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# Stability of the Surface Passivation Properties of Atomic Layer Deposited Aluminum Oxide in Damp Heat Conditions

Ismo T. S. Heikkinen<sup>1, a)</sup>, George Koutsourakis<sup>2</sup>, Sebastian Wood<sup>2</sup>, Ville Vähänissi<sup>1</sup>, Fernando A. Castro<sup>2</sup> and Hele Savin<sup>1</sup>

<sup>1</sup>*Aalto University, Department of Electronics and Nanoengineering, Tietotie 3, FI-02150 Espoo, Finland*  
<sup>2</sup>*National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, United Kingdom*

<sup>a)</sup>ismo.heikkinen@aalto.fi

**Abstract.** Surface passivation layers that are stable in the long term are becoming increasingly important in emerging architectures of crystalline silicon photovoltaics. In this work, we study the effect of elevated temperature and humidity on the surface passivation properties of 5 nm to 20 nm thick aluminum oxide (AlO<sub>x</sub>) layers grown using thermal Atomic Layer Deposition (ALD). ALD-coated p-type Float Zone (FZ) wafers were exposed to 40°C and 85°C in 85% relative humidity (RH), and the passivation properties of the AlO<sub>x</sub> films were monitored during the damp heat exposure at designated intervals by photoluminescence (PL) imaging. Additionally, minority charge-carrier lifetime, film charge, and interface defect density were measured before and after the exposure. The results indicated that even 5 nm AlO<sub>x</sub> layers were stable under the prolonged damp heat exposure, and that 20 nm thick passivation layers deposited using either water (H<sub>2</sub>O) or ozone (O<sub>3</sub>) as the oxidant in the ALD process had no major differences in passivation stability.

## INTRODUCTION

Atomic Layer Deposited (ALD) aluminum oxide (AlO<sub>x</sub>) is a versatile surface passivation material for crystalline silicon (c-Si) photovoltaics [1]. The high negative fixed charge density of the AlO<sub>x</sub> layer accounts for field-effect passivation, while the low interfacial defect density between the c-Si surface and the oxide provides efficient chemical passivation [2]. As the negative fixed charge of ALD AlO<sub>x</sub> repels electrons from the surface, it is especially efficient in the passivation of p-type silicon [3], although the passivation of both p- and n-type substrates [3, 5] as well as highly doped surfaces [6] is possible. Passivation layers are crucial for the operation of new solar cell architectures, especially Passivated Emitter and Rear Cell (PERC) devices. Degradation of surface passivation during processing and in harsh in-field conditions such as high illumination, temperature and moisture, can affect cell performance on a module level. In various studies, ALD AlO<sub>x</sub> has been shown to exhibit good thermal stability [7, 8] at conditions relevant to the necessary processing steps for solar cell fabrication. Regarding common solar cell operating conditions, Niewelt *et al.* studied the stability of AlO<sub>x</sub>-based surface passivation schemes under 1 sun illumination at 75°C, and showed that only minor degradation of surface passivation occurred for p-type substrates after 3700 hours of exposure [9]. In addition to degradation under illumination, the moisture sensitivity of passivation layers can be an issue if the encapsulating materials of solar modules fail to prevent moisture from reaching the surface of the cell [10]. Liang *et al.* studied how elevated temperature and moisture affected the surface passivation properties of 20 nm thick AlO<sub>x</sub> layers deposited using plasma-enhanced ALD (PE-ALD) [11, 12]. They reported that after approximately 230 hours of exposure at 85°C and 85% relative humidity (RH), the minority charge-carrier lifetime in p-type Float Zone (FZ) silicon wafers had decreased by 15%.

