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**Title:** Ozone-Based Atomic Layer Deposition of Al2O3 from Dimethylaluminum Chloride and Its Impact on Silicon Surface Passivation

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**Title: Ozone-based atomic layer deposition of Al₂O₃ from dimethylaluminum chloride and its impact on silicon surface passivation**

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DMACl (dimethylaluminum chloride) as aluminium source has shown promising potential to replace more expensive and commonly used TMA (trimethylaluminum) in semiconductor industry for atomic layer deposited (ALD) thin films. Here we modify the Al₂O₃ DMACl-process by replacing the common ALD oxidant, water, by ozone that offers several benefits including shorter purge time, layer-by-layer growth and improved film adhesion. We show that the introduction of the ozone instead of water increases carbon and chlorine content in the Al₂O₃ while long ozone pulses increase the amount of interfacial hydrogen at silicon surface. These are found to be beneficial effects regarding the surface passivation and thus final device operation. Heat treatments (at 400 °C and 800 °C) are found to be essential for high quality surface passivation similar to ALD Al₂O₃ deposited from conventional precursors, which is correlated with the changes at the interface and related impurity distributions. The optimal deposition temperature is found to be 250 °C, which provides the best chemical passivation after thermal treatments.

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# 1. Introduction

Many semiconductor devices nowadays include highly insulating metal-oxide thin films to allow smaller device dimensions and to prevent e.g. moisture from entering the devices. The metal oxides are also useful in providing a high quality passivation of dangling bonds at the semiconductor surface, which minimizes the recombination of the minority carriers and is therefore beneficial for the semiconductor device operation.[1,2] Such devices include e.g. photodetectors,[3] capacitors,[4,5] solar cells[6] and transistors.[7] The main deposition technology for metal oxides is atomic layer deposition (ALD) as it provides uniform coverage on complex structures combined with a precise control of the film thickness.[8,9] In ALD, high quality semiconductor-grade trimethylaluminum (TMA) is a commonly used aluminium (Al) source, however, in large scale production devices like solar cells and consumer electronics, the price of high-purity TMA may become an issue and therefore a lower grade TMA or even cheaper chemical, dimethylaluminum chloride (DMACl), has become an interesting alternative for the deposition of $Al_2O_3$ films.[10–13]

DMACl is an intermediate product in the TMA synthesis,[14] and is a mixture of two other Al precursors ($AlCl_3$[15,16] and TMA[17]). Therefore, DMACl-based ALD process is likely to show features from its parent compounds, *e.g.* the impact of chlorine (Cl) content in the film. Indeed, the first surface passivation results on DMACl based ALD $Al_2O_3$ have shown a comparable passivation quality and even better thermal stability when compared with that of TMA.[11] The higher thermal stability is likely due to Cl present in the films.[18]

The earlier work on DMACl has been relying on water as an oxidant in the ALD surface reaction. Usually, water is preferred in the ALD process as being harmless, allowing simpler deposition tool and providing a high quality of electrical passivation. However, water-based

ALD processes have been reported to suffer from local film delamination after high temperature heat treatments,[19–21] that is not acceptable for reliable operation of semiconductor devices. Replacing water with ozone as the oxidant, has been shown to suppress such film delamination in TMA-based process.[21,22] Furthermore, the ozone molecule is less sticky than water in the ALD system, thus being easier to purge especially in low temperature applications.[23–25] This decreases the ALD cycle time and results in cost savings. Additionally, ozone has been shown to create a more reactive silicon surface ($SiO_x$ layer) for the following reaction resulting in a layer-by-layer growth during the incubation period of ALD,[26–32] which has become important in the semiconductor industry when reducing the dielectric thickness to less than 10 nm.[18,33] Finally, although some studies show superior quality of ALD films deposited by ozone process with higher smoothness,[34] lower leakage current,[29,35] less defects and smaller flatband voltage shift,[35] there are also contradicting results especially regarding the surface roughness[36] and defect concentrations.[37]

Due to the contradicting results regarding differences of ozone over water in TMA process, it is currently unknown whether DMACl-process would benefit or suffer from the use of ozone. Here we studied the use of ozone as an oxidant in the DMACl based ALD $Al_2O_3$ process. The growth and elemental distributions of $Al_2O_3$ films were studied as a function of ozone pulse length and growth temperature. Furthermore, the impact of the heat treatments on the film properties were explored. Simultaneously, we studied the application of DMACl-ozone $Al_2O_3$ films for silicon surface passivation. Finally we discuss the correlation between the above mentioned film properties and the electrical characterization results describing the passivation quality. The results aim to provide insight in the passivation mechanism and optimal deposition parameters.

