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Novel Silicon Surface Passivation by $Al_2O_3/ZnO/Al_2O_3$ Films Prepared by Atomic Layer Deposition

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Abstract

In this paper, novel $Al_2O_3/ZnO/Al_2O_3$ stack is suggested as the silicon passivation layer for the solar cell application. It is confirmed by the experiment that the amount of the negative fixed oxide charge can be controlled by inserting ZnO inter layer (IL), which is explained by accepter-like defect (V_{Zn}, O_i, and O_{Zn}) formation from room temperature photo luminescence (RTPL) analysis. The effect of ZnO IL is investigated with varying the thickness of Al_2O_3 bottom layer by the electrical and physical analysis. The effective life-time measurement shows that the electronic recombination losses at the silicon surface are reduced effectively by optimizing the $Al_2O_3/ZnO/Al_2O_3$ stack.

1. Introduction

Surface passivation on the front and rear side of c-Si solar cells is very important because their efficiency is significantly affected by electronic recombination losses, primarily at the wafer surfaces. Normally, the surface recombination rate (U_S) from Schottky-Read-Hall (SRH) formalism [1] can be decreased by reducing the interface trap density by chemical passivation. Another method is reducing the density of one type of charge carrier at the surface by field-effect passivation [2]. Recently, the field-effect passivation by using Al_2O_3 which has the negative fixed charges near the Al_2O_3/c-Si interface has proved to be especially beneficial for passivating highly doped *p*-type c-Si surface [3]. Especially, Al_2O_3 prepared by atomic layer deposition (ALD) provides a high degree of surface passivation for *p*- and n-type c-Si. In this paper, for the first time, a new insulator structure of $Al_2O_3/ZnO/Al_2O_3$ stacks grown by ALD is suggested and the effect of a ZnO inter layer (IL) is investigated through the metal-insulator semiconductors (MIS) capacitors in terms of the field effect passivation for c-Si solar cells.

2. Experiment

MIS capacitors were fabricated on *p*-type (100)-oriented silicon wafers with a resistivity of 5-15 Ωcm. After conventional RCA cleaning of the silicon wafer and a dilute 1% HF strip for 1 min, $Al_2O_3/ZnO/Al_2O_3$ films were grown by ALD. ZnO layer was deposited as an IL using diethylzinc [$Zn(C_2H_5)_2$] and water, and Al_2O_3 for the top layer (TL) and bottom layer (BL) was deposited using trimethyaluminum [$Al(CH_3)_3$] and water, respectively. Ellipsometer measurements confirmed that ALD Al_2O_3 and ZnO film deposited at 200 ˚C is 1.4 and 1.7 Å thick per cycle, respectively. Considering that the fixed oxide charge is normally located approximately 2–3 nm from the oxide, the Al_2O_3 BL thickness was varied to 20 cycles and 30 cycles with ZnO IL thickness fixed as 5 cycles. 80-cycles Al_2O_3 films without ZnO IL are also considered as the reference condition. Ti and Al films 100 nm thick were deposited by RF magnetron sputtering to serve as the gate electrode and the backside contact of the Si wafer. Finally, all devices under test underwent a post-metallization annealing (PMA) process in a thermal furnace at 450 ˚C for 30 min with a forming gas (FG) (N_2:H_2=96 %:4 %) atmosphere. The cross section of the fabricated MIS capacitors used in this experiment is shown in **Fig. 1**. Capacitance-voltage (C-V) measurements were carried out with a HP 4284 A LCR meter. The room temperature photoluminescence (RTPL) measurement was taken at RT using a He-Cd laser line of 325 nm as the excitation source. The effect of the Zn and Al diffusion behaviors in the $Al_2O_3/ZnO/Al_2O_3$ stacks was also investigated by X-ray Photoelectron Spectroscopy (XPS) measurements.

3. Result and Discussion

Figure 2 shows the normalized C-V characteristic curves of the fabricated devices at a fixed frequency of 1 MHz. V_{FB} of devices with 30-cycle Al_2O_3 shifts to the largest positive direction and this means that there exists the largest negative fixed oxide charge ($-Q_{ss}$) as shown in **Fig. 3**. Here, to extract $-Q_{ss}$, V_{FB} shift from an ideal V_{FB} is calculated according to Al_2O_3 thicknesses as in the inset of **Fig. 3**. To find out the origin of $-Q_{ss}$, RTPL characteristic is investigated. As shown in **Fig. 4,** a narrow band edge (NBE) and deep level (DL) emission was observed at 380 (3.18), 420 (3.06), 521 (2.38), and 543 nm (2.28 eV) and $Al_2O_3/ZnO/Al_2O_3$/Si films have larger NBE and DL emission peak intensity than ZnO/Si films. The energy of the green emission is consistent with the oxygen antisite [O_{Zn}] level (521 nm [2.38 eV]) and the energy of 2.28 eV and 3.06 eV is with oxygen interstitial [O_i] and zinc vacancy [V_{Zn}], respectively. O_{Zn} can be formed from the interstitial oxides (O_i) and zinc vacancies (V_{Zn}), because the antisite oxide has relatively low formation energy [4]. Considering that $-Q_{ss}$ in ZnO films is related to accepter-like defects (V_{Zn}, O_i and O_{Zn}) [5], the increase of $-Q_{ss}$ in $Al_2O_3/ZnO/Al_2O_3$ stack can be explained by the enhanced formation of acceptor-like defects resulting from the chemical bonding between the Al_2O_3 and ZnO. For an efficient passivation layer, it is desirable the suggested stack has no effect on the interface trap density. To analyze the interface traps, the hysteresis characteristics of MIS capacitors with different Al_2O_3 BL thicknesses are investigated. **Figure 5** shows that in all devices, V_{FB} shifts to the positive direction, which can be attributed to hole trapping into the slow interface trap in the gate oxide. The hysteresis amount is increased when ZnO IL is adopted with 20-cycle Al_2O_3 BL but the 30-cycle Al_2O_3 BL devices have almost the same hysteresis amount with Al_2O_3 only devices even though a larger vertical electric field is forced. From the low-high frequency and the low frequency capacitance method, the fast interface trap characteristics are also investigated as shown in **Fig 6**. ZnO IL device with 20-cycle BL shows more increased fast interface trap density than Al_2O_3 only devices near V_{FB} energy level, which can be explained by Zn diffusing from ZnO into Al_2O_3, as revealed by XPS analysis in **Fig. 7**. But the hysteresis and capacitance analysis show that the interface degradation by Zn diffusion can be suppressed by optimizing Al_2O_3 BL thickness. **Figure 8** shows the effective lifetime values according to AL_2O_3 BL thicknesses. 30-cycle Al_2O_3 BL films with the largest negative fixed oxide charge have the largest effective lifetime. The effective lifetime measurement shows that the electronic recombination losses at the silicon surface are reduced effectively by the Al_2O_3/ZnO/Al_2O_3 stack.

