**Reduction of surface recombination velocity by rapid thermal annealing of p-Si
passivated by catalytic-chemical vapor deposited alumina films**

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Abstract

Excellent electrical-passivation of p-type Si (p-Si) in Si solar cells has been achieved by post-deposition rapid annealing of aluminum oxide (AlO_x) films prepared by catalytic chemical vapor deposition (Cat-CVD) using trimethyl aluminum (TMA) and O_2 . Extremely small surface recombination velocity of below 0.1cm/s has been obtained at post-deposition annealing temperatures in the range of 350-400 °C for an annealing time of 2 minutes. The reduction of surface recombination velocity has been attributed to band bending induced by a fixed negative charge density of 5×10^{11} charges/cm² and an additional small interface trapping density of around 10^{10} cm⁻²eV⁻¹.

Keywords,

Surface recombination velocity, Alumina passivation film, Solar cell, Cat-CVD, HW-CVD, Rapid thermal annealing

1. Introduction

Electrical passivation of p-Si surfaces to reduce surface recombination in crystalline Si solar cells is very important for increasing their conversion efficiency. It is becoming all the more important as solar cells are becoming thinner in order to reduce their cost [1-2]. Recently, there have been reports on Alumina (AlO_x) film-passivation techniques which can reduce surface recombination velocity (S_0) mainly by dint of band bending effect attributed to fixed charges induced by AlO_x films deposited on Si [3]. The creation of fixed charges is attributed to precursor gases, annealing of AlO_x films, and method depositing the films. Fixed charges have been created in AlO_x films deposited on Si using following deposition methods at various annealing temperatures, and annealing times : remote plasma enhanced chemical vapor deposition of tri-ethyldyaluminum and tri-sec-butoxide (400°C , 30 min.) [4], pyrolysis of aluminum tri-isopropoxide (510°C , 15 min.) [5], atomic layer deposition (ALD) of TMA and H_2O (300°C) [6], plasma-assisted atomic layer deposition (PA-ALD) of TMA and O_2 (425°C , 30min.) [7-9], plasma-enhanced chemical vapor deposition (PE-CVD) of TMA, CO_2 and H_2 (around 400°C) [10], sputtering of an aluminum target with O_2 ambient (500°C , 30min.) [11], spatial atomic layer deposition of TMA and H_2O ($350 - 425^\circ\text{C}$, 15min.) [12], and Cat-CVD

of TMA and O_2 (from 230 °C, cooled for 300min.) [13]. The surface recombination velocity obtained has been very small in all deposition methods mentioned above. It has been reported that post-deposition annealing is very effective in reducing surface recombination velocity [14-15]. We have already obtained extremely small surface recombination velocity (S_0) of below 0.1 cm/s in p-Si passivated by Cat-CVD deposited alumina films which have been cooled down slowly for several hours in vacuum [13]. The extremely small surface recombination velocity of below 0.1 cm/s in these films has been kept intact over one year [13]. However, the duration of the thermal treatment of several hours is too long for industrial applications.

In this study, the post-deposition annealing process has been investigated to achieve decrease of a surface recombination velocity by dint of the AlO_x film passivation. Film samples have been prepared by Cat-CVD deposition at varying annealing temperature (T_a) and time (t_a). The surface recombination at the interface between the AlO_x film and Si surface has been characterized by photoconductivity decay (PCD) curves and evaluated also by direct measurement of surface recombination velocities (S_0). Furthermore, fixed charge density (N_f) and interface trapping densities (D_{it}) have been obtained from capacitance voltage (C-V) curves measured for metal-oxide-semiconductor (MOS) diodes fabricated using AlO_x films. The annealing

temperature and time which achieves the smallest surface recombination velocity due to the AlO_x passivation films have been determined from PCD curves, measured surface recombination velocities, and fixed charge density. The mechanism for reduction of surface recombination velocity has been studied in terms of the behaviors of measured fixed charge density and interface trapping density.

