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Low surface recombination velocity in n-Si passivated by catalytic-chemical vapor deposited alumina films

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ABSTRACT

The surface recombination velocity (S_0) in n-type Si (n-Si) wafers has been reduced below 0.1 cm/s by dint of positive fixed charges created by alumina (AlOx) films deposited at a film-temperature of 230 °C by catalytic chemical vapor deposition (Cat-CVD) using trimethyl aluminum (TMA) and O_2. Positive fixed charges of the order of 10^{12} charges/cm^2 can be created in AlO_x films deposited under O_2/TMA flow-rate ratios in the range of 3.5–6.5. The extremely small S_0 has been confirmed to be obtainable mainly due to a band bending effect brought about by the positive charges. The polarity and amount of the fixed charges can be determined by the flow-rate ratio of O_2/TMA.

1. Introduction

Surface recombination velocity in crystal-Si solar cells is a dominant factor in determining their conversion efficiency [1,2]. This factor is becoming more dominant as the bulk thickness of Si wafer is being reduced to realize ~~a~~ reduction in cost. The surface recombination velocity in p-type Si (p-Si) has been reduced drastically due to alumina passivation films deposited by pyrolysis of aluminum triisopropoxide [3], atomic layer deposition (ALD) of TMA and H_2O [4], plasma-assisted ALD of TMA and O_2 [5–8], plasma-enhanced chemical vapor deposition (PE-CVD) of TMA, CO_2, and H_2 [9], spatial ALD of TMA and H_2O [10], and Cat-CVD of TMA and O_2 [11]. On the other hand, there have been some reports on the reduction of surface recombination velocity in n-Si due to AlO_x passivation films deposited by ALD of TMA and O_2 [7], and spatial ALD of TMA and H_2O [10]. These reports for n-Si have suggested that the reduction is caused by negative fixed charges in alumina films. However, negatively charged films bring the problem of parasitic shunting when applied to n-Si solar cells [12]. Therefore, it is necessary for passivation films in n-Si solar cells to have positive fixed charges instead. We have found newly that positive charges can also be created at the interface of AlO_x films on p-Si (AlO_x/p-Si) by AlO_x films deposited by O_2/TMA at flow-rate ratios below around 10 [11].

In this study, we confirm that S_0 decreases due to positive fixed charges in AlO_x films deposited on n-Si (AlO_x/n-Si) as well as investigate the process parameters which create positive fixed charges. The AlO_x films on n-Si have been deposited by varying O_2/TMA flow-rate ratios using Cat-CVD. The passivation performances at the AlO_x/n-Si interface have been characterized by photoconductivity decay (PCD) and evaluated by surface recombination velocity directly measured by the bi-surface photoconductivity decay (BS-PCD) method. Furthermore, interface trapping density (D_{it}) was obtained from capacitance–voltage (C–V) measurements of meal-insulator-semiconductor (MIS) diodes fabricated with AlO_x gates. The mechanism of reduction of S_0 has been studied in terms of the behaviors of fixed charge density (N_f) and D_{it}.

2. Experimental

AlO_x films on n-Si wafers were deposited by Cat-CVD using TMA and O_2 as the precursor gas. The experimental apparatus used in this study is shown in Fig. 1 [11]. Si substrates used for the samples were Czochralski (CZ) grown crystalline n-Si (100) wafers having a resistivity of 6 Ωcm with a mirror polished front-surface and a chemical-polished back surface. 2 cm × 2 cm samples were scribed from the wafers. The samples were slightly etched by a 2.5 wt.% hydrofluoric acid (HF) rinse to remove the native oxide and to obtain H-terminated surfaces, and then subsequently rinsed in deionized (DI) water prior to deposition. The samples were mounted on the sample holder 70 mm away form the catalyzer, and sample temperature (T_{sub}) measured by a thermography. An oxidation resistant 25 cm long and 0.2 mm diameter iridium wire was used as a catalyzer. The wire was wound around the holder in a W-shaped bend, and the catalyzer temperature (T_{cat}) measured by a radiation thermometer. The deposition of AlO_x films on the n-Si samples was carried out using N_2 gas as a carrier gas for the TMA which was introduced through the showerhead and O_2 gas was blown around the catalyzer. The films were deposited varying O_2/TMA flow-rate ratios in the range of 2–8 at a chamber pressure of 17 Pa, T_{cat} of 700 °C and T_{sub} of 230 °C. The flow rate of TMA was determined using the