## 2. Results and Discussion

### 2.1 DMACl-ozone as an ALD process

In an ALD process the growth per cycle (GPC) is an important parameter describing the growth of the film. If the GPC reaches a constant value after the incubation period of the ALD growth, it is a sign that the growth is pure ALD.[9] In our DMACl-ozone process, such GPC graph measured using ellipsometer is presented in **Figure 1** for samples deposited at 200 °C. From the figure we obtain a saturated GPC value of 0.76 Å/cycle if the ozone pulse time is 7 s or 20 s and we can see that the film growth is constant. Shorter pulse times resulted in non-uniform film thickness, however, the pulse time may be radically reduced using more powerful ozone generator.

The measured GPC is reasonable as compared to typical ALD $Al_2O_3$ processes[13] and only slightly lower than DMACl-water process (1.04 Å/cycle) obtained under the same ALD conditions.[11] When compared to ozone-based ALD processes, the GPC obtained here is comparable with TMA[33] (0.76 Å/cycle at 200 °C) while it is two times higher than that of $AlCl_3$[16] (0.4 Å/cycle at 300 °C). Although a longer ozone pulse in the ALD does not show a clear increase in the GPC, it indeed lead to a better film with a small increase in refractive index from 1.57 to 1.60 as measured in the as-deposited sample.
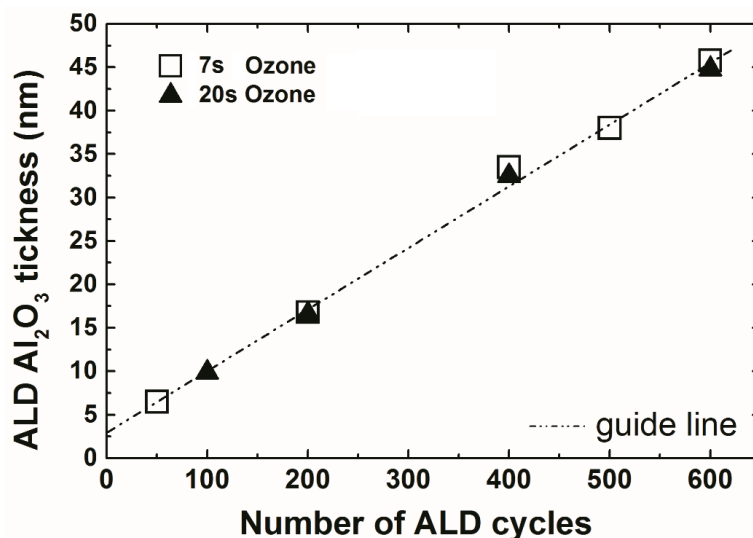
**Figure 1.** A linear growth of Al$_2$O$_3$ film as a function of the number of ALD cycles in DMACl-ozone process. 7 s or 20 s ozone pulse time was used in the ALD at the deposition temperature of 200 °C.

## 2.2. Ozone vs. water in DMACl-based Al$_2$O$_3$ process

Al$_2$O$_3$ films typically contain many impurities in addition to pure aluminum and oxygen. Such impurities may have a significant impact on the electrical film properties, GPC, and in our application, the passivation of silicon surface. **Table 1** compares the measured elemental concentration and impurities present in the DMACl-based Al$_2$O$_3$ film between ozone and water ALD processes. Elemental composition of the films is determined by Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) method.[38] We can see that the ozone-process leads to higher carbon (C) and chlorine (Cl) concentration, which are more than tenfold and threefold, respectively. This is in agreement with earlier reported TMA-ozone ALD Al$_2$O$_3$ films, in which ozone lead to higher C content than corresponding TMA-water process, 1 at.% as compared with 0.2 at.%, respectively.[37]

