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Effect of substrate pretreatments on the atomic layer deposited Al_2O_3 passivation quality

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The authors show here that the passivation quality of Al_2O_3 is highly sensitive to the surface condition prior to the atomic layer deposition, affecting especially the thermal stability of the film. Pretreatments like diluted HCl bath or preheating at 200 °C both improved significantly the passivation quality and thermal stability of the films. In addition, the authors observed that a thin chemical SiO_2 layer resulting from diluted HCl solves the blistering problem often encountered in H_2O based atomic layer deposited process. Finally, the authors show that the chemical oxide protects the surface from contaminants, enabling long storage times in a dirty ambient between the cleaning and the film deposition. © 2014 American Vacuum Society.
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I. INTRODUCTION

In recent years, Al_2O_3 has been considered as one of the most promising dielectric passivation layers for p- and n-type as well as p+ surfaces.¹ The excellent passivation of Al_2O_3 is based on the combination of a low defect density and a negative fixed charge at the $\text{Si}/\text{Al}_2\text{O}_3$ interface. Moreover, a thin SiO_2 interlayer between the Si substrate and the Al_2O_3 layer was recently found to play a significant role in the surface passivation.²

Conventionally, an HF dip that removes any native or chemical oxide present on the surface is often used before atomic layer deposited (ALD) films. However, recent experiments have shown rather controversial results regarding the effect of hydrophilic (thin SiO_2) or hydrophobic (HF treated) surfaces on the passivation quality and thermal stability of Al_2O_3 films.^{3,4} The differences were explained by the different chemistry used for the formation of the thin SiO_2 interlayer.⁵ Here, we study the possibility to use diluted SC2 treatment (SC2)⁶ as a last cleaning step and compare the results to the standard HF dip. Diluted SC2 solution has many benefits as compared to standard RCA; not only it consumes less expensive chemicals but also results in lower particle levels.⁷

In the industrial batch ALD process, throughput is increased by preheating the samples in a separate furnace prior to the film deposition. However, the effect of preheating on the passivation quality has not been studied before. Similarly, there is no report on the effect of the wafer storage ambient on the passivation quality, which should be of importance to the practical industrial applications. Here, we investigate both issues and find quite surprising results.

In our study, we put special emphasis on the passivation quality after rapid thermal anneal (firing) used in the solar

cell processing as a final step for metal contact formation, since it is often reported to deteriorate the passivation quality of the Al_2O_3 films. As a final step, we study the effect of the above mentioned pretreatments on the blistering of the Al_2O_3 film and discuss the passivation mechanisms in detail.

II. EXPERIMENT

As a first step, the wafer surfaces were RCA cleaned followed by either a modified standard cleaning solution (SC2, $\text{HCl}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$)^{6,7} (SC2) or a dip in HF. The process sequences of this study are shown in Fig. 1. For the wafer storage test, (process sequence A) the samples were kept either in an ISO 5 or in an ISO 8 class cleanroom for a week prior to the ALD deposition.

Surface passivation was done by 20 nm of Al_2O_3 deposited in an industrial batch ALD reactor (Beneq P800) on both sides of p-type Magnetic Czochralski (Double Side Polished, 4 in., $\sim 3 \Omega\cdot\text{cm}$) silicon wafers with oxygen concentration below 10 ppma. Trimethylaluminum (TMA) was used as the aluminum source and the combination of H_2O and O_3 as the oxygen source.⁸ Passivation was activated with a postdeposition anneal at 400 °C for 30 min in N_2 atmosphere. Additionally, some samples went through a firing step in a rapid thermal anneal (RTA) furnace at 800 °C for 3 s after the postdeposition anneal. The actual wafer temperature was measured by a contact thermocouple in the RTA furnace. The influence of a separate preheating step prior to the ALD deposition was evaluated for some of the samples (process sequence B). In this experiment, the samples were heated in 200 °C for 120 min in a special preheating oven. The preheating was followed by direct loading of wafers into the batch ALD reactor, which is kept constantly at the deposition temperature. This method increases the ALD throughput as during the deposition of the wafers, the next batch can be already preheated. The oven was located

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Fig. 1. (Color online) Different process sequences used in the study. (a) The process flow of the storage ambient test and (b) the preheating experiment.

in an ISO 8 class cleanroom (same as the ALD reactor) and could be filled with nitrogen.

Injection level dependent lifetimes were measured with quasisteady state photoconductance (QSSPC, Sinton WCT-120) to evaluate the passivation quality. Ellipsometer (PLASMOS SD 2300) was used to measure the film thicknesses and blistering was studied with an optical microscope.

III. RESULTS AND DISCUSSION

A. Surface cleaning

In the literature, the firing step is considered as a harmful step for the passivation quality for ALD Al₂O₃.^{8–10} In our study, we observe the same phenomenon in the samples that experienced an HF dip before the deposition (Fig. 2). However, in the case of SC2 cleaned samples, the measured lifetime is actually increased after firing resulting in lifetime nearly 3 ms. The thin chemical SiO₂ layer resulting from the diluted SC2 cleaning probably has a similar role as the previously reported ALD grown thin SiO₂ layer.¹ This behavior can be explained, for example, by the hydrogen release from the Al₂O₃/Si interface^{1,11} and/or from the Al₂O₃ film, which can result in blistering^{12,13} as discussed in Sec. III D.

Fig. 2. (Color online) Minority-carrier lifetimes measured at an injection level of $5 \times 10^{15} \text{ cm}^{-3}$. Al₂O₃ was deposited either directly after SC2 or HF dip or after storing the wafers one week in a cleanroom of two different levels.

