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Investigation of New Stacking Surface Passivation Structures with Interfacial Tuning Layers on p-type Crystalline Silicon for Solar Cell applications

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Abstract

We fabricated Y_2O_3-ZrO_2 composition film (YZO) on Al_2O_3 for the field effect passivation with high negative fixed charge densities on p-type Si. The surface recombination velocity was improved down to 30 cm/s after annealing at 400 °C. High thermal tolerance was confirmed over 600 °C by inserting 2-nm-thick ZrO_2 layer between YZO and Al_2O_3 interface. This result showed ZrO_2 layer work as protecting barrier of Al and Y interdiffusions.

1. Introduction

In the crystalline Si solar cells, traditional full aluminum rear contacts on p-type solar cells is going to be replaced by the partial rear metallization contacts through the dielectric passivation layer such as a passivated emitter and rear cell (PERC) structure, whose cell efficiencies are reported beyond 20 % [1]. In the structure, it is essential to have superior passivation properties at the rear surface as well as front one. The surface passivation properties can be improved by the effects of the chemical passivation and field effect passivation to suppress the minority carrier recombination at the Si surface [2].

The passivation layer for p-type Si is desired to have high density negative fixed charges, which can induce the effective field effect passivation [3]. We have investigated the 15 % Y_2O_3-85 % ZrO_2 composite film (YZO) for the field effect passivation and found significantly large negative fixed charge density [4]. In the case, we also verified the negative fixed charges were originated in the film, therefore they increased with increasing the film thickness. On the other hand, the Al_2O_3, which is well known as the superior passivation film for p-type Si, has electrical dipole at the interface between Si and provides the similar desired effects as negative fixed charges [5]. Therefore, YZO/Al_2O_3 stacking structure should provide both benefits of negative fixed charge in the film and electric dipole at the interface resulting in the superior field effect passivation. We have confirmed, however, the interdiffusion of Al and Y occurred and deteriorated the passivation properties especially after high temperature thermal treatment. In this study, we proposed YZO/ZrO_2/Al_2O_3 stacking structure in order to protect interdiffusion and investigated passivation properties depending on ZrO_2 thickness.

2. Experiment

A p-type silicon of 15-30 Ωcm (MCZ, 770 μm, (100)) was used as a substrate. 10-nm-thick Al_2O_3 passivation films were symmetrically deposited on the both front and rear surfaces of the silicon substrate by batch-type ALD (atomic layer deposition) technique. After Al_2O_3 deposition, post-deposition annealing (PDA) was performed at 450 °C for 30 min in nitrogen atmosphere. Then, the ZrO_2 and sub sequential 20-nm-thick YZO films were deposited on the Al_2O_3 layer in the same sputtering system at room temperature. After the deposition, additional post-deposition annealing (A-PDA) was performed at 400-800 °C for 30 min in a pure oxygen atmosphere. The effective lifetimes of the YZO/ZrO_2/Al_2O_3 passivated substrates were measured by the microwave-detected photo-conductance decay (Semilab, WT-2000) measurements. For the capacitance-voltage (C-V) measurements, the Pt gate electrodes were fabricated on the front YZO film, and rear side films were removed to form an ohmic contact with the silicon substrate. To determine the depth profiles of the chemical states, X-ray photoelectron spectroscopic (XPS) measurements (Thermo Scientific, K-alpha) were performed with Ar sputtering system.

3. Results and Discussion

Figure 1 shows maximum surface recombination velocities (S_{max}) of YZO/ZrO_2/Al_2O_3/Si structure as a function of A-PDA temperatures. When the A-PDA at 600 °C or less is performed on the Al_2O_3 layer with "pre" PDA, S_{max} is almost constant at approximately 130 cm/s. on the other hand, S_{max} is deteriorated over 10000 cm/s when the A-PDA performed at 800 °C. A high temperature oxidized annealing of Si should grow low quality thermal oxide between Si and Al_2O_3 layer, which deteriorates interface properties. When the YZO/ZrO_2 structure was employed, S_{max} shows almost the same passivation level as Al_2O_3/Si for the as deposited YZO film. However, S_{max} of employing 5-nm-thick ZrO_2 layer is increased, approximately 1000 cm/s, it is considered longer sputter process for the ZrO_2 insertion induced damage on the Al_2O_3 film. After the 400 °C A-PDA process, S_{max} is significantly improved to the surface passivation level of 30 cm/s. Higher temperature