**Table 1.** A comparison of the elemental concentrations measured in the bulk of the $Al_2O_3$ films between DMACl-ozone and DMACl-water ALD. 400 ALD cycles were deposited at 200 °C.

| ALD recipes | Elemental concentration (atom. %) | | | | |
|---|---|---|---|---|---|
| | H | C | O | Al | Cl |
| DMACl ozone | 4.1±0.4 | 1.4±0.2 | 55±2 | 36±2 | 3.4±0.3 |
| DMACl water[11] | 4.5±0.4 | <0.1 | 57±2 | 37±2 | 1.2±0.1 |

The results are also indirectly supported by ellipsometer and X-ray reflectivity (XRR) measurements, *i.e.* the measured refractive index (1.57) and film mass density (2.8 g/cm$^3$) are lower with ozone process than with water process (1.60 and 3.0 g/cm$^3$, respectively). The higher amount of film impurities indicates that the reaction between DMACl and ozone is less complete than DMACl-water reaction when the same deposition conditions are applied. This may explain the differences observed in GPC. On the other hand, the film adhesion is found to be better with the ozone process, *i.e.* we did not observe any blisters in the DMACl-ozone process after thermal treatments, which is in agreement with the earlier study that showed superiority of ozone over water regarding film delamination (in case of TMA-based process).[22]

**2.3. Effect of thermal treatment**

ALD is considered a low temperature process but often after the film deposition, the sample needs to undergo one or several high temperature process steps in the device fabrication sequence. Sometimes such temperature steps can improve the film quality, sometimes they degrade the film. In case of $Al_2O_3$, the optimal temperature to reach a high level passivation has been around 400 °C.[10] We selected two typical heat treatments, 400 °C and 800 °C referred as LT and HT, respectively, to study their impact on the DMACl-ozone based $Al_2O_3$ films.

We use minority carrier lifetime as a measure for the surface passivation. Typically lifetime values close to milliseconds are needed for efficient semiconductor device operation, see *e.g.* the correlation to solar cell conversion efficiencies in Ref. [10,39]. An additional measure of interface quality includes interface defect density ($D_{it}$), which describes how well the dangling bonds at the interface are passivated and is often called as chemical passivation. $D_{it}$ should be thus minimized and $D_{it}$ values below $1 \times 10^{11}$ eV$^{-1}$cm$^{-2}$ have been reported in case of high quality interfaces.[40] Third electronic parameter that is relevant for the surface passivation is called negative charge density ($Q_f$). It describes how efficiently the minority carriers are pushed away from the surface and thus recombination minimized at the interface. Therefore it is often called as field effect passivation. $Q_f$ should be maximized for the best performance and values above $3 \times 10^{12}$ cm$^{-2}$ are often targeted in thermal ALD process.[40]