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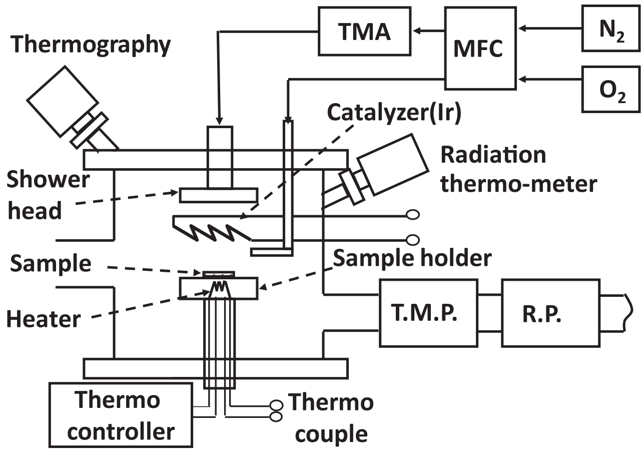

Fig. 1. Schematic illustration of apparatus used for film deposition.

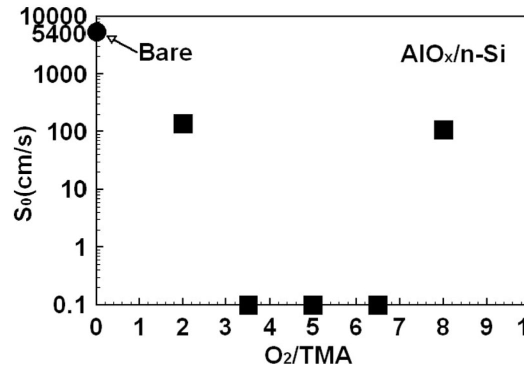

Fig. 3. Surface recombination velocity (S_0) measured for various flow-rate ratios of O_2/TMA.

equivalent N_2 flow rate to satisfy the vapor-pressure of TMA. Subsequent to deposition, the samples were naturally cooled over 5 h under vacuum. The AlO_x film thicknesses were measured to be in the range of 1.8–3.2 nm for the samples deposited at O_2/TMA flow-rate ratios of 2–8 by a spectroscopic ellipsometer (ALPHA-SE, J.A. Woolam Co., Inc.) considering a two layer model composed of an AlO_x layer and a SiO_2 layer. The SiO_2 film thicknesses were measured to be 1.08 nm. The surface recombination at the interface between the film and n-Si was characterized by the initial decay in photoconductivity decay (PCD) curve measurements and also evaluated by S_0 determined by BS-PCD method from two PCD-curve measurements using contactless techniques [13–16]. 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 2.3×10^{13} cm^{-2}. S_0 at the interface was directly measured by applying BS-PCD method using a BS-τ life-time profiler from Hemmi, Inc. N_f was calculated from the flat band voltage shift of C–V curves measured at 1 MHz. D_{it} was measured varying the signal frequency in the range of 10 Hz–1 MHz using the conductance method [17] with a signal amplitude of 20 mV for the MIS diodes consisting of an AlO_x insulator film and an aluminum-gate electrode 500 μm in diameter.

