THE STUDY OF Al$_2$O$_3$ PASSIVATION BY CORONA CHARGE

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ABSTRACT: The dependence of emitter saturation current density and interfacial trap density of Al$_2$O$_3$ passivated silicon samples on deposition and post deposition conditions is investigated in detail. The films are deposited by thermal and plasma-assisted atomic layer deposition. A corona discharge is used to apply more negative charge in Al$_2$O$_3$, negatively charged dielectric, for analyzing the passivation properties. Our results show there are clear differences in the interface defect density and charge density for films deposited using different oxidants, with plasma-assisted films exhibiting the lowest mid-gap defect density and the highest charge density. The application of negative charge causes the embedding of some of this charge in the film and a reduction in the emitter saturation current density, especially for samples annealed at relatively low temperature. Following the application of negative charge, differences in surface passivation (emitter saturation current density) of films deposited using different oxidants or at different temperatures largely disappear

Keywords: Al$_2$O$_3$, corona charge, annealing

1 INTRODUCTION

Recently Al$_2$O$_3$ atomic layer deposition (ALD) has become of great interest due to its excellent passivation performance caused partly by a high density of negative charge. Negatively charged dielectric layers are important for high-efficiency silicon solar cells because of their excellent surface passivation for p-type crystalline silicon (c-Si) and boron-diffused emitters based on the field effect passivation caused by a high density of fixed charge $(Q_f)$. The quality of surface passivation also depends on the interface trap density $(D_{it})$ within bandgap due to traps that occur at the interface between the silicon and the passivating dielectric. Low $D_{it}$ is required for good passivation. The effective passivation of Al$_2$O$_3$ is attributed to a low value of $D_{it}$ in the range of $10^{12}$ cm$^{-2}$ eV$^{-1}$ around mid-gap in combination with a high density of fixed negative charge up to $10^{13}$ cm$^{-2}$ [1, 2].

To reach a high level of surface passivation a post-deposition anneal is indispensable. The plasma-assisted ALD deposited Al$_2$O$_3$/Si interface properties, $D_{it}$ and $Q_f$, have been measured as a function of the temperature of the post-deposition anneal [1]. The influence of annealing on the field-effect passivation properties of the films and the level of chemical passivation of the films have also been investigated, with corona charging used as a powerful tool to characterize the field-effect passivation provided by thin-films on c-Si [3].

In the field of photovoltaics, corona charge has generally been utilized for material characterization by modifying the surface charge density. This allows, for example, determination of fixed charge density in dielectrics [4]. Corona charging could also be used to effectively and permanently change the charge state of dielectric films.

In this study, we investigate the effect of annealing temperature and oxidant (O$_3$, H$_2$O or oxygen plasma) on the properties of ALD deposited Al$_2$O$_3$ films and the Al$_2$O$_3$/Si interface. Further, study the possibility of embedding additional negative charge using corona charging to reduce surface recombination at the Al$_2$O$_3$ interface.

2 EXPERIMENTAL PROCEDURE

10 Ω-cm n-type Float-zone Si (100) wafers with a thickness of 255 μm were used as substrates for lifetime measurements. The 100 Ω-cm boron diffusion was performed on both sides of the wafers using BF$_3$ as the diffusion source. After boron diffusion, the wafers received a standard RCA clean with a final HF dip prior to deposition to remove the native oxide. Then a 20 nm thick ALD Al$_2$O$_3$ film was deposited on all samples in a Beneq TFS 200 series reactor. The films were prepared by alternating trimethylaluminum (TMA) exposure and various oxidant precursors including O$_3$, H$_2$O$_2$, and O$_2$. Thermal ALD Al$_2$O$_3$ was deposited at 200°C and plasma assisted (PA) ALD at 150°C. The wafers were cut into quarters and received different thermal post-deposition annealing (PDA). The inductively coupled photoconductive decay (PCD) technique was used to determine $J_{inj}$ as a function of injection level [5, 6]. The value of $J_{inj}$ is extracted from the effective carrier lifetime in high injection.

Corona charge was deposited sequentially using identical deposition parameters on both surfaces of the Al$_2$O$_3$ coated samples. The initial investigations presented in this work focused on the deposition of negative charge only; this polarity was chosen for its tendency to strengthen the field-effect passivation at Al$_2$O$_3$/Si interface. For 12 minutes, a -6KV potential was applied to the steel needle, which was 14 cm above the sample. The negative ions originating from the tip of the wire in the discharge were most probably CO$_3^-$ ions [7].

The deposited corona charge was measured using a Kelvin probe, KP020 in KP Technology Ltd. Each sample was then subjected to rapid thermal annealing (RTA) process that involved the rapid (30°C/s) increase to the post-deposition annealing temperature previously used for that particular sample. These set temperatures were kept for 30 seconds before rapid cooling. The RTA was performed in forming gas ambient.