**Figure 2** shows that the as-deposited sample presents only a poor passivation (lifetime around 5 µs) due to high $D_{it}$ ($3 \times 10^{12}$ eV$^{-1}$cm$^{-2}$ ) and low $Q_f$ ($2 \times 10^{11}$ cm$^{-2}$) value. The LT improves the passivation, which is typical behavior for ALD Al$_2$O$_3$ films. The HT step, on the other hand, is often found detrimental for such films.[10] In DMACl-ozone process, on the contrary, HT step improves the passivation close to millisecond. CV measurement reveals that the enhancement of passivation results from both better chemical and stronger field effect passivation, which is similar behavior than reported earlier for the DMACl + water process.[11,41] Thus, the qualitative behavior is similar to the water process. The exact values should not be compared yet as we will see they are impacted by the ozone pulse length and deposition temperature.
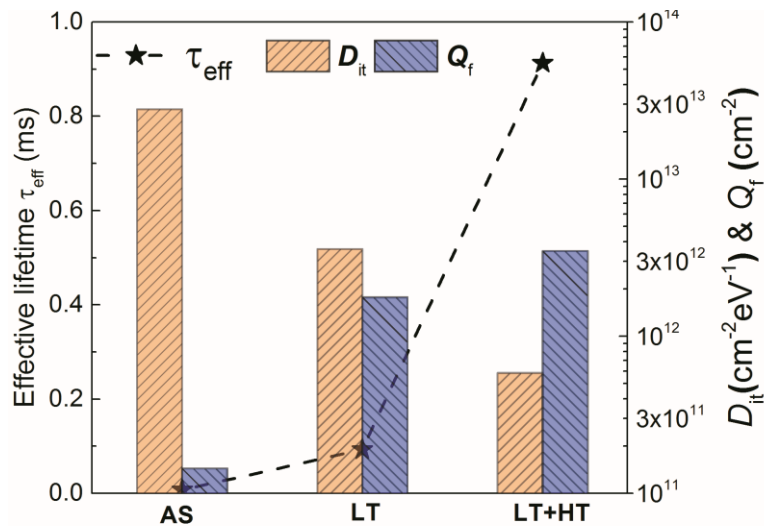
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**Figure 2.** The evolution of passivation quality of ALD Al$_2$O$_3$ film with different thermal treatments. The samples were measured right after ALD (AS), after anneal in N$_2$ at 400 °C for 30 min (LT), and after second anneal at 800 °C for 3 s (LT+HT). 100 ALD cycles were deposited at 200 °C with 7 s ozone and 0.2 s DMACl pulse lengths.

**Figure 3** shows the elemental depth profile of Al$_2$O$_3$ film for as-deposited sample with 7 s ozone pulse (b) and after the heat treatments for both 7 s (c) and 20 s (d) ozone pulse lengths. The main difference between the as-deposited and the heat treated samples is the lower impurity hydrogen and chlorine content after the heat treatment. The chlorine is quite evenly distributed over the film but for hydrogen and carbon some non-homogeneities can be observed. The slightly different measurement parameters used for the samples in Figure 3.b) and d) forbid additional conclusions from the shape of these two depth profiles.
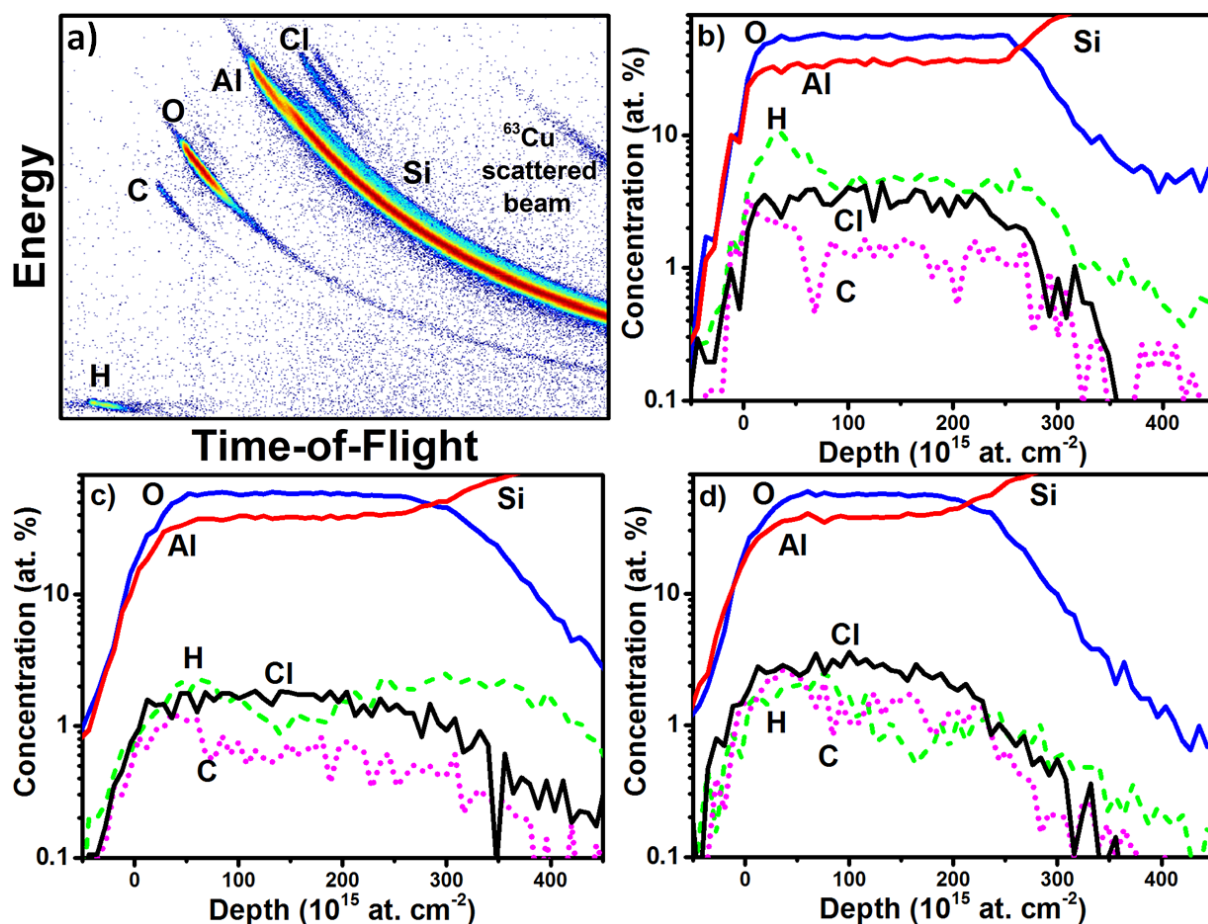
**Figure 3.** In ToF-ERDA measurements different masses can be separated by measuring time-of-flight and energy for each recoil atom in coincidence. Elemental depth profiles of $Al_2O_3$ films: b) as-deposited with 7 s ozone pulse time, c) after LT + HT treatment with 20 s ozone pulse and d) after LT + HT treatment with 7 s ozone pulse. The histogram in a) corresponds to depth profiles in c). The film was deposited at 200 °C with 400 ALD cycles. Note: because of the sectional overlap of Al and Si at the $Si/Al_2O_3$ interface in the histograms, the depth profiles for Al and Si were plotted as one.