In this work, we study the passivation stability of uncapped 5 nm, 10 nm, and 20 nm thick ALD aluminum oxide layers in damp heat conditions. The films were deposited with thermal ALD, which has the potential for batch processing, and thus wider applicability than PE-ALD at the industrial scale. As thin ( $\leq 10$  nm) passivation layers are preferable over thicker films to keep the costs of industrial solar cell processing low [13], we study the influence of passivation layer thickness on the degradation rate. AlO<sub>x</sub> passivation films are often capped with plasma-enhanced

chemical vapor deposited (PE-CVD) silicon nitride ( $\text{SiN}_x$ ) [13-15], which acts as an antireflection coating (ARC) and an efficient moisture barrier [16]. However, solar cells and photodetectors making use of the black silicon (bSi) texture on the front side do not necessarily require ARCs [17-19], and thus have bare  $\text{AlO}_x$  on the light-absorbing side of the device. The most common oxidant for ALD  $\text{AlO}_x$  is water ( $\text{H}_2\text{O}$ ), but using ozone ( $\text{O}_3$ ) as the oxidant can provide faster ALD cycling, and yield better surface passivation with superior thermal stability [20]. Therefore, the effect of the oxidant in the damp heat degradation is also considered in this study.

## EXPERIMENTAL DETAILS

Square p-type 156 mm  $\times$  156 mm FZ wafers (1-3  $\Omega\text{cm}$ ,  $\sim$ 160  $\mu\text{m}$ ) were used as the substrate material. The wafers were first cleaned with standard RCA solutions and annealed in an oxygen ambient at 1050°C for 30 min to deactivate intrinsic defects in FZ wafers [21]. After the pre-treatment steps, the wafers were coated with 5, 10, or 20 nm  $\text{AlO}_x$  films deposited using trimethylaluminum (TMA) and  $\text{H}_2\text{O}$  as precursors. In addition, a 20 nm thick  $\text{AlO}_x$  film was deposited by changing the oxidant to  $\text{O}_3$ . All ALD coatings were prepared using a Beneq TFS-500 ALD tool.

Prior to the damp heat experiments, effective minority charge-carrier lifetime  $\tau_{\text{eff}}$  was measured from the wafers with the Quasi Steady-State Photoconductance (QSSPC) method using a Sinton Instruments WTC-120 equipment. The effective maximum surface recombination velocity  $S_{\text{eff,max}}$  was calculated from  $\tau_{\text{eff}}$  at a minority carrier density of  $1 \times 10^{16} \text{ cm}^{-3}$  assuming infinite bulk lifetime. The wafers were quartered, and one quarter of each sample was exposed to damp heat conditions in an environmental chamber after initial characterization. The quarters were first placed in 40°C/85% RH for 168 h, and subsequently to 85°C/85% RH for 264 h to accelerate the potential degradation process. Photoluminescence (PL) imaging was used to monitor the potential degradation on a wafer level after 4 h, 48 h, 96 h, and 168 h cumulative exposure times in both conditions, and additionally after 264 h in 85°C/85% RH. Total film charge  $Q_{\text{tot}}$  and interface defect density  $D_{\text{it}}$  were measured after annealing and after exposure to damp heat with contactless CV (COCOS) [22] using a Semilab SDI PV-2000A instrument. Figure 1 summarizes the procedure for sample preparation and experiments.