3. Results and discussion

Fig. 2 shows PCD curves obtained for mirror-surface samples and those having AlO_x films deposited only on the mirror surface of n-Si substrates with varying O_2/TMA flow-rate ratios in the range of 2–8. Here, the O_2/TMA gas flow-rate ratio is simply labeled as O_2/TMA in the figures throughout this paper. During measurement the mirror surface was irradiated by a pulse laser for the photo-carrier excitation. As seen in the figure, the curve for the bare Si-wafer decays faster initially due to high surface recombination velocity of 5400 cm/s obtained from Fig. 3. The two curves for AlO_x films with O_2/TMA flow-rate ratios of 2 and 8 initially decay slightly, suggesting relatively reduced S_0. The curves for AlO_x films with O_2/TMA flow-rate ratios of 3.5–6.5 initially display no-decay, suggesting extremely small surface recombination velocity. Fig. 3 shows S_0 measured as a function of O_2/TMA flow-rate ratios. S_0 for the bare silicon sample prior to HF etching is very large at 5400 cm/s, but decreases to 109 cm/s for O_2/TMA flow-rate ratio of 2. It decreases below 0.1 cm/s for O_2/TMA flow-rate ratios in the range of 3.5–6.5, and increases to 109 cm/s again at O_2/TMA flow-rate ratio of 8. This suggests extremely small S_0 due to band bending effect brought about by fixed charges in the AlO_x films and/or reduction of interface trapping density. This band bending is caused by either the negative or positive fixed charges. Fig. 4 shows two representative C–V curves measured for AlO_x films deposited with O_2/TMA flow-rate ratio of 2 and 3.5 along with an ideal curve calculated as reference. The curve with flow-rate ratio of 3.5 shifts toward the negative voltage direction which suggests creation of fixed positive charges at the AlO_x/n-Si interface. The fixed charge density for various flow-rate ratios of O_2/TMA was calculated from the flat band voltage shift from that of the ideal C–V curve. This shift is calculated considering the work function difference between the Al gate and n-Si, and the film thicknesses of AlO_x and SiO_2 at the interface. The N_f was then plotted against O_2/TMA flow-rate ratios. The polarity of the fixed charges is positive for O_2/TMA flow-rate ratios in the range of 2–8. The results suggest that the magnitude of the fixed charge density is affected by the O_2/TMA flow-rate ratios. The largest N_f was obtained for O_2/TMA flow-rate ratio of 3.5. Fig. 6 shows S_0 as a function of N_f, which indicates that S_0 is reduced below

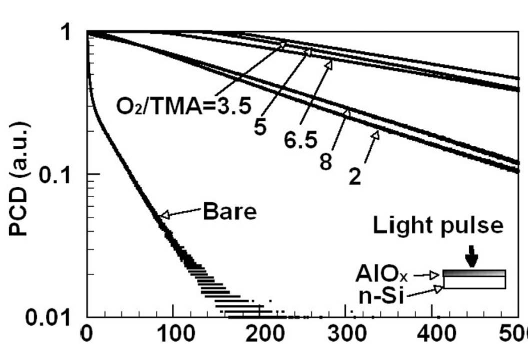

Fig. 2. Photoconductivity decay (PCD) curves observed by BS-τ lifetime profiler for laser impulse irradiated AlO_x films prepared under various O_2/TMA flow-rate ratios.

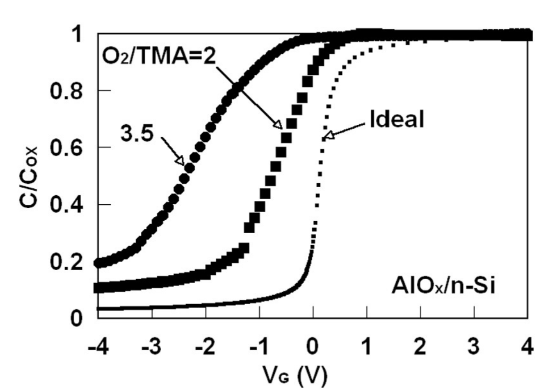

Fig. 4. C–V curves measured for two representative flow-rate ratios of O_2/TMA.

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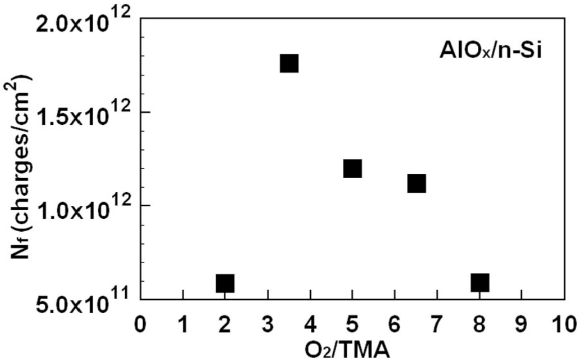

Fig. 5. Positive fixed charge density (N_f) determined by flat-band voltage shifts.

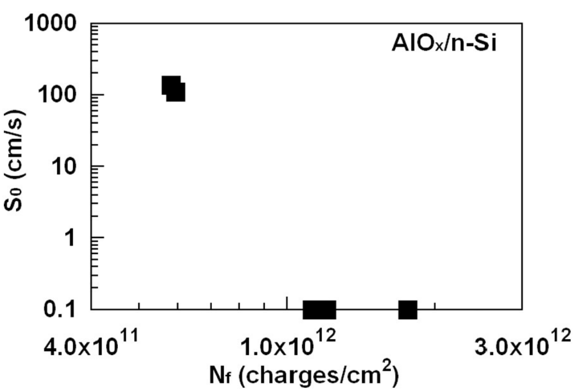

Fig. 6. Measured surface recombination velocity (S_0) as a function of positive fixed charge density(N_f).