B. Storage ambient

In the industrial process, wafers sometimes need to be stored in a buffer area after the cleaning process and before the ALD process. It has not been studied before whether the possible contamination build-up during the storage will affect the surface passivation quality. In our study, the wafers were dipped in HF and kept in an ISO 5 or an ISO 8 cleanroom ambient for a week before the film deposition. SC2 cleaned wafers were also stored in ISO 8 cleanroom for a reference purpose.

Figure 2 shows that the storage ambient has a significant effect on the passivation quality in HF-dipped wafers. First, higher lifetimes are reached if the wafers are kept in an ISO 5 class cleanroom before the film deposition. During this time, a native oxide is formed on the wafer surface leading to an improved lifetime. However, storing the samples in a dirtier ambient lowers the lifetime as compared to the same-day deposited samples due to the contamination from the atmosphere. Second, the lifetime of HF dipped samples drops significantly after firing step regardless of the cleanliness of the storage ambient. This is in contrast with the sample that was processed directly after the HF-dip.

A protective thin chemical SiO₂ layer from SC2 cleaning on the surface, on the other hand, has the opposite effect. There was no degradation in the lifetime after storing the wafers in a dirty ambient. Moreover, the firing even increased the lifetime as already shown in Fig. 2. In the industrial production fab, if an HF-dip is a mandatory step before the film deposition, shortening the delay time between cleaning and Al₂O₃ deposition or storing the cleaned wafers in nitrogen is probably needed to avoid the performance decrease.

C. Preheating

Traditional batch ALD tool usually requires quite a long time (2–3 h) to heat up the substrates to the deposition temperature in a vacuum, which is impractical and expensive as compared to the deposition time of 10–20 nm of Al₂O₃ (10–20 min). In order to increase the tool utilization for the film deposition and to fulfill the high throughput requirement

FIG. 3. (Color online) Minority-carrier lifetime measured at an injection level of $5 \times 10^{15} \text{ cm}^{-3}$. Al_2O_3 was deposited either directly after SC2 or HF dip or after the preheating at N_2 or ambient atmosphere.

by the industry, a separate preheating step is performed before loading the substrates into the ALD tool. It is important to understand how the preheating affects the Si/ Al_2O_3 interface and the passivation, as we have seen above that the passivation quality of the ALD film is very surface sensitive.

Figure 3 shows the effect of the preheating steps on the minority carrier lifetime either at N_2 or at ambient atmosphere in an ISO 8 class cleanroom. The preheating does not affect much the postannealed lifetime in samples with SC2 cleaned surface. On the contrary, the lifetime after firing is sensitive to the preheating and the heating needs to be carried out in N_2 atmosphere to maintain high passivation after firing. This behavior can be explained by the fact that O_2 in an ambient atmosphere speeds up the silicon surface oxidation and results in a loss of protective H-termination by the incorporation of the possible contamination from the air.^{14–16}

Interestingly, if the same preheating is carried out for the wafers with SC2 cleaning, the lifetime is increased after firing resulting lifetimes above 3 ms. Thereby, the preheating is not only speeding up the process itself but also enhances the passivation quality. It is also worth to note that in this case N_2 atmosphere is not needed but ambient is enough. This result supports the previous conclusion that the thin chemical SiO_2 layer protects the surface from ambient contamination.

D. Blistering

It is well known that so called blisters (local film delamination from the substrate) can appear in Al_2O_3 films if water is used as an oxidant in the ALD reaction and the film thickness exceeds 10 nm.¹⁷ The blisters are known to deteriorate the surface passivation,¹³ and could therefore explain our lifetime degradation in HF dipped samples after firing as seen in Fig. 2. In our study, the samples were inspected with an optical microscope in order to see if the different pretreatments have any effect on the appearance of the blisters.

Figure 4 shows the microscope images of the selected samples with varying surface pretreatment after postannealing and firing. If the surface experienced an HF-dip before the film deposition, some blisters appeared on the surface [Figs. 4(a) and 4(b)] although the preheating made the blisters much smaller [Fig. 4(b)]. No blisters were observed if SC2 was used as a last step before the film deposition [Figs. 4(c) and 4(d)]. Previously, it has been proposed that blisters form at the interface by gas build-up during annealing.^{12,13,18} Since the ALD growth is strongly dependent on the starting surface, the steady-state growth is obtained faster on the SC2 cleaned as compared to HF dipped Si, where lower reactivity of TMA and longer incubation time has been observed.¹⁹ It is likely that in the case of thin chemical SiO_2 layer resulting from SC2 cleaning, there are less hydrogen residues at the interface, which decreases the amount of released hydrogen thus preventing the blistering.¹⁷

IV. SUMMARY AND CONCLUSIONS

We have studied the thermal stability of the ALD Al_2O_3 thin films with a special emphasis on the substrate cleaning and heating prior to the film deposition. We found that the harmful blisters disappear if we have a thin chemical SiO_2 layer on the silicon surface prior to the ALD process. Moreover, we observed that an industrially viable preheating prior to the ALD process either in N_2 or air greatly improves the firing stability of the Al_2O_3 film. The stability is further improved if the film is deposited on top of the previously mentioned chemical SiO_2 layer.

FIG. 4. (Color online) Optical microscope images of the samples that experienced different surface pretreatments (a) HF dip, (b) HF dip followed by preheating, (c) SC2 cleaning, and (d) SC2 cleaning followed by preheating. All the samples were postannealed and fired.

We also studied the effect of the ambient in which the samples are stored between the surface treatment and the actual film deposition on the surface passivation. In general, we observed that it is critical to deposit the Al_2O_3 film directly after HF dip. However, a thin chemical SiO_2 film was once again found beneficial: even after storage in the dirty ambient (ISO 8) the passivation quality of the Al_2O_3 was found to be excellent.

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