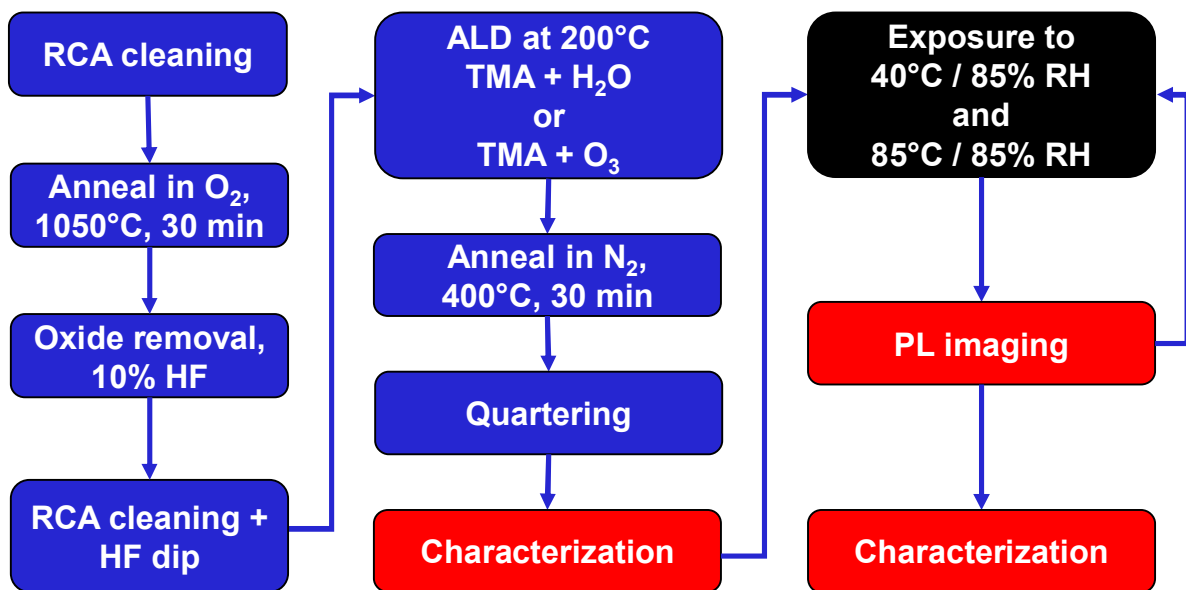


FIGURE 1. Procedure for sample preparation, damp heat exposure, and characterization using PL imaging as well as QSSPC and contactless CV measurements.

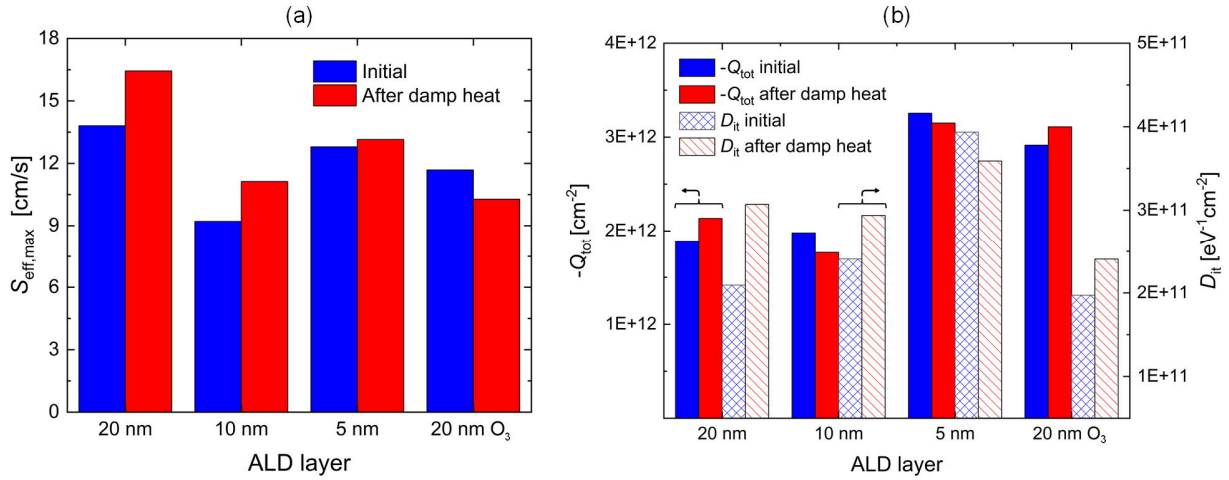


FIGURE 2. (a)  $S_{\text{eff,max}}$ , and (b)  $Q_{\text{tot}}$  and  $D_{\text{it}}$  for all samples before and after exposure to damp heat.