2. Experimental

Aluminum oxide films were deposited on p-Si wafers by Cat-CVD using TMA and O_2 as the precursor gas. The experimental apparatus used in this study is shown in Fig. 1. Si substrates used for the samples were Czochralski (CZ) grown crystalline p-Si (100) wafers having a resistivity of $10 \text{ } \Omega\text{cm}$ with a mirror-polished front surface and a chemically-polished back surface. $2 \times 2 \text{ cm}^2$ samples were scribed from the wafers. The samples were then slightly etched by a 2.5 wt% hydrofluoric acid (HF) rinse to remove the natural oxide to obtain a H-terminated surface, and rinsed in deionized (DI) water prior to deposition. The samples were mounted on the sample holder 7 cm away from the catalyzer. The samples were heated from the back side by radiation from a Chromel alloy-wire heater mounted in a zigzag manner on a ceramic plate as shown in Fig. 1. The sample temperature (T_{sub}) was measured by a thermography. An oxidation resistant

25 cm long, 0.2 mm diameter iridium wire was used as the catalyzer. The wire was wound around the holder in a W-shaped bend, and the catalyzer temperature (T_{cat}) was measured by a radiation thermometer. The deposition of AlO_x films on the p-Si samples were carried out using N_2 gas as a carrier gas for the TMA which was introduced through the shower head and O_2 gas was independently blown around the catalyzer. The films were deposited for 15 min. at T_{sub} of 240 °C under O_2 /TMA gas flow-rate ratio of 15 and a chamber pressure of 17 Pa. The flow rate of TMA was determined using the equivalent N_2 flow rate to satisfy the vapor-pressure of TMA. Subsequent to deposition, as senn in Fig. 2, the samples were annealed by elevating the sample temperature to the maximum annealing temperature (T_a) which was kept constant for the annealing time (t_a) of several minutes in N_2 ambient at a pressure of 10^5 Pa. The samples were prepared varying T_a in the range of 250-420 °C for $t_a = 2\text{min.}$, and then varying t_a in the range of 1–10 minutes with $T_a = 400$ °C. The AlO_x film thicknesses of the samples were measured to be in the range of 2.1-3.1 nm by a spectroscopic ellipsometer (ALPHA-SE, J.A. Woolam Co. Inc.) using two-layer model composed of an AlO_x layer and a SiO_2 layer. The surface recombination at the interface in $\text{AlO}_x/\text{p-Si}$ was characterized by the initial decay in photoconductivity decay curves measured and evaluated also by the surface recombination velocity (S_0) measured using contactless

techniques [16-19]. In this experiment, the photoconductivity change was detected by a reflected 500 MHz electromagnetic wave. Excess carriers were created by impulse-irradiation of 904 nm laser diode with a photon flux density of $7.7 \times 10^{12} \text{ cm}^{-2}$. Surface recombination velocities in the samples were directly determined by applying bi-surface photoconductivity decay (BS-PCD) method to two PCD curves measured by a BS- τ lifetime profiler equipment from Hemmi Inc.[16-19]. Fixed charge density (N_f) was obtained from the flat-band voltage shift of C-V curves measured at 1 MHz. Interface trapping density (D_{it}) was measured varying the signal frequency in the range of 10 Hz –1 MHz using the conductance method [20] with a signal amplitude of 20 mV for MIS diodes consisting of the AlO_x insulator film and an aluminum-gate electrode of 500 μm in diameter.

3. Results and discussion

Figure 3 shows PCD curves measured for the bare mirror-surface sample, the as-deposited sample, and those prepared varying T_a in the range of 250-420 °C, when the pulse laser for photo-carrier excitation was irradiated on the AlO_x film surface of samples. As seen in the figure, the curve for the as-deposited sample decays slowly compared with that for the bare samples. The curves for T_a of 350–400 °C display

