Evaluating the Impact of Thermal Annealing on Al_2O_3/c-Si Interface Properties by Non-Destructive Measurements

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***Abstract* — The interface properties of Al_2O_3/c-Si are critical for both chemical and field-effect passivation. However, the impact of thermal annealing on the interface is challenging to investigate in a non-destructive manner. In this work, we combine non-contact corona-voltage measurements with Brewster's angle Fourier transform infrared spectroscopy (FTIR). Both measurements are fast and non-destructive which allowing instant diagnosis of the interface quality. The interface charge (Q_{tot}) and interface defect densities (D_{it}) both show a strong dependence on the annealing temperature. The change of Q_{tot} could be attributed to the different oxygen concentration at the interface. The pre-grown chemical oxide reduced the D_{it} resulting in the lowest saturation current density (J_0) of 2.15 fA after a 450 ºC annealing. The linear relationship between J_0 and D_{it} Q_{tot}^{-2} is shown for the samples annealed at 350 to 450 ºC, and it provides instant information of the passivation quality without requiring a symmetrical sample.**

***Index Terms* — aluminum oxide, infrared spectroscopy, Berreman effect, surface passivation, atomic layer deposition, interface.**

I. Introduction

Al_2O_3 provides excellent passivation on lightly doped and p^+ doped c-Si due to its low interface defect density combined with charge carrier population control by a high negative charge density, and it is currently the *de facto* standard for the passivation of the rear of the industrial passivated emitter and rear cells (PERC)[1]–[4]. The origin of the fixed charge can be attributed to the interstitial oxygen atoms in the AlO_x film [5]. The as-deposited AlO_x film contains a significant amount of OH groups at the interface due to the incomplete reactions during the first ALD cycles. A post-deposition annealing process releases H atoms and reconstructs the Al-O-Si bonding resulting in an O-rich layer at the AlO_x/c-Si interface detected by X-ray photoelectron spectroscopy (XPS) [6]. This suggestion agrees with high-resolution electron energy loss spectroscopy (EELS) measurements on cross-sectional transmission electron microscopy (TEM) samples[7], [8]. After annealing, a high ratio of tetrahedrally bound Al was found at the interface due to the aluminum silicate interlayer where a negative charged tetrahedral SiO_4 phase dominates[9]. Both excess oxygen atoms in Al_2O_3 and the tetrahedrally coordinated SiO_4 could contribute negative charge in Al_2O_3 film[5], [10]. However, the measurement requires a high vacuum environment and the removal of the upper AlO_x layer.

In this work, non-destructive measurements were employed to evaluate the interface quality. The impact of thermal annealing on the electrical properties and interfacial O content were shown by a non-contact corona-voltage measurement and Brewster's angle FTIR, respectively. These results will then be correlated to the level of surface passivation. It will be shown for the first time that the level of surface passivation directly correlated to the atomic density of the interfacial SiO_x film.

II. Experimental

The Si substrates used in the experiments were double-side polished 280 μm, boron doped, Float-zone (FZ) wafers with a resistivity of 1-10 Ω·cm. Prior to Al_2O_3 deposition, the wafers were cleaned by a standard Radio Corporation of America (RCA) cleaning process which includes two steps. The first step (RCA1) which removes the surface organic residues was performed in a mixed solution of ammonium hydroxide (NH_4OH), hydrogen peroxide (H_2O_2) and deionized (DI) water. After rinsing in DI water, the samples were cleaned in a second mixed solution (RCA2) of hydrochloric acid (HCl), H_2O_2 and DI water. This step removes the metallic contamination and leaves a thin chemical oxide in the c-Si surface. The Al_2O_3 film was deposited by plasma enhanced (PE-) atomic layer deposition (ALD, Fiji G2, Cambridge Nanotech, Veeco/CNT Inc.) using an oxygen plasma as the oxidant. The Al precursor, dimethylaluminum isopropoxide (98%, STREM Chemicals, Inc.), was heated to 50 ºC and delivered by Ar gas with a flow rate of 20 sccm. The delivery line and chamber walls were heated to 150 ºC. Before starting a deposition, the substrate was stabilized for 30 min at 200 ºC with Ar and O_2 flows of 50 and 30 sccm, respectively. The process pressure was at ~160 mTorr. The precursor pulse time was set to 0.4 s, and the reactor chamber was purged for 10 s after precursor pulse and oxygen plasma exposure. ~25 nm thick AlO_x films layer were grown on the substrate. After the depositions, the samples were subjected to thermal annealing in a rapid thermal process system (RTP-600xp, Modular Process Technology) with an N_2 flow of 5000 sccm at target temperatures for 10 min.