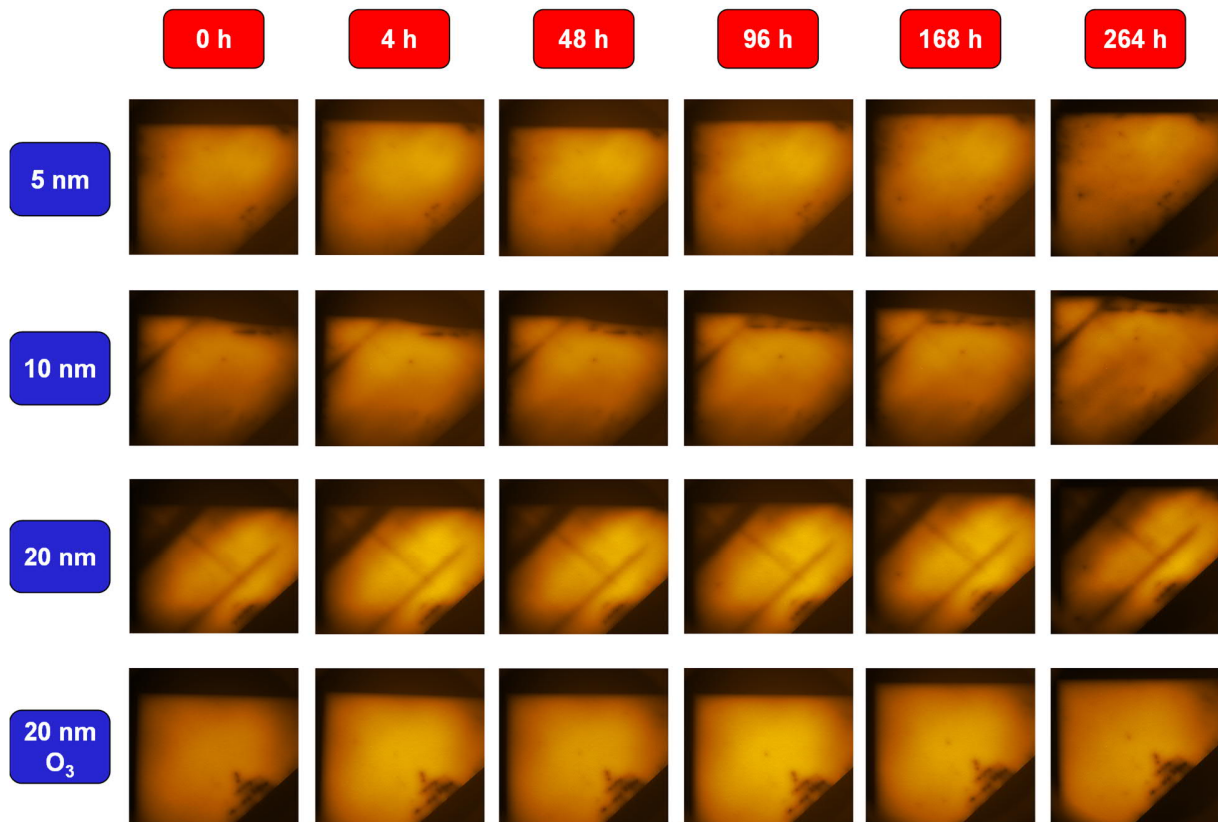
## RESULTS AND DISCUSSION

After the annealing step, the minority charge-carrier lifetime at  $1 \times 10^{16} \text{ cm}^{-3}$  minority carrier density was in the range of 580 to 870  $\mu\text{s}$  for all samples. Figure 2(a) shows  $S_{\text{eff,max}}$  for all samples before and after exposure to damp heat. The  $S_{\text{eff,max}}$  values corresponding to the initial lifetimes were approx. 13 cm/s for the 5 nm, 9 cm/s for the 10 nm, 14 cm/s for the 20 nm and 12 cm/s for the 20 nm O<sub>3</sub> sample. For all samples, the values were in a similar range compared to previous studies on ALD AlO<sub>x</sub>-passivated p-type FZ silicon [5, 23], so efficient surface passivation was confirmed with all film thicknesses and both oxidants. After the 264 h exposure to 85°C/85% RH, the lifetimes were in the order of 490 to 780  $\mu\text{s}$ , which corresponded to approx. 13 cm/s for 5 nm, 11 cm/s for 10 nm, 16 cm/s for 20 nm and 10 cm/s for 20 nm O<sub>3</sub>. For all samples except the 20 nm layer,  $S_{\text{eff,max}}$  was on a similar level before and after the damp heat exposure, so no major degradation of the surface passivation properties was observed. For the 20 nm sample, the reduction of lifetime was approximately 16%, which was in a similar range as reported in [12]. Nevertheless, none of the samples were significantly degraded after the 264 h long damp heat exposure, and  $S_{\text{eff,max}}$  remained at a level that is applicable for solar cells [8].