## 2.4. Effect of ozone dose in the ALD process

The role of the ozone pulse length in the ALD is studied further in this section to see if it has

impact on passivation and/or elemental distributions. First, **Figure 4** shows the effect of ozone

pulse length on the passivation quality. After bare LT treatment increasing ozone pulse length

up to 20 s improves the passivation quality by providing better chemical passivation as seen

from reduced $D_{it}$ (orange columns). A 40 s ozone pulse time shows no further increase in

passivation due to saturation of the ALD process. After LT + HT treatments the pulse length

does not seem to impact much the chemical passivation but $D_{it}$ remains quite low in all samples

(pink columns). Regarding the field effect passivation ($Q_f$), the pulse length seems not to have

any influence. The HT treatment boosts the $Q_f$ by more than 50% to the level of about $3.4 \times 10^{12}$

$cm^{-2}$ independent on the ozone pulse length. When compared to water-based DMACl process,

the passivation quality is comparable with the ozone process (lifetime in ms range). This also

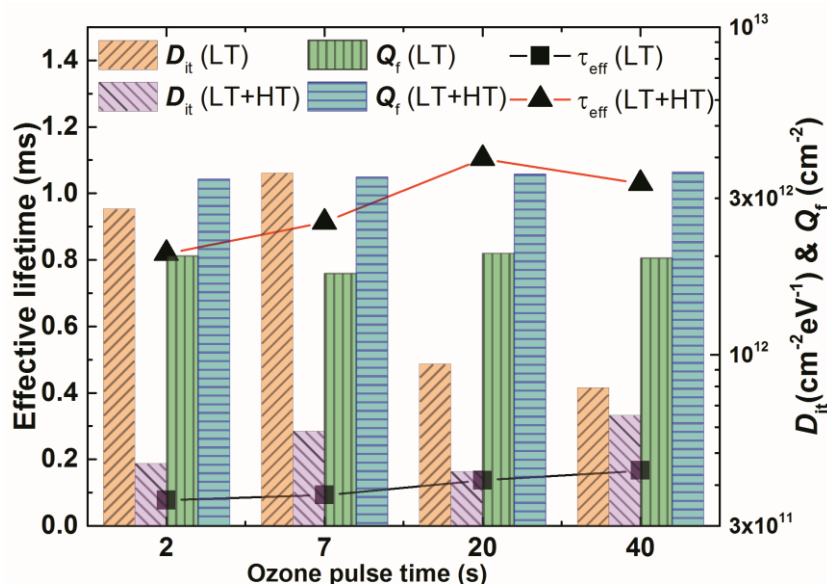applies to $D_{it}$ and $Q_f$ values, especially with 20 s pulse width.



