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Characteristics of surface passivation of ozone- and water-based Al_2O_3 films grown by atomic layer deposition for silicon solar cells

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ABSTRACT

We investigated the effects of the thermal stability of atomic layer deposition (ALD) oxidants on the surface passivation of ALD-Al_2O_3 film. The results showed good passivation at temperatures not greater than 780 °C. However, we found that Al_2O_3 films with an ozone oxidant showed better surface passivation at high temperatures than the water-based samples. The Al_2O_3 films with a water oxidant yielded an additional interfacial oxide upon high-temperature annealing. In the case of the ozone-based samples, the interfacial Si—O bonds that formed during deposition were more stable. This structural change degraded chemical passivation, which increased the interface-trap density to ~10^{12} eV^{-1} cm^{-2}. The passivation performance of ALD-Al_2O_3 films showed that at temperatures over 780 °C the passivation quality was affected more by defective passivation at the Si/SiOx interface than by a negative-fixed charge.

1. Introduction

Al_2O_3 films grown by atomic layer deposition (ALD) are attractive materials for the surface passivation of high-efficiency crystalline silicon solar cells [1–5]. It is well-known that ALD-grown-Al_2O_3 films' excellent surface passivation on crystalline Si substrates is due to field-effect passivation induced by negative-fixed charge as well as chemical passivation due to low interface defect density [1–5]. Thermal ALD is sensitive to surface conditions and interfacial properties due to the surface reaction of alternative precursor supplies. Therefore, the characteristics of ALD-Al_2O_3 films grown by using H_2O as the oxidant are strongly dependent on the hydroxyl groups [5]. Alternatively, because of ozone's higher activity for ligand elimination in metal-oxide ALD, ozone (O_3)-based ALD-Al_2O_3 films have the advantages of not only minimizing the formation of OH and related defects but also reducing oxygen deficiency [6]. On the other hand, there is not much information on how these two reactants affect the surface-passivation stability of Al_2O_3, because screen-printed silicon solar cells are subject to a high-temperature firing process for contact to a metal electrode.

In this study, we compare the thermal ALD passivation stabilities of Al_2O_3 for H_2O and O_3 as the primary oxidants.

2. Experimental details

Al_2O_3 films were formed on solar-grade silicon wafers and deposited by ALD in a NCD Lucida batch-type reactor. All solar-cell samples were fabricated on boron-doped p-type monocrystalline silicon wafers of 1–2 Ω-cm resistivity, 180 ± 20 μm thickness, and 156 mm × 156 mm size.

The Cz Si wafers were cleaned by a standard Radio Corporation of America (RCA) cleaning method of SC-1, SC-2, and HF-dip immediately prior to Al_2O_3 deposition. A 20 nm-thick Al_2O_3 layers were deposited at 250 °C. Trimethylaluminum (TMA) was used as the Al precursor and with either H_2O or O_3 as the oxygen precursor. O_3 was injected into the reactor in a flux 1 SLM at a concentration of 220 g/Nm^3 using an MKS AX8560 ozone generator. After ALD Al_2O_3 growth, the wafers were annealed at 450 °C for 30 min in a forming gas ambient (FGA) and fired at 780 °C for 4 s. All temperature readings were obtained using a thermocouple. To examine the thermal stability of the passivation performance on ALD Al_2O_3 passivation layer, the wafers were treated for 4 s at 830 °C, which temperature exceeded the firing temperature by 50 °C.

The carrier lifetimes were measured with Sinton WCT-120 Quasi Steady State Photoconductance equipment at an injection level of 5×10^{15} cm^{-3}. Each measurement was performed thrice and the results were averaged for five samples of surface area 156 mm × 156 mm. The interfacial characteristics were determined by X-ray photoelectron spectroscopy (XPS) and capacitance-coltage (C-V) measurements. The C-V measurements were performed on a MIS capacitor that was formed by the evaporation of a 300 nm aluminum electrode. The interface-defect densities were measured by the conductance method [7].