no-decay initially, suggesting extremely small S_0 due to the band bending effect. Fig. 4 shows PCD curves for the samples prepared by varying t_a in the range of 1–10 minutes. As seen in the figure, the decay is sensitive to t_a and the PCD curve at $t_a = 2$ min. indicates no-decay initially, suggesting the smallest surface recombination obtained. Therefore, the PCD curves in Fig. 3 were measured under $t_a = 2$ min. S_0 measured using BS-PCD method is shown in Fig. 5 as a function of annealing temperature. S_0 for the bare silicon sample prior to HF etching is very large as at 11275 cm/s and decreases to 179 cm/s for the as-deposited sample. S_0 for T_a from 350-400 °C decreases below 0.1cm/s, and S_0 for the higher T_a of 420 °C increases to 300 cm/s. These behaviors are in good agreement with those seen in Fig. 3. Until now, we were able to find that the annealing temperature in the range of 350- 400 °C and the annealing time of 2 min. are optimum conditions in order to achieve extremely small S_0 by rapid post-deposition annealing. Reduction of S_0 is attributed to band bending due to fixed charges. In order to obtain magnitude of fixed charges, C–V curves for MIS diodes fabricated using AlO_x films annealed at T_a of 250 – 420 °C were measured. The C-V curve measured for AlO_x annealed at T_a of 400 °C is shown in Figure 6 along with the ideal curve as a reference. The curve for 400 °C shifts in the positive voltage direction suggesting creation of negative charges. Figure 7 shows the fixed charge densities (N_f) as a function of

annealing temperature, where N_f is determined from the flat band voltage shift in measured C-V curves as shown in Fig. 6. As seen in the figure, large negative fixed charges of above 3.7×10^{11} charges/cm² are obtained at T_a of 350 – 400 °C corresponding to T_a which obtains very small S_{0s} . This implies that very small S_0 is caused by band bending effect attributed to fixed negative charges created by post-deposition rapid thermal annealing. Figure 8 shows S_0 as a function of N_f . The S_0 is strongly depended on the magnitude of N_f . Extremely small S_0 data of below 0.1 cm/s is obtained by fixed negative charge density greater than 3.7×10^{11} charges/cm². These extremely small two sets of S_0 data correspond to S_0 data obtained at annealing temperatures of 350 and 400 °C. It seems that the abrupt reduction of S_0 and extremely small S_0 data are obtained by dint of the fixed negative charges. Surface recombination velocity is dependent not only on band bending but also on interface trapping density (D_{it}). Figure 9 shows the behavior of interface trapping density taken at the mid-gap for the samples in Fig. 8 prepared by varying T_a from 250-420 °C together with D_{it} for the as-deposited sample. The interface trapping density seems to be constant around 10^{10} cm⁻² eV⁻¹ and not dependent on the fixed charge densities of the order of 10^{11} charges/cm² created by post-deposition rapid anneal process in this study. Therefore, it can be concluded

that the abrupt reduction to small S_0 is caused by change in band bending due to change in fixed negative charges created corresponding to the change of anneal temperature.

4. Conclusion

The effects of post-deposition rapid thermal annealing on AlO_x films deposited on p-Si by Cat-CVD have been investigated in order to reduce surface recombination as the AlO_x films enable to adapt for use as passivation films of crystalline Si solar cells. Extremely small surface recombination velocity below 0.1 cm/s in p-Si with AlO_x films deposited at substrate temperature of 240 °C has been obtained by post-deposition rapid thermal annealing at temperatures in the range of 350-400 °C for an annealing time of 2 min. It can be explained that the extremely small S_0 has been reduced below 0.1 cm/s by dint of the band bending effect attributed to negative charges greater than 3.7×10^{11} charges/cm² and by the small interface trapping density of around 10^{10} eV⁻¹cm⁻².

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Figure captions

Fig. 1 Schematic illustration of apparatus used for film deposition and post-deposition rapid thermal annealing.

Fig. 2 Time chart used for film deposition and post-deposition thermal annealing.

Fig. 3 Photoconductivity (PCD) curves observed by BS- τ for $\text{AlO}_x/\text{p-Si}$ samples prepared by varying post-deposition annealing temperature, as-deposited and bare wafers (without AlO_x films).

Fig. 4 PCD curves observed by BS- τ for $\text{AlO}_x/\text{p-Si}$ samples prepared by varying post-deposition annealing time.

Fig. 5 Surface recombination velocity (S_0) measured as a function of post-deposition annealing temperature (T_a).

Fig. 6 One example of C-V curve shift attributed to fixed charges generated by post-deposition annealing temperatures.

Fig. 7 Fixed charge density (N_f) as a function of post-deposition annealing temperature.

Fig. 8 Surface recombination velocity (S_0) as a function of fixed charge density (N_f).

Fig. 9 Interface trapping density (D_{it}) as a function of fixed charge density.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9