film thickness increasing, the unpassivated surface of the substrate is passivated gradually by AlO_x and the thin film becomes uniform and dense. The decrease of the oxygen concentration at the interface means the ratio of oxygen to aluminum reduces with the increase of cycles. So the negative

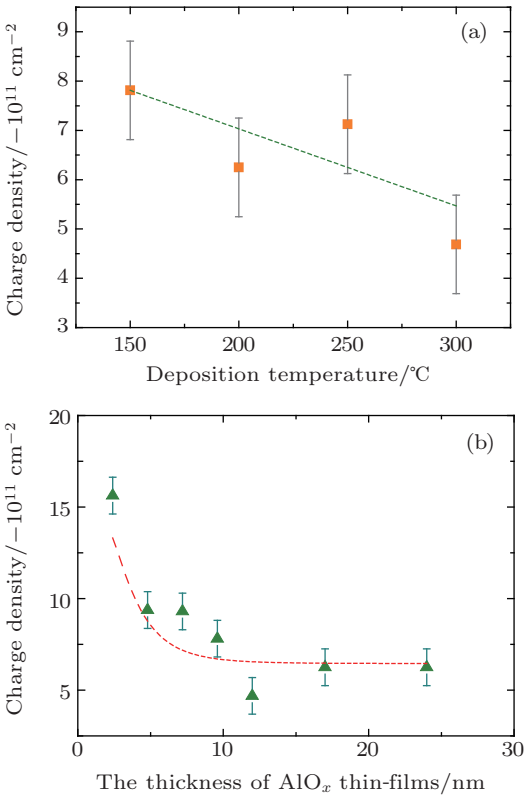


Fig. 2. (color online) Variations of charge density with (a) deposition temperature and (b) the thickness of AlO_x thin-film, with the dashed lines being guides to the eye.

charge defects are reduced too. Therefore, the negative charge density drops off gradually, and it is finally kept at a value of $-(6.25\pm1)\times10^{11}$ cm^{-2}. The apparent decline in charge density at 12 nm might be due to the calibration errors for AlO_x thin films during the corona charge experiment. The highest fixed negative charge density of $-(1.56\pm1)\times10^{12}$ cm^{-2} in a 2.4-nm thick AlO_x film is achieved. This result is in accordance with the earlier reported result,[11] which indicates the existence of strong negative charge field.

The Al_2O_3 dielectric layer can contain a high density of built-in negative charges,[16,17] which can build an electric field at the interface between the film and the silicon substrate. In this way, the minority carrier (electron) concentration at the interface can be effectively reduced by the effect of electrostatic-shielding and, consequently, the surface recombination velocity is reduced. Further, the surface recombination velocity decreases with the increase of negative charge density.[18] Therefore, the higher negative charge density is important for improving the performance of the solar cell. The relationship between the solar cell efficiency and charge density has been simulated by the PC1D simulator. The PC1D implements the one-dimensional drift-diffusion model to solve the fully coupled nonlinear equations for the quasi-one-dimensional transport of electrons and holes in a crystalline semiconductor device, with the emphasis on a photovoltaic device. The numerical program used for modeling semiconductor solar cells is based on the three semiconductor equations, consisting of Poisson's equation, current density equation and continuity equation. Parameters in Table 2 are used in the simulations. The results are shown in Fig. 3, where it is clearly indicated that the solar cell efficiency increases with the increase of fixed negative density. Illustrated in Fig. 3 is the numerical model for simulation. When the fixed negative charge is zero, the corresponding cell efficiency is 17.75%. However, the efficiency can reach up to a maximal value of 20.81% when the fixed negative density is -1×10^{13} cm^{-2}. Besides, the V_{oc} and the J_{sc} are both increased, which indicates that the fixed negative charge density in the passivation layer is of great significance for improving the performance of a solar cell.

Table 2. Physics parameters used as input data for PC1D simulation.

Device area	1 cm^2	Dielectric constant	11.9
Front surface texture depth	9 μm	Energy bandgap	1.124 eV
Front surface reflectance	5%	Intrinsic carrier concentration	10^{10} cm^{-3}
Back surface reflectance	100%	Front surface recombination rate	10^3 cm/s
Front surface charge	0	Back surface recombination rate	10^5 cm/s
n-type diffusion sheet resistance	79.45 Ω/sq	Testing temperature	25 °C
p-type doping concentration	9.999 Ω·cm	Testing voltage	−0.8 V ∼ 0.8 V
Substrate thickness	500 μm	Input optical power	100 mW/m^2
Contact resistance	0.015 Ω	Light source	AM 1.5

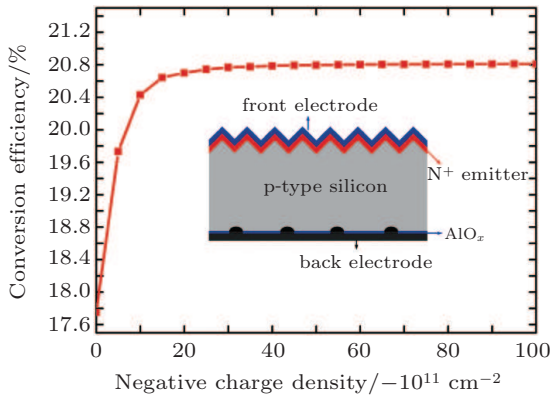


Fig. 3. (color online) Simulated solar cell efficiency as a function of negative charge density of the passivation layer.

In our experiment, the highest fixed negative charge density can reach up to -1.56×10^{12} cm^{-2} when the thickness of the AlO_x film is 2.4 nm. The performance of the solar cell is calculated by the PC1D using the different AlO_x film thickness values to passivate the rear surface of the p-type silicon solar cell. The device parameters are identically set to those in Table 2. The simulation results are listed in Table 3, showing a strong increase of conversion efficiency due to Al_2O_3 passivating the rear surface of the p-type silicon. The sample without AlO_x results in a conversion efficiency of 17.75%. However, with 2.4-nm thick AlO_x passivating the rear surface of the p-type silicon, the cell efficiency of 20.66% can be obtained . Although our results have demonstrated that ALD Al_2O_3 with a thickness of 2.4 nm is beneficial to passivating the back surface of silicon solar cells, it is still far from the theoretical value (29%). The loss of the efficiency is mainly related to practical problems, such as light reflection from the front surface and the relatively high surface recombination velocity.

Table 3. Simulation results of the solar cell by ALD-Al_2O_3 simulated using PC1D.

Film thickness/nm	V_{oc}/mV	J_{sc}/(mA/cm^2)	Conversion efficiency/%
0	574	38.13	17.75
2.4	650.3	39.33	20.66
4.8	637.6	39.3	20.38
9.6	637.2	39.3	20.37
12	631.8	39.28	20.23
18	614.6	39.15	19.65
24	614.6	39.15	19.65

4. Conclusion

In the present paper, a high level of fixed negative charge density can be obtained on p-type CZ Si by thin AlO_x film prepared by the ALD technique. Results show that the thickness of the film plays an important role in determining the charge density of the AlO_x film. The AlO_x with a thickness of 2.4 nm results in the highest negative charge density (-1.56×10^{12} cm^{-2}) after having been annealed at 400 °C. Furthermore, the cell efficiency increases with the increase of charge density, which is demonstrated by the PC1D simulator. With ALD-Al_2O_3 passivating the rear surface of p-type silicon, the cell efficiency of 20.66% can be obtained, and it is 2.91% higher than that without Al_2O_3 passivation.

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