**Figure 4.** Passivation quality of samples deposited using different ozone pulse times. The samples were measured after LT and LT+HT treatments. 100 ALD cycles were deposited at 200 °C. Note the logarithmic scale in y2 axis

Afterwards, the samples with 7 s and 20 s ozone pulse times are selected for element analysis

and the results are presented in Fig. 3c) and d). The stronger hydrogen peak at the interface of

the 20 s sample could be related to the stronger oxidation of silicon surface with longer ozone

pulse time. The role of the hydrogen at the interface will be discussed in chapter **2.6**.

## 2.5. Effect of ALD deposition temperature

ALD deposition temperature is known to have a strong impact on the deposited film properties.

**Figure 5** shows the evolution of surface passivation quality at ALD temperatures ranging from

150 to 300 °C when either LT or both LT and HT heat treatments are performed subsequently. When increasing deposition temperature from 150 to 250 °C, a clear increase in the passivation quality is seen due to the notable reduction of $D_{it}$ and the optimal deposition temperature for DMACl + ozone process is 250 °C. This is slightly higher than the normal passivation temperature reported for TMA (200 °C).[42] The result is in agreement with earlier observations that Cl-based precursors with ozone typically allow higher growth temperatures than water-based ALD.[18] This is because ozone processes do not suffer from the decreasing OH-groups at the reaction surface when increasing the deposition temperature.[18,43]

Similar to the TMA-based thermal ALD $Al_2O_3$ passivation,[42] further increase in ALD temperature to 300 °C will deteriorate the chemical passivation. The reason is believed to be related to a lower amount of hydrogen present in the film and will be discussed later in the paper. Regarding the field effect passivation, increasing temperature in ALD results in slightly lower $Q_f$ at the interface, which can be explained by the shield effect of positively charged interfacial silicon oxide layer formed at higher ALD temperatures.[44] Nevertheless, the decrease in the field effect passivation is rather small. In general, the ALD deposition temperature range between 200 to 250 °C results in the surface passivation quality that is sufficient for most semiconductor devices.
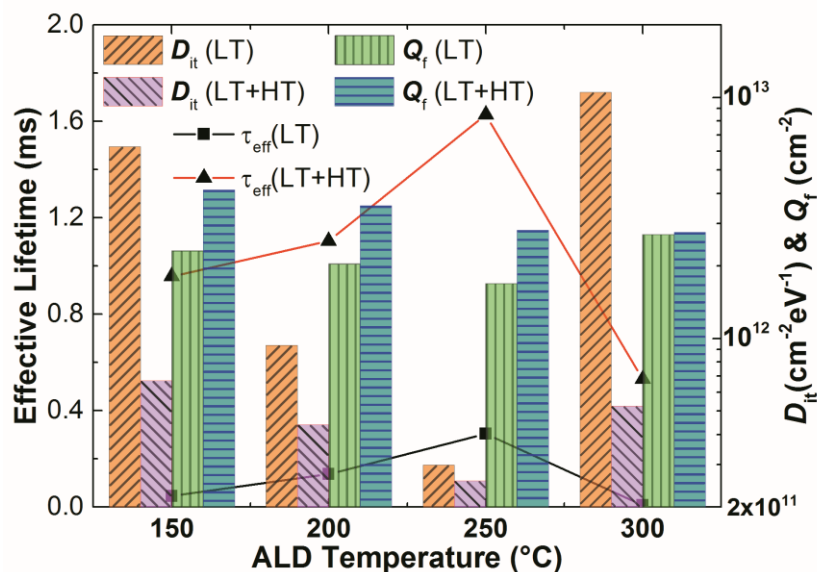
**Figure 5.** Passivation quality of samples deposited at various ALD temperatures. The samples were measured after LT treatment or after LT + HT treatment. All samples experienced 100 ALD cycles with 20 s ozone pulse time.

