FT-IR and TPD Analysis of Ozone-Based Atomic Layer Deposited AlO_x Passivation Films for Crystalline Silicon Solar Cells

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1. Introduction

To reduce the cost of power generation by crystalline silicon (c-Si) based solar cells, both the reduction of the material cost by decreasing of wafer thickness and the increase of conversion efficiency of the solar cells are required. In order to realize them, development of passivation film for p-type silicon is one of the most important issues.

Recently, AIO_x has been studied by many researchers as a surface passivation material for p-type c-Si. The AlOx films were fabricated by several techniques, such as plasma enhanced chemical vapor deposition, sputtering, and plasma enhanced atomic layer deposition [1-3]. Regardless of the deposition technique, fabricated AlO_x films have a common feature that passivation quality is improved by thermal annealing after the deposition. However, for most deposition techniques, c-Si substrates are heated during the deposition. Therefore, it is difficult to separate the effects of heating during deposition and thermal annealing after deposition on the passivation quality. Therefore, we used an ozone based atomic layer deposition (O₃-ALD) technique which enable the deposition without heating [4,5]. The passivation quality of AlO_x films deposited by the O₃-ALD was also improved by the thermal annealing. In order to obtain a better understanding of the heating and annealing effects, the structural changes of AlO_x films are evaluated by Fourier transform infrared spectroscopy (FT-IR) and temperature programmed desorption (TPD) analyses.

2. Experimental

AlO_x passivation films were symmetrically deposited on both the front and rear surfaces of a p-type (100) silicon substrate (MCZ, $\rho = 15-30 \ \Omega \cdot \text{cm}$, 770 µm) by a batch O₃-ALD method. Trimethylaluminum (TMA, Al(CH₃)₃) and ozone were used as the aluminum source and oxidant, respectively. The depositions were carried out at various temperatures from room temperature to 350 °C. The postdeposition annealing was carried out in the air at the temperature of 400 to 500 °C for 60 min. Chemical bonds in the AlO_x films were evaluated by attenuated total reflectance (ATR) FT-IR. For TPD analysis, a sample was placed in the vacuum chamber, and heated over 500 °C with a heating rate of 10 K/min. The desorbed gases were analyzed by a quadrupole mass spectrometer.

3. Results and Discussion

From the TPD analysis, amounts of gas desorption from the sample deposited at room temperature (RT-sample RT-50) and the sample deposited with heating (heated sample : 200-30, 300-30) were maximized at 310 and 370 ^oC, respectively. Figure 1 shows representative gas desorption spectra. As shown in Fig.1, the amount of gas desorption from the RT-sample is several orders of magnitude larger than that from the heated samples. Here, mass numbers 15 is attributed to CH₃ from TMA. In the case of the heated samples, aluminum-methyl group bonds are dissociated by thermal energy and ozone. However, in the case of the RT sample, the bonds are dissociated by ozone only. Therefore, there are many residual methyl groups in the RT sample. Mass number 44 is attributed to and CO₂. The gas desorption spectrum of mass number 28 is similar with that of mass number 18. Therefore, mass number 28 is attributed not to N₂ but to CO. It can be considered that the residual methyl groups are changed to hydroxy and carboxyl groups by ozone.



Fig. 1 Gas desorption spectra of mass number 15 (upper) and 44 (lower).

Figure 2 shows infrared absorption spectra of the RT-samples with and without postdeposition annealing. In the case of the as-deposited sample, characteristic absorptions can be seen at $1300 \sim 1700$ and $600 \sim 1000$ cm⁻¹. The former is attributed to C=O bonds in carboxyl group, and the latter is attributed to Al-O bonds. The absorption related to C=O bonds is almost none in the RT-samples with postdeposition heating. In the case of heated samples, the absorption is almost none, too. This result supports the result of TPD analysis. In other words, the time for ozone exposure during ALD is not enough to break the aluminum-methyl group bonds

Figure 3 shows the magnified figure of Fig.2. Two peaks can be recognized at near 700 cm⁻¹ (peak 1) and at 850~900 cm⁻¹ (peak 2). In spite of different postdeposition conditions, the wavenumber of the peak 1 seems almost constant. On the contrary, the wavenumber of the peak 2 is different in each case. The wavenumber of peak 2 in the as-deposited sample is near 850 cm⁻¹, and that in the sample with postdeposition heating is near 900 cm⁻¹. In the case of the as deposited RT-sample, the methyl, carboxyl, and hydroxy groups are remained. Therefore, a part of Al-O back bonds might be Al-C bonds. By the postdeposition annealing, the gases are released from the RT-sample, a part of Al-O back bonds might include dangling bonds. The peak 2 of the heated samples shifts to more higher wavenumber region. In this case, the methyl groups are released during the deposition. Therefore, numbers of Al-C bonds and dangling bonds in the heated samples might be lower than those in the RT-sample. These differences in back bonds may affect the peak 2 position. The relation between peak 2 position and fixed charge density in the AlO_x film is under consideration.

4. Conclusions

The structural changes of AIO_x films prepared by O_3 -ALD are evaluated by FT-IR and TPD analyses. In the as-deposited RT-sample, methyl, hydroxyl and carboxyl groups exist in the AIO_x film, and they are desorbed by the postdeposition annealing at around 310 °C. As a result of thermal annealing, the structure of AIO_x film was changed.

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Fig.2 Infrared absorption spectra of RT-samples with and without postdeposition annealing (solid line ; as-deposited, dash-line ; annealing at 500 °C for 60min, dash-dot line ; sample after TPD analysis).



Fig.3 Magnified figure of Fig.2 (keys are the same as those of Fig.2).