For the investigation of the Al$_2$O$_3$/Si interface properties, MIS (metal / insulator / semiconductor) capacitor structures were fabricated. Samples used for C-V measurements were CZ p-type, 1-10 Ω-cm (100)
wafers without emitters. After a standard RCA clean, an Al$_2$O$_3$ layer around 20 nm thick was deposited at 200 °C. Prior to measurement, 100 nm thick Al dots were evaporated on the front and GaIn contacts were formed on the rear of the samples. No post-metallization anneal was given to these devices. A high frequency (HF) curve sweeping the bias voltage from 0 V in the positive direction was measured to take samples to flatband conditions and slightly beyond. Once the flatband voltage ($V_{FB}$) is known, a bias corresponding to the maximum positive sweep voltage was applied for a certain time to try to charge up the film to a steady state condition that will then not change during the subsequent measurements. After stabilization, a high frequency and a quasi-static ($QS$) capacitance-voltage ($C-V$) sweep were carried out to determine interface trap density of the samples. These C-V curves were measured from inversion to accumulation in order to reduce spurious effects due to inversion-layer response time [8]. High frequency C-V measurements were accomplished at 1 MHz, and quasi-static C-V measurements were carried out with different sweep rates of 0.1 and 0.02 V/s for compensation resulting from leakage current [9].

The defect density was calculated using the Castagne and Vapaille method [10].

3 RESULTS AND DISCUSSION

The Kelvin probe technique is used to characterize the magnitude of negative corona charge on Al$_2$O$_3$ films. In most cases, the surface charge density can be calculated simply from the measured charge in the surface work function difference after corona charging, $Q_s = \epsilon \left( \frac{e_{ox} - d_{ox}}{d_{ox}} \right)$, where $\epsilon_{ox}$ is the dielectric permittivity of the oxide and $d_{ox}$ is the thickness of the oxide, because the potential drop across the space charge region under the Al$_2$O$_3$/Si interface can be neglected when the measurement is carried out appropriately.

![Figure 1: Surface charge density as a function of corona charging time for negative corona needle potentials](image)

Figure 1 illustrates the measured values of surface charge density for a range of corona charging times. After 12 minutes of charging, the surface charge density reaches ~-7×10$^{12}$ cm$^{-2}$. The electric field across the Al$_2$O$_3$/Si interface (resulting from the sum of the corona surface charges and fixed charges near the interface in the Al$_2$O$_3$ films) is ~1-1.5MV/cm under these conditions, depending on the fixed charge density. An electric field of this magnitude is insufficient to result in tunnelling of carriers from the Si substrate into the dielectric [11].

![Figure 2: Negative charge density and interface trap density at midgap of (a) O$_3$, (b) H$_2$O, and (c) O$_2$ plasma ALD Al$_2$O$_3$ annealed at 350°C-450°C before/after corona charging and RTA](image)

Fig. 2 shows the fixed charge density in the films, as determined from $V_{FB}$ values obtained from the first voltage sweep, usually from 0 to 3V. Note that the calculation of charge density from $V_{FB}$ usually assumes that all the charge is located at the Si-dielectric interface. If the charge is located some distance into the dielectric, the actual charge density must be greater to account for the same value of $V_{FB}$. For films that have not been corona charged, the assumption of charge being located at the interface is expected to be valid, since experimentally the fixed charge in Al$_2$O$_3$ films has been found to be located very close to the interface [12]. For films following corona charging, the location of the additional charge is less clear. However, the increase in
The charge densities of Al$_2$O$_3$ become higher after corona charging and this trend is more distinct at low annealing temperature. This additional charge would be expected to provide more effective field passivation for p-type surfaces. The embedded corona charge could therefore play a role in improving field-effect passivation. The charge density of O$_3$-based Al$_2$O$_3$ increases after corona charging. However, already fully activated H$_2$O and O$_2$ plasma-based Al$_2$O$_3$ samples annealed over 400°C have almost the same charge density after corona charging. The effect of RTA on charge density of corona-charged samples indicates that the negative charges are maintained or decrease slightly after redistribution into the oxide.

![Figure 3: QS and HF C-V curves for the O$_2$ plasma-based ALD films annealed at 400°C before/after corona charging and RTA.](image)

The interface trap densities ($D_{it}$) at midgap extracted from the CV measurements are also shown in Fig. 2. The overall $D_{it}$ at midgap decreases with the post-deposition annealing temperature. The hydrogen content of the Al$_2$O$_3$ films has been found to be very important for the chemical passivation of c-Si obtained from the Al$_2$O$_3$ films [14]. Lowest $D_{it}$ values are generally obtained at the higher anneal temperature of 450°C. O$_2$ plasma-based Al$_2$O$_3$ films deposited at 150°C have significantly lower $D_{it}$ values compared to H$_2$O-based Al$_2$O$_3$ deposited at 200°C. This may be because the former has a higher hydrogen content than the latter [14], resulting in better H termination of interface defects during annealing. Also overall the process is nearly temperature-independent when H$_2$O is used. By contrast, O$_3$-based Al$_2$O$_3$ exhibit a high $D_{it}$ at low annealing temperature and low $D_{it}$ at high annealing temperature.

