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Ozone-based batch atomic layer deposited Al_2O_3 for effective surface passivation

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Abstract

In this paper we compare water and ozone as oxidants in the Al_2O_3 ALD reaction in terms of surface passivation quality. The experiments show that O_3 produces a high negative charge density up to $7 \cdot 10^{12} \text{ cm}^{-2}$ even in as-deposited film, which is different from water based Al_2O_3 that requires a separate annealing step to activate the negative charge. In general, the ozone process produces lower interface defect density (D_{it}) and higher negative charge density, which contributes to the higher lifetime value than corresponding water process. Most importantly, ozone-based Al_2O_3 shows much better firing stability than water-based Al_2O_3 . Ozone concentration is also shown to play a role in the surface passivation quality. Finally, we found out that inserting a water pulse after the ozone pulse can lower the D_{it} further resulting in even higher lifetime.

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Keywords: Atomic layer deposition; ozone; aluminum oxide; Si surface passivation

1. Introduction

Atomic layer deposited Al_2O_3 has shown excellent passivation performance on c-Si surface [1]. In photovoltaics (PV) water is most often used as an oxidant in ALD process, even though it is well known that ozone-based Al_2O_3 can yield even better passivation performance [2,3]. However, it is known from semiconductor field that batch ALD requires much higher precursor dose than single wafer ALD to achieve short processing time and high-quality film. Thereby, semiconductor industry typically uses very

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high ozone concentration. In PV field, on the other hand, it is unknown how the c-Si surface passivation quality depends on the ozone concentration and whether such high concentrations are actually needed.

Here we study the surface passivation and interface characteristics of ALD Al_2O_3 using ozone as oxidant. We compare the results with pure water process as well as with combination of ozone and water process.

2. Experimental details

The silicon wafers used in the experiments were 4'' DSP magnetic CZ p-type wafers of resistivity $\sim 3 \Omega\text{cm}$ with oxygen concentration below 10 ppma. They were cleaned in a 1 % HF solution for 60 s to remove the native silicon oxide at the surface. Al_2O_3 layers of 20 nm were deposited with Beneq TFS500 batch ALD reactor at 200 °C. TMA was used as Al precursor and three different combinations of oxidants were used *i*) water *ii*) ozone *iii*) ozone + water pulse. Concentrations of ozone were varied according to Table 1, in which ozone concentrations are defined by the ozone molar ratio in the deposition chamber, which represents the real ozone concentration nearby the substrate surface. After ALD the wafers were annealed at 400 °C for 30 min followed by a firing step at 800 °C for 3 s. The lifetimes were measured by Sinton WCT-120 Quasi Steady State Photoconductance (QSSPC) equipment at an injection level of $5 \cdot 10^{15} \text{ cm}^{-3}$. The lifetime measured by QSSPC is an average of a surface area of approximately 20 cm^2 . Microwave photoconductivity measurements were performed to check the homogeneity of the lifetime. The interface characteristics were measured on each lifetime sample by means of Capacitance-Voltage (CV) measurements after evaporation of 200-300 nm of aluminum contacts in order to create MIS capacitances. The measurements were performed at a frequency of 1 MHz with a gate voltage ranging from -6 to +5 volts and the interface defect densities were measured by the Terman method.

Table 1. Conversion table of the O₃ concentrations used

	Concentration 1	Concentration 2
Output O ₃ (g/Nm ³)	48	168
Output O ₃ (wt%)	3.3	11.3
O ₂ flow rate (SLM)	0.25	0.25
N ₂ flow rate (SLM)	0.4	0.4
O ₃ mole ratio* (%)	0.85	2.94
Sample index	1	3
Corresponding samples	O ₃ (1)	O ₃ (2) H ₂ O+ O ₃ (2)

* O₃ mole ratio: $(\text{O}_3 \text{ mole})/(\text{O}_3+\text{O}_2+\text{N}_2)\text{mole} \times 100$

3. Results and discussion

3.1. Passivation studied by lifetime

Figure 1 shows the minority carrier lifetime results after annealing and firing in case of three different precursor sets and two different ozone concentrations. All ozone samples have much higher lifetimes than water samples. Moreover, the lifetime is seen to increase with the ozone concentration, and an addition of water before the ozone pulse can further improve the lifetime. Firing decreases the lifetime in all samples but the trend remains the same. The lifetime values are still relatively high after the firing step, around 2 ms, for the samples prepared from water and ozone. It is important to note that we did not observe any blistering in ozone samples, which is in agreement with the higher lifetime values. On the contrary, blistering was observed on the pure water sample as reported before [4]. Moreover blistering was also observed after annealing of the $\text{H}_2\text{O} + \text{O}_3$ samples but to a lower extent; blister size was smaller and the density was lower than in the case of the pure water sample. It can be seen on Figure 1 that in this case, blistering does not seem to be an important cause of lifetime reduction since the lifetime of the sample processed with the combined mechanism is still over 2 ms.