A-PDA processes resulted into two divided groups. First, the effect of surface passivation is kept at approximately 70 cm/s with 2-nm-thick ZrO_2 because of the damage recovery. Otherwise S_{max} are increased with more than one order of magnitude after the A-PDA higher than 400 ^oC. Therefore it is apparent from Fig. 1, the 2-nm-thick ZrO_2 insertion was quite effective for the high thermal tolerance. 5-nm ZrO_2, however, was not effective for the improvement in the temperature tolerance. The XPS depth profile measurement indicates the reaction between Zr and Si after 800 ^oC annealing. The improvement of S_{max} means a decrease of D_{it} and/or increase of Q_{eff}. Effective fixed charge densities of $YZO/ZrO_2/Al_2O_3/Si$ structures extracted from C-V characteristics are shown in Fig.2. For the as-deposited samples, the negative fixed charge density slightly increases with YZO on the Al_2O_3 implying the YZO with and without ZrO_2 insertion provided additional fixed charge on the Al_2O_3. After the 400 ^oC A-PDA process, the Q_{eff} with YZO layer increases significantly, while Q_{eff} without YZO layer shows slight decrease probably due to the poor SiO_2 formation the interface as described above. The oxide films deposited by sputtering process usually includes a lot of oxygen vacancies (Vo), in which Vo is well known as indicating positive fixed charge. Thus, A-PDA process in a pure oxygen atmosphere should deny the Vo defects and increase negative fixed charge in the YZO films. This increase of negative Q_{eff} is good correlation with the improvement of S_{max} due to the enhancement level of field effect passivation. After the A-PDA processes over 600 ^oC, the fixed charge were change from negative to positive. Since Al_2O_3/Si structures show negative Q_{eff} even after the annealing, the YZO/ZrO_2 film structure should include large amount of positive Q_{eff}. M. Houssa et al. reported that annealing temperature above 500 ^oC for ZrO_x/SiO_x structure produces significant amount of positive charges which is caused by the crystallization of ZrO_2 layer [6].

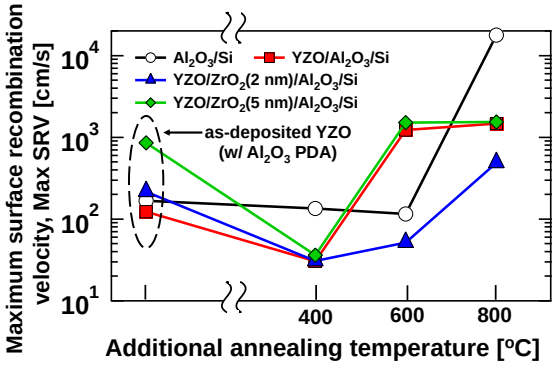

Fig.1 Maximum surface recombination velocities as a function of annealing temperature. The open circle shows Al_2O_3/Si as a reference. Close symbols show different ZrO_2 thickness.

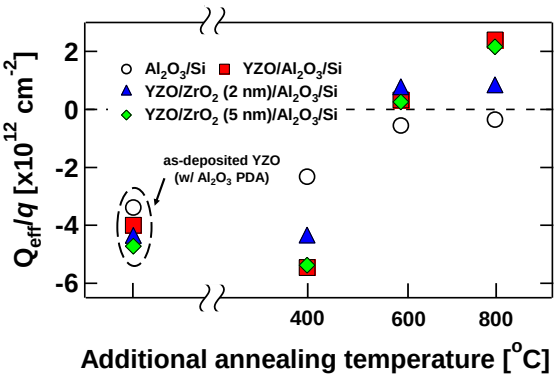

Fig.2 Fixed charge density as a function of annealing temperature.

3. Conclusions

We investigated the Zr based new surface passivation material with stacking structure. The surface recombination velocity was improved below 30 cm/s after annealing at 400 ^oC. High thermal tolerance was confirmed by inserting 2-nm-thick ZrO_2 layer at the YZO/Al_2O_3 interface. We verified the optimum thickness each layer and succeeded in the interdiffusion control between Al and Y for the superior performances.

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