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Plasma nitridation of atomic layer deposition (ALD) Al_2O_3 by NH_3 in plasma-enhanced chemical vapor deposition (PECVD) for silicon solar cell

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ABSTRACT

We investigated the effect of plasma nitridation of atomic layer deposition (ALD) Al_2O_3 films of crystalline Si wafers. Nitridation using NH_3 plasma treatment in a plasma-enhanced chemical vapor deposition for various RF plasma powers was performed on Al_2O_3 to form aluminum oxynitride (AlON). The plasma nitridation of the Al_2O_3 layer grown by ALD demonstrated a significant improvement in the passivation performance of a crystalline silicon solar cell. Indeed, the best values of open-circuit voltage and carrier lifetime for the AlON film at 400 W were 660 mV and 200 μs, respectively. The results of this experiment indicate that utilization of AlON film is a feasible means of improving the passivation performance of crystalline Si solar cells.

1. Introduction

The surface passivation performance of Al_2O_3 films is an attractive dielectric means of improving the efficiency of crystalline silicon solar cells [1–3]. It is well known that Al_2O_3 films grown by atomic layer deposition (ALD) exhibit excellent surface passivation on crystalline Si wafers, due to the field-effect passivation induced by negative-fixed charge and the high level of chemical passivation resulting from a low interfacial defect density [4–7]. The surface passivation performance of ALD Al_2O_3 films has been found to depend on post-treatment such as annealing and capping layering [3,8]. For high-efficiency passivated emitter and rear contact (PERC) silicon solar cells, an amorphous SiNx:H layer deposited by means of plasma-enhanced chemical vapor deposition (PECVD) is routinely utilized for anti-reflection at the front side and as a capping layer at the rear side of the ALD Al_2O_3 passivation layer. The structure of Al_2O_3/SiNx passivation experience plasma exposure on the Al_2O_3 passivation layer in PECVD. Nitridation of films by nitrogen and ammonia plasma exposure has often been employed in the solar cell and semiconductor device field [9,10]. AlON films can form in a similar way at the Al_2O_3/SiNx interfacial layer. Notably, it has been reported that AlON films have a higher density of negative fixed charge than do Al_2O_3 films [9,10].

In this study, we evaluated the passivation performance of ALD Al_2O_3 films after NH_3 plasma nitridation by PECVD.

2. Experimental details

In the present experimentation, we employed p-type crystalline Czochralski (Cz) Si wafers of 1–2 Ω-cm resistivity, 180 ± 20 μm thickness and 156 × 156 mm^2 overall size. First, surface damage caused during wafer sawing was removed by etching in 10% NaOH solution. The Cz Si wafers were cleaned by standard Radio Corporation of America (RCA) cleaning immediately prior to Al_2O_3 deposition. ALD Al_2O_3 films of about 10 nm thickness were deposited at 250 °C with trimethylaluminium ($Al(CH_3)_3$, TMA) and de-ionized water (H_2O, DIW) as reactants. One cycle of thermal ALD-Al_2O_3 growth consisted of a pulse of TMA, followed by a pulse of DIW, each carried by a flow of nitrogen and separated by purge time. After ALD-Al_2O_3 growth, plasma nitridation of the Al_2O_3 layer was carried out by PECVD with a gaseous mixture of N_2 and NH_3. A 13.56-MHz RF plasma generator provided power to the upper electrode while the lower electrode and reactor wall were maintained at ground potential. Several plasma parameters having been tested, the total pressure and total gas-flow rate were fixed at 700 mTorr and 330 sccm, respectively. To examine the passivation performance of the plasma nitridation on the ALD Al_2O_3 passivation layer, the effect of RF plasma power was studied at 100, 200, 300, 400 and 500 W. To avoid plasma-induced damage, for each RF power, the Al_2O_3 film was exposed to NH_3 plasma at 400 °C for 2 min.

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The passivation properties were characterized by quasi-steady-state photoconductance (QSSPC) measurement of the effective lifetime. Secondary ion mass spectroscopy (SIMS) was employed to evaluate and compare the depth profiles of the elements before and after the plasma nitridation process. The interface change was analyzed with reference to X-ray photoelectron spectroscopy (XPS) and Photoluminescence (PL) results.

3. Results and discussion

Fig. 1 plots the effective carrier lifetime and implied V_{oc} of the ALD Al_2O_3 films measured by quasi-steady-static photoconductance (MODEL: SINTON WCT-120) after NH_3 plasma nitridation. The effective minority carrier lifetime was determined at an injection level in the range of 1×10^{15} cm^{-3}. The effective lifetime of the ALD Al_2O_3 films was about 65 μs. As seen in Fig. 1(a), the lifetime was improved from 65 μs to about 200 μs with increasing RF plasma power. This improvement was saturated at ~400 W. The implied V_{oc} value of the ALD Al_2O_3 films for the solar-grade Si wafer was about 620 mV, which increased dramatically with increasing RF plasma power. The maximum implied V_{oc}, 660 mV, was obtained after exposure to 400 W RF plasma power. To examine the effect of the NH_3 plasma nitridation, post-deposition annealing (PDA) was carried out at 450 °C forming gas-anneal ambient for activation of the passivation. The implied post-PDA V_{oc} value was about 650 mV. These results can be considered to be clear representations of the effect of NH_3 plasma nitridation. We also employed one-side polished p-type Cz Si wafers of 1–10 Ω-cm resistivity, 525 ± 20 μm thickness to examine passivation performance. For the semiconductor-grade Si wafer using same procedure, the carrier lifetime and V_{oc} values were 2.1 ms and 670 mV, respectively, after 400 W NH_3 plasma nitridation. These values could increase up to reported level [11] using optimal post annealing condition. In our study, we focused on passivation performance of plasma nitridation after ALD-Al_2O_3 deposition.