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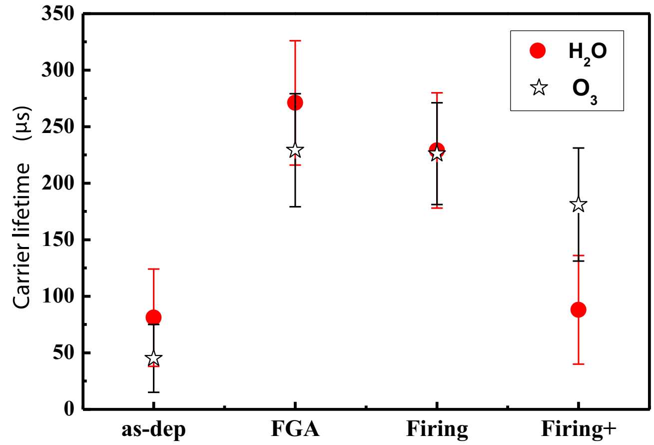

Fig. 1. Carrier lifetimes of ozone- and water-based Al_2O_3 films on solar-grade silicon wafers as functions of the annealing temperature.

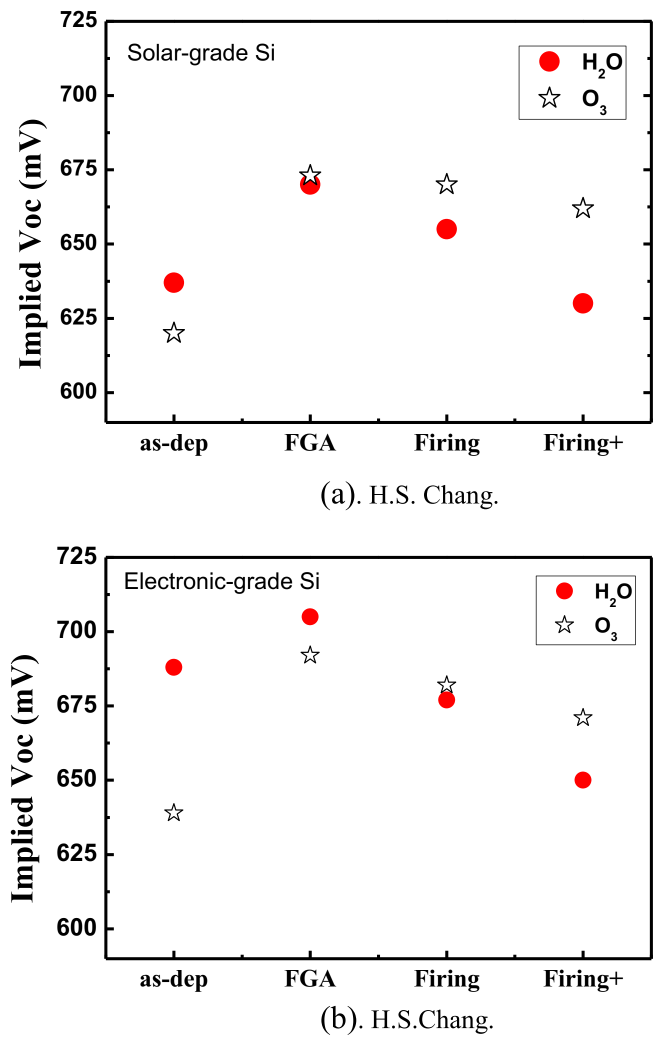

Fig. 2. Implied V_{oc} of ozone- and water-based Al_2O_3 films on (a) solar-grade, and (b) electronic-grade silicon wafers as functions of the annealing temperature.