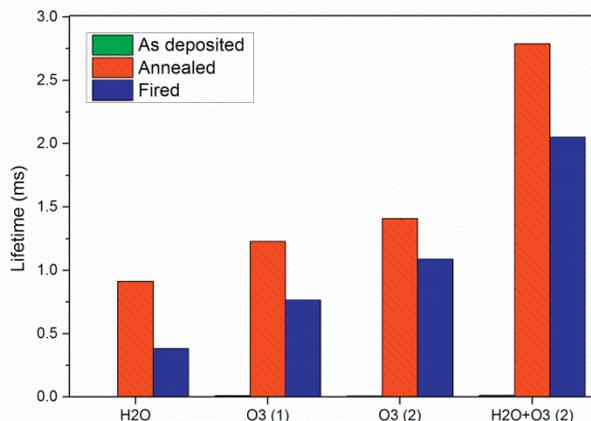


Fig. 1. Lifetime as a function of ALD ozone concentration processed in single wafer (TFS500) tool with three different precursors i) water ii) ozone iii) water+ozone.

3.2. Passivation mechanism studied by CV

Figure 2 shows the interface characteristics of the different samples before and after the heat treatments. The as-deposited charge and defect densities are much higher in the case of ozone than in the case of water. After the annealing step the defect density of the ozone samples decreases drastically while the charge density remains rather stable as it has been reported before [5]. Such values are usually not achievable with water-based ALD deposited at such a low temperature [6], which proves the superior quality of the ozone mechanism. Furthermore the D_{it} values decrease when the ozone concentration increases, suggesting that the quality of the interface is related to the oxidizing power of the oxygen source.

The results after the firing step show that the interface defect density increases and negative charge density decreases, which explains the lower lifetime values obtained after firing. Further investigations are ongoing to study the firing stability of the samples with lower ozone concentration.

Moreover, a clear difference in interface defect density can be observed between the combined H₂O + O₃ sample and the pure ozone samples after annealing, which seems to correlate with the obtained lifetime values. With the combined process, D_{it} values as low as $5 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ can be reached after the annealing while the charge is still high - over $4 \times 10^{12} \text{ cm}^{-2}$. This improvement can be explained by the combination of the two ALD mechanisms. First, the water pulse introduces hydroxyl groups in the layer according to the well-known ALD mechanism [7,8]. As a consequence, these inserted groups improve the interface oxidation during the post-annealing step. They are also likely to be hydrogen sources, which will further improve the passivation of silicon. The subsequent ozone pulse provokes a different mechanism [9] that can improve the interface further by preventing carbon insertion and the formation of metal-metal bonds and thus contributes to the low defect density. From these observations, the D_{it} reduction seems to be a major cause of the lifetime increase with the ozone concentration.

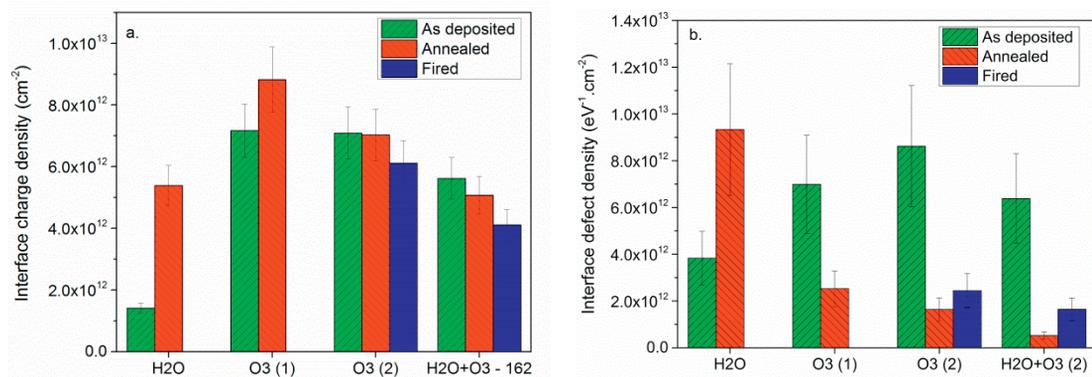


Fig. 2. Measured (a) negative charge density; (b) interface defect density before and after the heat treatments. The numbers 1 and 2 refer to the ozone concentration (see Table 1)

4. Conclusions

We have demonstrated that ozone-based batch ALD Al₂O₃ process can result in excellent surface passivation and has many benefits as compared to corresponding water-based process. The results can be explained by the interface characteristics, i.e. lower interface defect density and high negative charge density. Moreover, ozone concentration turned out to be an important parameter since the passivation could be improved by increasing it by a factor of three.

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