Figure 2(b) presents the results for  $Q_{\text{tot}}$  and  $D_{\text{it}}$ . Initially,  $Q_{\text{tot}}$  was  $-3.3 \times 10^{12} \text{ cm}^{-2}$  for 5 nm,  $-2.0 \times 10^{12} \text{ cm}^{-2}$  for 10 nm,  $-1.9 \times 10^{12} \text{ cm}^{-2}$  for 20 nm, and  $-2.9 \times 10^{12} \text{ cm}^{-2}$  for the 20 nm O<sub>3</sub> sample, and the film charge remained comparable for all samples before and after the exposure. This does not agree with results previously reported in [12], where the damp heat exposure lead to a reduction of  $Q_{\text{tot}}$  due to the formation of AlO(OH). In this study only minor differences in the  $D_{\text{it}}$  values before and after the damp heat exposure were observed. Initially,  $D_{\text{it}}$  was  $3.9 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$  for 5 nm,  $2.4 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$  for 10 nm,  $2.1 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$  for 20 nm, and  $2.0 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$  for the 20 nm O<sub>3</sub> sample. The  $D_{\text{it}}$  of the 5 nm sample stayed at the initial level after the exposure, while it slightly increased for all the other samples, although none of the changes were high enough to significantly deteriorate the passivation properties. The most pronounced increase occurred for the 20 nm sample (up to  $3.0 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$ ).

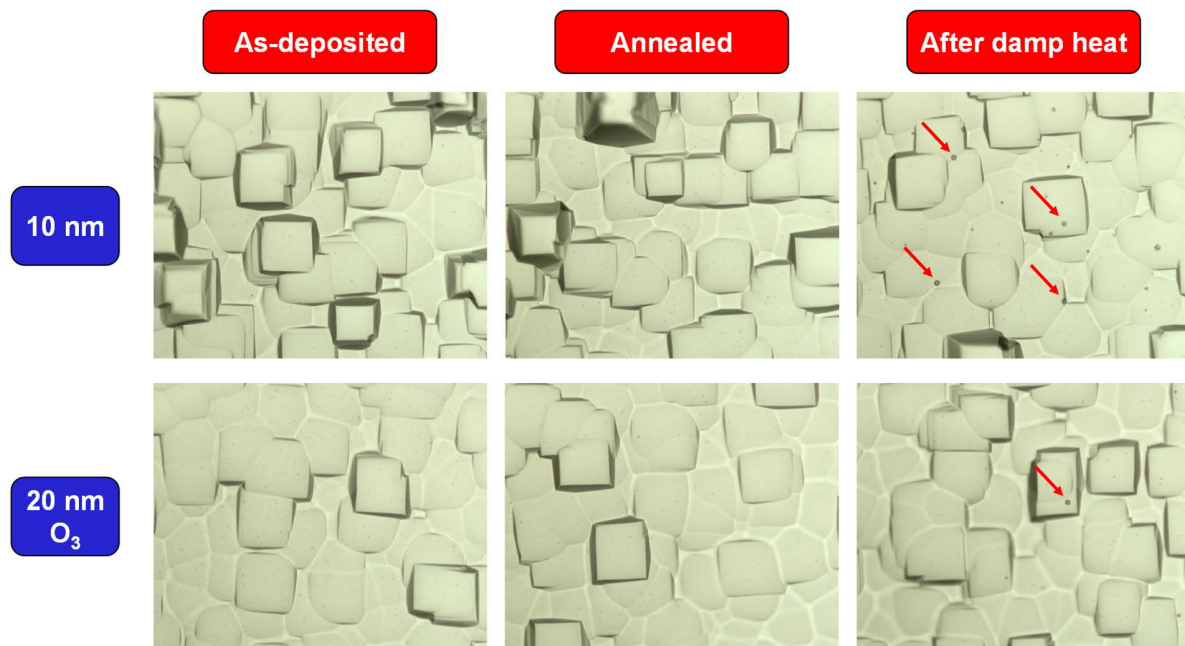
PL imaging was used to study the spatial dependence of the passivation stability at a wafer level to observe whether the passivation performance would degrade uniformly or from point-like defects. PL maps taken before damp heat exposure verified uniform passivation quality, but low-signal areas were observed in all samples. These areas potentially arose from defects in the individual Si wafers or from sample handling during fabrication, which could account for the variance in  $S_{\text{eff,max}}$  between different film thicknesses. Throughout the exposure to the 40°C/85% RH conditions, the intensity of the PL signal remained unchanged for all samples, and no point-like degradation propagating from pinhole defects in the passivation layers was observed. Therefore, the temperature was raised to 85°C while maintaining the relative humidity at 85% in order to accelerate the possible degradation. The same samples were exposed to 85°C/85% RH for an additional 264 hours, and PL images taken at designated intervals are presented in Fig. 3. Again, the intensity of the PL signal for all samples was stable throughout the exposure, with some small local degradation potentially observed after 264 hours. The passivation quality was demonstrated to be stable at the wafer level for the investigated timescales of this work. Nevertheless, 85°C/85% RH conditions were rather harsh for