4. Conclusions

Al_2O_3/ZnO/Al_2O_3 stacks for the surface passivation of c-Si solar cells are suggested for the first time. From electrical and physical analysis, the optimal process condition of Al_2O_3/ZnO/Al_2O_3 film is studied in terms of the field effect and chemical passivation. C-V analysis shows that 30-cycle Al_2O_3 films have the largest negative fixed oxide charge and smallest interface trap density. From RTPL analysis, the negative fixed oxide charge is found to be caused by zinc vacancy [V_{Zn}], oxygen interstitial [O_i] and oxygen antisite [O_{Zn}]. In 20-cycle BL case, the device shows increased interface trap density with smaller -Q_{SS} by near-interface defects resulting from Zn diffusing from ZnO into Al_2O_3 as revealed by XPS analysis. The effective lifetime measurement shows that the optimized Al_2O_3/ZnO/Al_2O_3 stack is very effective for the field effect passivation at the silicon surface.

Acknowledgements

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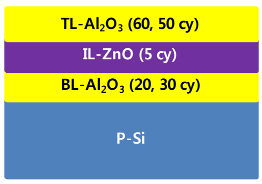

Fig. 1. Cross section of MIS capacitors with Al_2O_3/ZnO/Al_2O_3 stacks

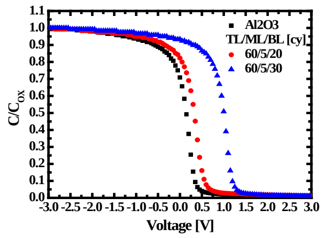

Fig. 2. C-V curves in devices with diffrent Al_2O_3 BL thicknesses.

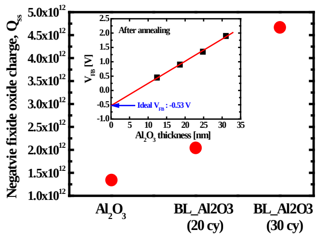

Fig. 3. Variation in negative fixed oxide charge (-Q_{SS}) according to different Al_2O_3 BL deposition thickness. Inset shows ideal V_{FB} extracted from the dependence on Al_2O_3 thickness.

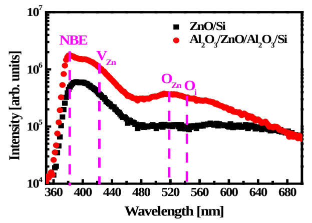

Fig. 4. RTPL in ZnO (500 cy)/Si and Al_2O_3 (160 cy)/ZnO (500 cy)/Al_2O_3 (160 cy)/Si films. In this analysis, thicker film is used than the real structure.

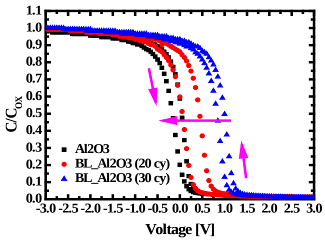

Fig. 5. The hysteresis characteristics of MIS capacitors at a frequency of 1 MHz. The gate voltage is swept from +3 to -3 V and vice versa.

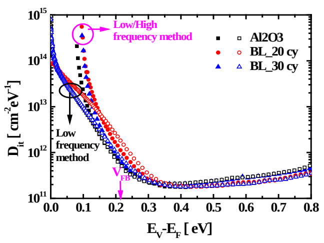

Fig. 6. Extracted results of fast interface trap density according to Al_2O_3 BL thicknesses by low/high and low frequency capacitance method.

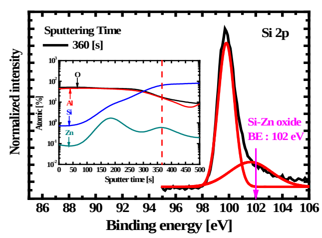

Fig. 7. Curve-fitting of Si 2p in 20-cycle Al2O3 BL. Inset shows XPS depth profiling.

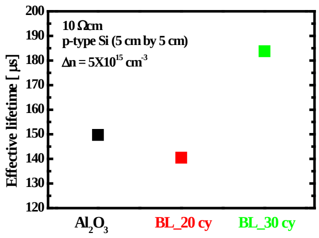

Fig. 8. Effective lifetime in Al_2O_3 BL thicknesses.