We also studied the effect of ALD temperature on ALD growth and elemental composition as shown in **Figure 6**. Figure 6a shows that the refractive index (RI) increases continuously with temperature, from 1.56 at 150 °C to more than 1.64 at 350 °C. Similarly, the film density increases from 2.7 g/cm³ at 150 °C to 3.0 g/cm³ at 250 and 300 °C. This increasing film density has a connection to the concentration of impurities, which is in accordance with the results shown in Figure 6.b. Increasing the ALD temperature is thus a straightforward way to improve the DMACl-ozone $Al_2O_3$ refractive index and reduce the impurities in the film. The GPC behavior, on the other hand, is not that straightforward as it has a minimum at 200 °C. The sample deposited at 150 °C has lowest film density and highest impurity level but it results in abnormally high GPC. This is an indication that the surface reaction at lower temperature is just less complete.
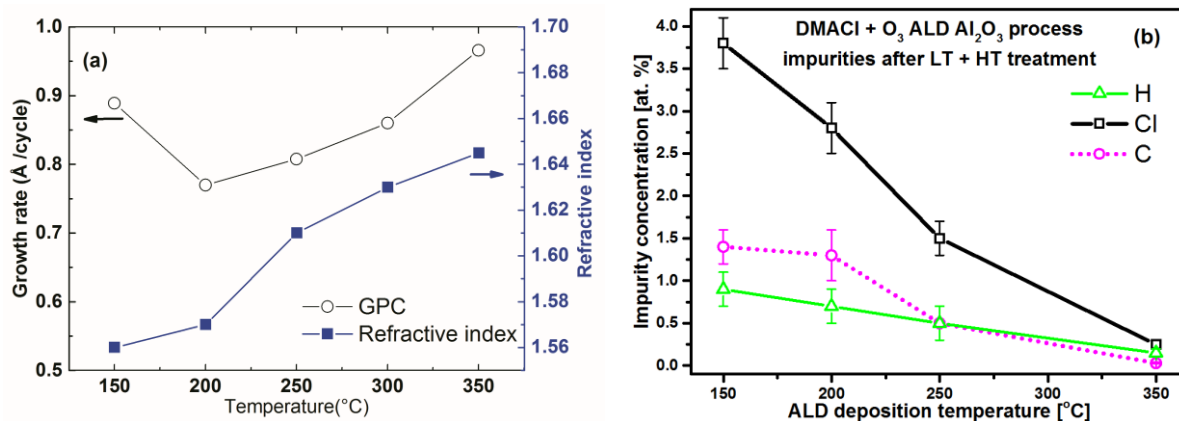
**Figure 6.** Influence of ALD temperature on (a) GPC and refractive index in as-deposited samples (b) impurity (H, C, Cl) concentration measured after LT and HT treatment.

### 2.6 Discussion about the chemical passivation

As mentioned earlier $D_{it}$ is used to quantify the quality of chemical passivation of the silicon surface. Many studies have shown that the chemical passivation, and thus $D_{it}$, is affected by the amount of hydrogen present at the silicon/passivation layer interface. For example, a high quality thermal $SiO_2$ passivation can be further improved by annealing at $H_2$ ambient, which reduces the interface defect density from $1 \times 10^{12}$ cm$^{-2}$ to lower than $10^{10}$ cm$^{-2}$.[45] Regarding thermal ALD $Al_2O_3$ deposited on silicon, a thin interfacial $SiO_x$ is formed during the first cycles of the ALD[10] and it usually has a thickness around ~1-2 nm.[46,47] At this interfacial $SiO_x$ layer the silicon-hydrogen bonds determine the chemical passivation of the $Al_2O_3$ film.[10,41,48,49] Therefore, the elemental profiles and especially hydrogen profiles are valuable in understanding the passivation mechanism provided by DMACl-ozone ALD $Al_2O_3$ process. However, it is good to note that so called hydrogenation usually requires thermal energy to form Si-H bonds. Therefore we cannot compare the H profiles of as-deposited and annealed samples (Figure 3) to make conclusions about chemical passivation.