These phenomena can be explained by the result of Elliot et al [15]. The authors suggested that the low electronic density of the films deposited using O$_3$ at low temperature means that the layer is composed of Al$_2$O$_3$ with voids. The rugged morphology of the films deposited using O$_3$ than their H$_2$O counterparts as the oxygen source can be traced to an inhomogeneous distribution of immobile protons at low temperatures on the surface. As the ALD cycle proceeds, the action of O$_3$ regenerates protons, frozen in an uneven distribution, which then undergo no further reaction with gas-phase O$_3$. Over many cycles, the mode of film deposition will therefore resemble island growth and will result in a rough, porous, low-density film. This may also be the reason why O$_3$-based Al$_2$O$_3$ shows higher $D_{it}$ at low anneal temperature compared to other Al$_2$O$_3$ films.

For the Al$_2$O$_3$ films with relatively high $D_{it}$ ($>10^{12}$ cm$^{-2}$eV$^{-1}$) after relatively low post-deposition annealing, the chief effect of corona charging is the decrease of $D_{it}$. The change in $D_{it}$ after corona charging decreases with increasing anneal temperature. Also, most of Al$_2$O$_3$ samples subjected to a post-charging RTA exhibit almost the same midgap $D_{it}$ at high annealing temperature, but increasing midgap $D_{it}$ at low annealing temperature. The reasons for the change in $D_{it}$ following corona charging are not clear, but suggest further hydrogenation of the interface. It is clear that the film properties depend greatly on the post deposition anneal temperature, with low anneal temperatures leading to films whose properties are far more easily altered by subsequent treatments. As a consequence, corona charging is not always a ‘non-invasive’ technique, in the sense of not altering the film bulk or interface properties, although this appears to hold for samples annealed at a sufficiently high temperature.

The emitter dark saturation current density $J_{0e}$ is influenced by the net charge in the passivation film (in other words, the sum of the interface, bulk and surface charge densities) as well as by changes in the interface defect density. Figure 4 shows the effect of annealing, corona charging and RTA on $J_{0e}$. It is clear that the 350 °C annealed sample has the biggest impact from corona charging, resulting in the decreased $J_{0e}$ of Al$_2$O$_3$ coated emitters. This figure also shows that corona charging can decrease the $J_{0e}$ difference among samples. The important thing is that saturated $J_{0e}$ values (following corona charging) of Al$_2$O$_3$ films are almost the same regardless of oxidant precursor and annealing temperature. It is analogous to the surface recombination velocity trend of p-type SiO$_2$/Si of various base doping concentrations after positive corona charging [16]. This is despite the different interface defect densities observed by C-V measurements.

The differences in $J_{0e}$ values before and after corona charging of samples annealed over 400°C are very small. Apparently the passivation of Al$_2$O$_3$ annealed at 450°C is robust. In terms of corona damage, however, increases of $J_{0e}$ after post-charging RTA reveals that charge redistribution through RTA can bring about reduction in passivation. As post-deposition annealing temperature is higher, the degree of change caused by corona charging and RTA has a tendency to be smaller. Also, the $J_{0e}$ values after post-charging RTA at 350°C are lower than those of PDA-treated initial state unlike samples, annealed at 450°C with relatively low initial $J_{0e}$.
maintaining almost the same. It means corona charging and RTA can enhance the passivation of ill-passivated $\text{Al}_2\text{O}_3$.

![Figure 4](image_url) 

**Figure 4:** Saturation current density for $\text{O}_3$, $\text{H}_2\text{O}$, and $\text{O}_2$ plasma ALD $\text{Al}_2\text{O}_3$ before/after corona charging and RTA in terms of annealing temperature at minority carrier density of $1 \times 10^{16}$.

4 CONCLUSION

In conclusion, we have demonstrated that the passivation of corona charge deposited on the surface of $\text{Al}_2\text{O}_3$-passivated silicon is influenced by fixed charge density and interface trap density. For low anneal temperatures, corona charging appears to result in the embedding of additional negative charges in the films, as well as a reduction in the interface defect density. Also the application of negative charge results in a decrease in $J_{le}$ of ALD $\text{Al}_2\text{O}_3$ passivated B-diffused emitters. The saturated $J_{le}$ values in the range of $1-3 \times 10^{14}$ A/cm$^2$ implies that negative corona charge results in some enhancement of $\text{Al}_2\text{O}_3$/$\text{Si}$ interface. The $\text{Al}_2\text{O}_3$ field-effect passivation itself is enhanced by additional negative charge.

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6 REFERENCES