Contactless corona-voltage measurements (PV-2000 tool, Semilab Inc.) were used to extract the interface state density (D_{it}) and the total deposited charge (Q_{tot}) required to reach flat band condition. Q_{tot} is a combination of fixed charge (Q_f) and interface trapping charge (Q_{it}), where Q_f is the main component on a well-passivated surface. The interfacial silicon oxide was detected by Fourier transform infrared (FTIR) (Nicolet 5700, Thermo Fisher) spectroscopy with a *p*-polarizer and a variable angle holder. The impact of annealing temperature on the level of passivation was qualified by the saturation current density

(J_0) determined from minority carrier lifetime measurements obtained using the quasi-steady-state photoconductance (QSSPC) decay method (Sinton, WCT-120) on a symmetrical Al_2O3/c-Si(p)/Al_2O_3 structures.

III. Results

A. Interface properties

To investigate the impact of the thin oxide on the interfacial properties, the chemical oxide layer was intentionally left on the surface (labelled RCA2) and the remainder of the samples were etched in an HF (1%) solution (labelled HF) to remove the surface oxide. After the deposition of AlO_x films, the samples were annealed from 350 to 500 ºC for 10 min. Fig. 1(a) shows the impact of the annealing temperature on the Q_{tot}. For both of HF and RCA2 samples, Q_{tot} showed a linear increase at the temperature range from 350 to 450 ºC from 2.06×10^{12} to 2.64×10^{12} cm^{-2} and from 2.38×10^{12} to 2.64×10^{12} cm^{-2} for HF and RCA2 treated samples, respectively. The trend of decreased Q_{tot} at higher annealing temperatures was also observed for the AlO_x films prepared by thermal ALD using trimethyl aluminum (TMA) as the Al precursor [9]. The origin of higher Q_{tot} could be the higher O content close to the interface. At these annealing temperatures, the RCA2 samples showed a higher charge density than that of HF samples indicating that the pre-grown chemical SiO_x provides or enhances the O content in AlO_x at the interface.

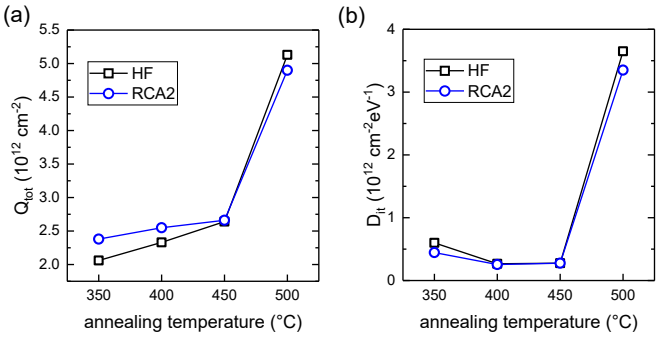

Fig. 1 Q_{tot} (a) and D_{it} *(b)* as a function of annealing temperature.

At annealing temperatures of 350 and 400 ºC, the D_{it} of RCA2 samples was found to be lower than that of HF samples, but the difference was negligible at 450 ºC, as shown in Fig. 1(b). It indicates that the chemical oxide reduces the interface defects when the annealing temperature is lower than 400 ºC, but the surface modification is insignificant when the annealing temperature is higher than 450 ºC. The lowest D_{it} of 2.67 and 2.54×10^{-11} $cm^{-2}eV^{-1}$ was obtained after annealing at 400 ºC for HF and RCA2 pre-treated samples, respectively. After annealing at 500 ºC, both Q_{tot} and D_{it} increased rapidly.