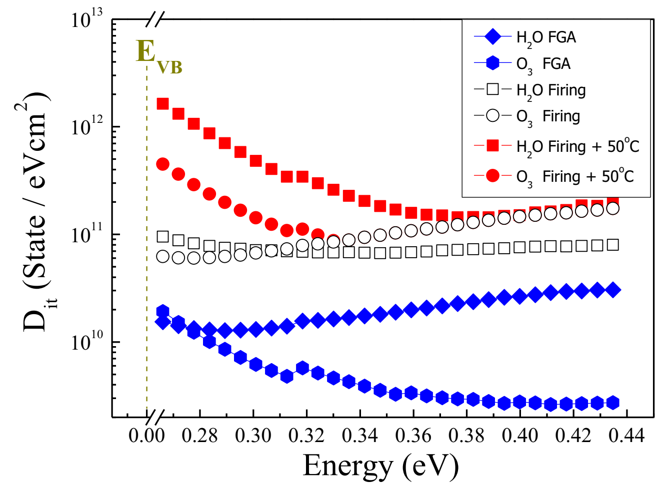

Fig. 3. Interface-trap density as function of energy in the Si band gap, as determined for Al/20 nm Al_2O_3/p-Si metal-insulator-semiconductors by the conductance method.

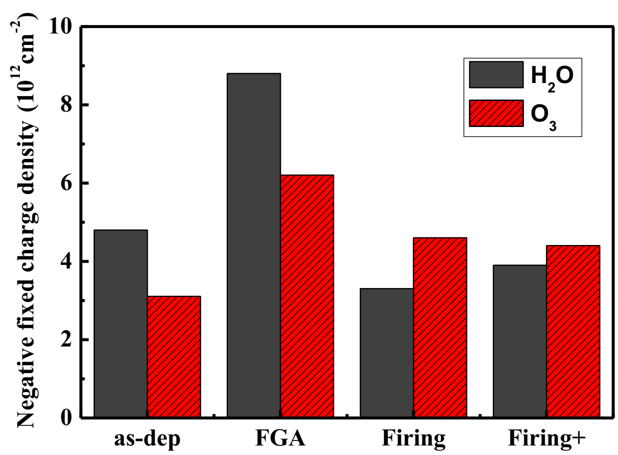

Fig. 4. Negative-fixed-charge density for ozone- and water-based Al_2O_3 films as functions of the annealing temperature.

3. Results and discussion

Fig. 1 plots the carrier lifetime as a function of thermal treatment for an ALD Al_2O_3 film using the oxidants H_2O and O_3. For the as-deposited samples, the water-based Al_2O_3 film showed a longer carrier lifetime than the ozone-based film. It is known that FGA treatment imparts the longest carrier lifetime to ALD Al_2O_3 films [8–10]. The average values of carrier lifetime for the water-oxidant and ozone-oxidant samples were 271 and 230 μs, respectively. The average carrier lifetimes after the firing process were similar, on the order of 225–230 μs. There was significant degradation of the lifetime value for the water-based sample after thermal treatment at a temperature 50 °C higher than the firing temperature. The average carrier lifetime for the ozone-based sample was 180 μs. This value, though less than that after firing, still corresponds to a good level of passivation. In other words, the degradation in the passivation of the ozone-based Al_2O_3 layer was less than that of the water-based Al_2O_3 layer after firing at a temperature 50 °C higher (firing + 50 °C).

Fig. 2(a) plots the implied open-circuit voltages (V_{oc}) of the H_2O- and O_3-oxidant Al_2O_3 films as a function of thermal treatment. The water-based films show a better V_{oc} than the ozone-based films, similar to the trend observed with carrier lifetimes. The Al_2O_3 films yielded the best values of V_{oc}: 670–673 mV for the FGA. The ozone-based samples were less degraded after both normal firing and firing at 50 °C higher temperature, as reflected in the V_{oc} values 670 and 662 mV respectively. In constant, the V_{oc} of the water-based film reduced to 655 mV after firing; it drastically reduced to 630 mV after firing 50 °C higher. Though there are differences in the levels of wafer quality, the electronic-grade silicon wafer shows an effect on passivation similar to that on temperature, as shown in Fig. 2(b). There were significant changes