bare wafers, as these are the conditions usually applied to encapsulated PV modules in accordance with the IEC 61215-1-1 standard.



**FIGURE 3.** PL images of all samples at designated intervals of exposure at 85°C/85% RH. At 0 h, the samples had already been at 40°C/85% RH for 168 hours.

In order to elucidate the potential degradation mechanisms behind the slight increase  $D_{it}$ , optical microscope images were taken from the samples. Figure 4 shows microscope images from 10 nm and 20 nm  $O_3$  samples taken with a 50× magnification as-deposited, annealed, and after exposed to damp heat. The observed surface textures are typical for Si wafers after chemical polishing, and while the surface was not fully planar, the detection of defects at the surface was still possible. In all samples, there were no observable defects on the surface in the as-deposited and annealed states, but after the damp heat exposure clear point-like defects had appeared. All samples made using  $H_2O$  as the oxidant showed multiple defects, while in the 20 nm  $O_3$  sample only singular defects were observed, as highlighted by the red arrows in the figure. As a potential explanation for these observed defects, we hypothesize that the annealing step caused the passivation film on these samples to blister [24, 25], but the scale of the blisters was so small that such features could not have been observed under an optical microscope. During the damp heat exposure, the degradation of the passivation film propagated from the blisters, which was seen as the point-like defects in the passivation film. In the  $AlO_x$  films deposited with  $H_2O$  a significant amount of blistering could have occurred. These blisters exposed the bare Si surface to the gaseous water molecules, which accelerated the degradation process as speculated in [12] by acting as starting points for the point-like degradation. Both thinner passivation films, such as the 5 nm sample in this case, and using  $O_3$  as an oxidant possibly reduced the amount of blistering [25], which would provide better resilience against the damp heat degradation. However, the experiments should be carefully repeated with a larger amount of samples to test the validity of this hypothesis.



**FIGURE 4.** Optical microscope images from the 10 nm and 20 nm  $O_3$  samples as-deposited, annealed, and after exposed to damp heat. While blisters were not visible on the sample surface after annealing, clear point-like defects were visible after damp heat exposure, as highlighted with red arrows.

## CONCLUSIONS

The surface passivation properties of 5, 10, and 20 nm  $AlO_x$  layers were found stable for 264 hours in 85°C/85% RH based on QSSPC and contactless CV measurements as well as PL imaging. No major changes in  $S_{eff,max}$ ,  $Q_{tot}$ ,  $D_{it}$ , or the PL signal were observed after damp heat exposure compared to the initial values. Optical microscope images of the sample surfaces showed point-like defects after the damp heat exposure in all samples, but more defects were observed in samples deposited with  $H_2O$  than with  $O_3$ . Based on this observation, we hypothesized that the amount of blistering influenced the degradation rate of surface passivation under damp heat, but this speculation is not in agreement with previous reports on the damp heat degradation of surface passivation [12]. Therefore, systematic studies on the role of blisters in the degradation of ALD  $AlO_x$  passivation are needed to shed light on the exact degradation mechanisms.

Further interests include the degradation experiments of ultrathin (~2 nm) passivation layers in order to study their stability under high illumination and in damp heat conditions. Degradation studies of similar samples is to be implemented under PV module standard damp heat testing conditions of 85°C/85% RH for 1000 h. The passivation stability of  $AlO_x$  passivation layers deposited on planar and bSi using industrially viable spatial ALD (SALD) will also be investigated.

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