In order to better understand these passivation phenomena, SIMS, PL and XPS analyses were performed under 100 and 400 W plasma nitridation conditions.

Fig. 2 shows the SIMS depth profiles of Al, O, H, and N for the 100 and 400 W plasma nitridation treatments. Such depth profiles obtained at oblique angles using a low-energy Cs^+ beam can be used to accurately measure elemental distributions. And in fact, the results showed clearly the nitrogen incorporation by NH_3 plasma nitridation. With increasing RF plasma power, SIMS profiles of Si and N show more nitridation at the Al_2O_3/Si interface resulting in more SiN formation and more release of Si atoms into the Al_2O_3 layer. A part of the surface Si could be explained by surface roughness at the high plasma power [8]. The nitrogen concentration in the interfacial region and on the surface of the 400 W AlON film was much higher than in the case of the 100 W version. In both sample films, the hydrogen was mainly at the Al_2O_3/Si interface. It was apparent that the interfacial H concentration was not increased by higher plasma power. However, in the 400 W AlON film, the hydrogen profile was broadened near the interface, indicating growth of the oxide layer. The distribution of Si, Al, and O in the 400 W AlON, moreover, indicated that the oxynitride layer in the interfacial region had become wide. The oxynitride in the interface of the sample nitrided at 400 W, in fact, was very noticeably increased. This phenomenon, which has been linked to the change of interfacial bonds resulting from the reduction of interfacial defects, can enhance surface passivation [9–13].

To confirm the reduction of the interfacial defect densities, a PL spectral analysis was performed on the ALD Al_2O_3 and AlON films. Strong PL emission in the 450–600 nm spectral range was observed for the ALD Al_2O_3 film, as shown in Fig. 3. Its maximum was observed at about 520–560 nm. This emission reflected the interfacial defects [12], which act as carrier recombination sites. As is apparent in Fig. 3, plasma treatment caused a shift of the PL emission to the short wavelength for the 100 W samples. A relatively weak PL emission in the 300–450 nm spectral range was observed for the 100 W AlON, whereas for the 400 W AlON, no PL emission was detected. Based on these PL results, it could be concluded that the main contribution to the PL spectra of our samples was from the interfacial-defect-based carrier recombination. The high interfacial defect concentration obviously was reduced by the formation of AlON film.

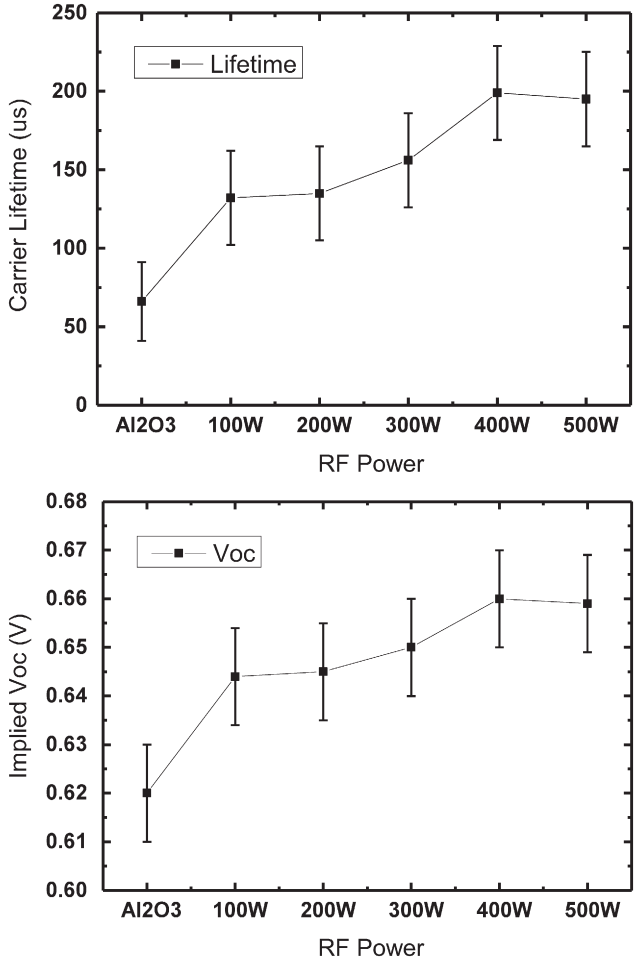

Fig. 1. Change of (a) effective carrier lifetime and (b) implied V_{oc} with RF processing power.

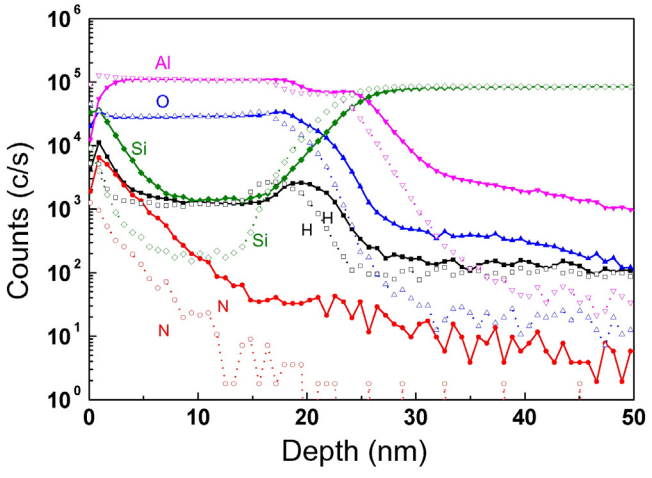

Fig. 2. SIMS depth profiles of ALD Al_2O_3 films nitrided at 100 and 400 W plasma power. The open and closed symbols represent 100 and 400 W power, respectively.