B. FTIR of SiO_x

To investigate the impact of annealing temperature on the interface properties, FTIR measurements were carried out using *p*-polarized incidence light and a variable angle sample holder. Fig. 2(a) shows the absorption spectra of PE-ALD AlO_x film annealed at 400 ºC at the angle of incidence from 10 to 74º. When the incident angle is lower than 30º, slight interference fringes were visible due to interference in the silicon substrate. These interference fringes were eliminated by using an incident angle of 74º which is Brewster's angle for c-Si. The other advantage of non-normal incident light is to enlarge the signal of longitudinal optical (LO) phonon vibrational mode of SiO_x which strongly absorbs *p*-polarized light at non-normal angles of incidence (the Berreman effect [11]). This angular behavior can also be seen in Fig. 2(a). The intensity of SiO_x LO peak at 1238 cm^{-1} increased at higher incidence angles. Therefore, the angle of incidence was set to 74º for the following measurements. It should be noted that the SiO_x film is only 1-2 nm thick in this case. Hence, Brewster angle FTIR is remarkably sensitive to the critical SiO_x interface layer, and this sensitivity is exploited in the remainder of this work.

The atomic density of the SiO_x film can be calculated from the frequency of the longitudinal optical (LO) and transverse optical (TO) phonon modes in SiO_x [12]. In AlO_x/c-Si structure, the signal of SiO_x TO peak is weak due to the thickness, and it overlaps with Al-O LO phonon peak at 900-1000 cm^{-1} [13] which makes it difficult to determine the peak position. On the contrary, the SiO_x LO peak is easily identified and shows a strong correlation with the annealing or oxidation temperature [14], [15]. Table 1 summarizes the relationship between LO mode peak frequency and the calculated SiO_x atomic density in literature, and the higher wavenumber of SiO_x LO peak indicates higher atomic density. A high wavenumber of SiO_x LO peak also indicates the x value it closer to 2 in the SiO_x layer[16], [17].

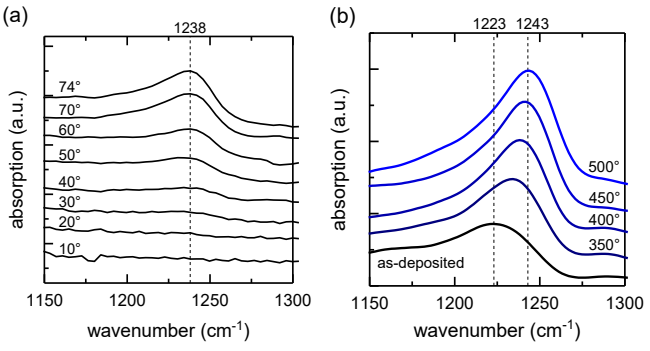

Fig. 2 (a) FTIR absorption spectra of PE-ALD AlO_x annealed at 400 ºC for various incident angle. (b) Evolution of SiO_x LO mode peak at annealing temperature of 350 to 500 ºC.

Table 1 Reported atomic density of SiO_x calculated from the LO and TO phonon modes.

TO mode (cm^{-1})	LO mode (cm^{-1})	atomic density (cm^{-3})	reference
1090	1256	2.28×10^{22}	[12]
1065	1243	1.93×10^{22}	
1057	1234	1.84×10^{22}	[15]
1057	1226	1.57×10^{22}	

Fig. 2 (b) shows the SiO_x LO mode peak of the as-deposited and annealed samples. The as-deposited film showed a broad peak at 1223 cm^{-1} which could be attributed to the SiO_x layer formed on the c-Si substrate during the first few cycles of oxygen plasma. After annealing, the peak became sharper and shifted to higher wavenumber, implying that the atomic density of SiO_x increased after annealing. The low quality of the SiO_x layer in the as-deposited AlO_x film is consistent with the fact that a post-annealing process treatment is essential for PE-ALD AlO_x films to activate the surface passivation [3]. The change of the SiO_x stoichiometry could be attributed to the relocation of O atoms from the interface OH groups which reconstruct Si-O-Al bonding during annealing [6]. The peak positions showed a strong dependence on annealing temperature, and it shifted to 1243 cm^{-1} after annealing at 500 ºC. The shift of LO peak position reveals that more interstitial O atoms presented close to the interface at the higher annealing temperature.