0.1 cm/s due to positive N_f of the order of 10^{12} charges/cm^2. However, this reduction in S_0 may be due to the decrease in the interface trapping density. The behavior of measured D_{it} is shown in Fig. 7 as a function of the surface potential (ϕ_s). The D_{it} seems to be influenced by the O_2/TMA flow-rate ratios. The decrease of D_{it} at O_2/TMA flow-rate ratio of 3.5 seems to correspond to the smallest S_0 in Fig. 3. Fig. 8 shows behavior of D_{it} at the flat band plotted against N_f. A large N_f of 1.8×10^{12} charges/cm^2 appears to cause the small D_{it} of 2×10^9 eV^{-1} cm^{-2}. However, in some other data in the figure, there seems to be no correlation between D_{it} and N_f. Furthermore, D_{it} in Fig. 8 decreases by around one order, in spite of that, as seen in Fig. 3, S_0 decreases by four orders. Therefore, it is suggested that an extremely large decrease in S_0 is mainly caused by the band bending effect due to the existence of positive fixed charge density of the order of 10^{12} charges/cm^2 and that reduction in D_{it} at large N_f assists in the reduction of S_0.

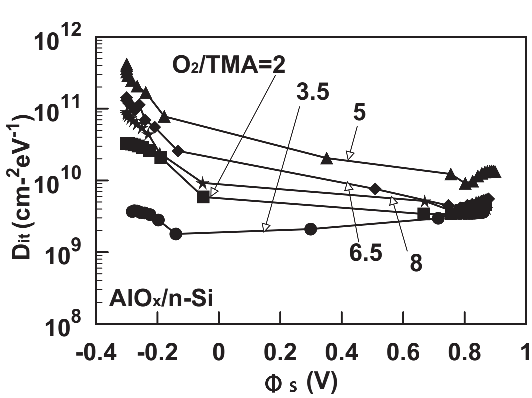

Fig. 7. Measured interface trapping density (D_{it}) as a function of surface potential.

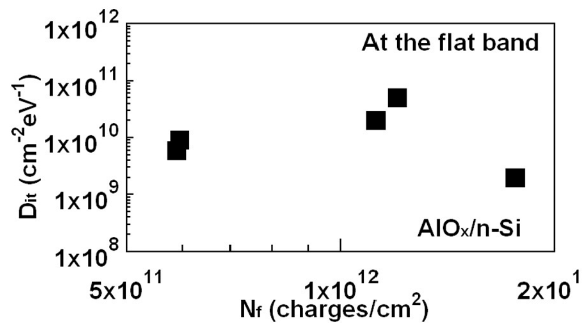

Fig. 8. D_{it} plotted against N_f.

As seen in Fig. 5, positive charges in n-Si were obtained at O_2/TMA flow-rate ratios in the range of 2–8. This was predicted from the data on charges created in p-Si in a previous work by the authors [11]. We can say that positive charges are created in O_2/TMA flow-rate ratios around 10 and below in this study whereas previous work [11] by the authors showed that negative charges are created in O_2/TMA flow-rate ratios above around 10 in the AlO_x films deposited by using the Cat-CVD. The results that charges obtained in O_2 rich ambient are negative while those obtained in Al rich ambient are positive seem to be consistent with the results obtained by first-principles calculations [18,19].

4. Conclusion

The creation of positive fixed charges and its effect on reducing surface recombination in n-Si can be attributed to AlO_x films deposited by Cat-CVD in order to obtain excellent passivation films for crystalline n-Si solar cells. Positive fixed charges can be created in AlO_x films deposited at O_2/TMA flow-rate ratios around 10 and below. The surface recombination velocity measured was reduced to below 0.1 cm/s for O_2/TMA flow-rate ratios in the range of 3.5–6.5. It was confirmed that extremely small surface recombination velocity is obtained mainly due to band bending effect brought about by positive fixed charges of the order of 10^{12} charges/cm^2. The decrease in D_{it} at large N_f also assists in the reduction of S_0.

Acknowledgments

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