C. J_0 and annealing temperature

Fig. 3(a) shows the J_0 as a function of annealing temperature. The J_0 of both RCA2 and HF samples decreased with increasing annealing temperature below 450 ºC, which implies better surface passivation after higher annealing temperatures. The J_0 strongly increased after annealing at 500 ºC. This rapid change was consistent with the evolution of the D_{it} and Q_{tot} as is shown in Fig. 1. This degradation of surface passivation at high annealing temperature was also reported in the previous study which showed that both thermal and PE-ALD TMA Al_2O_3 films degraded after prolonged annealing at 500 ºC [18].

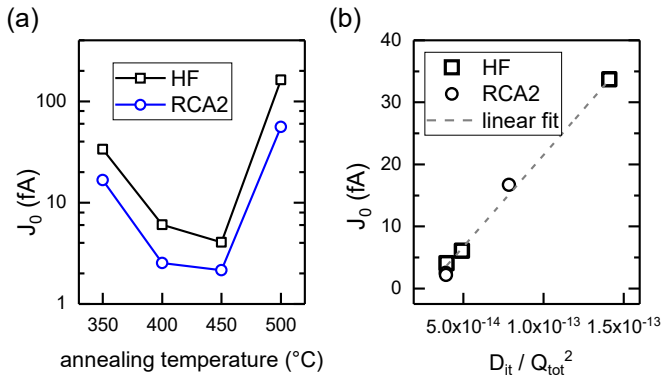

Fig. 3 (a) J_0 of Al_2O_3 films on *p*-type c-Si as a function of annealing temperature (b) J_0 as a function of $D_{it}\ Q_{tot}^{-2}$.

The RCA2 samples showed lower J_0 values compared to the HF samples, indicating that the chemical oxide improves the interface quality which is consistent with previous studies where TMA was used as the Al precursor [19]. A lowest J_0 value of 2.15 fA was obtained from the RCA2 sample with a post-annealing temperature of 450 °C. The surface passivation of Al_2O_3 films is a combination of chemical and field-effect passivation which could be determined by D_{it} and Q_{tot}, respectively. The reciprocal recombination rate is proportional to D_{it} and Q_{tot}^{-2} [20]. Figure 3(b) shows the J_0 value of the samples annealed at 350 to 450 ºC as a function of $D_{it}\ Q_{tot}^{-2}$. For both RCA2 and HF samples, the J_0 fits the linear relationship. This is consistent with the first order scaling of surface passivation as a function of fixed charge and interface defect density[21].

IV. Conclusion

We demonstrated a strong dependence of Q_{tot} and D_{it} on the post-annealing temperature by non-contact corona-voltage measurement. When the annealing temperature was increased from 350 to 450 ºC an increase in fixed charge density was detected which could be attributed to the higher O content at the interface. The as-deposited Al_2O_3 film contained a significant amount of OH groups at the interface, and the post-annealing process reconstructed the Al-O-Si bonding. This reaction is strongly related to the annealing temperature, and it results in a higher O content interface when the annealing temperature is higher, observed on the SiO_x interlayer by Brewster angle FTIR. Chemically pre-grown thin SiO_x also increased the Q_{tot} and resulted in a low recombination loss at the interface. The lowest J_0 of 2.15 fA was obtained from the RCA2 sample with a post-annealing temperature of 450 °C. These non-destructive measurements provide an instant diagnosis of the interface qualities.

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