The XRR analysis made on DMACl-ozone ALD $Al_2O_3$ samples revealed a clear difference in interfacial $SiO_x$ layers between different samples. As the thickness of the $SiO_x$ layer is quite

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thin (0.5- 1.2 nm based on the XRR analysis), it is hard to give exact quantitative values for the thickness and the density. However, it is clear that both the $SiO_x$ layer thickness and the density increased with longer ozone pulse and higher ALD deposition temperature.[28] As the diffusivity of hydrogen in $SiO_2$ is two orders of magnitude higher than that in $Al_2O_3$ at high temperature,[50] hydrogen originating from the $Al_2O_3$ film can diffuse through the oxide layer to the silicon surface, accumulate near the $SiO_x$/Si interface,[32,49,51] and form passivating Si-H bonds to reduce the surface defect density. On the other hand, if the $Al_2O_3$ film is not initially hydrogen-rich, there is not enough hydrogen at the silicon/$SiO_2$ interface after thermal anneal to passivate the dangling bonds. This was the case when the ALD deposition temperature was increased to 350 °C and as a result the passivation suffered from increased $D_{it}$.

While hydrogen may diffuse from the $Al_2O_3$ towards the Si/$SiO_2$ interface during anneal, it may also diffuse out from the film, which is called effusion. From the surface passivation point of view, effusion is an unwanted phenomenon since it reduces the amount of hydrogen at the Si/$SiO_2$ interface and thus reduces chemical passivation. Normally, hydrogen effusion is more severe with lower film density, which was the case in the sample deposited at 150 °C that probably even contained voids.[36] Since the film density increases with ALD deposition temperature and ozone pulse length, $Al_2O_3$ film most likely blocks the effusion of hydrogen during heat treatment in all other samples. This may provide a possible explanation for the hydrogen accumulation at the silicon/$SiO_2$ interface.

## 3. Conclusion

A study on the DMACl and ozone -based ALD $Al_2O_3$ processes and their performance on the passivation of silicon wafer is carried out. The DMACl-ozone process resembles TMA-ozone process in reactant saturation condition, but with slightly lower GPC. Above 200 °C, increasing

ALD growth temperature increases GPC and film density but also lowers the amount of impurities in the $Al_2O_3$. Regarding composition of light elements present in the films, about 4.1% hydrogen and 3.4% chlorine is found in the as-deposited sample grown at 200 °C. Longer ozone pulse time is found to lower the impurity concentration except the hydrogen at the $Si/Al_2O_3$ interface.

Surface passivation quality as a function of heat treatments, ozone pulse time and ALD growth temperature is studied by monitoring the change in the effective lifetime, interface defect density and negative charge density. In the case of DMACl and ozone -based ALD $Al_2O_3$ process a low temperature treatment at 400 °C for 30 min seems not to provide enough thermal energy to activate the passivation while high temperature treatment (800 °C for 3 s) remarkably improved the passivation by lowering the interface defect density and increasing the field effect.

Longer ozone pulse in an ALD is found to have a positive effect on the final passivation quality probably due to higher interfacial hydrogen concentration. The increase of the ALD temperature to 250 °C, is found to lead to better chemical passivation and higher film GPC. In addition, DMACl-ozone process seems to solve the blistering problem of ALD $Al_2O_3$ films during thermal treatments. The obtained results show that DMACl-ozone $Al_2O_3$ process can be used for efficient surface passivation for semiconductor devices.

**4. Experimental Section**

Double side polished 4" p-type semiconductor-grade Magnetic Czochralski-grown silicon wafers with 400 μm thickness, ~3 Ω·cm resistivity and (100) crystal orientation were used as starting material. The first process step was a short dip in a hydrofluoric (HF) acid solution to remove the native oxide. Shortly after the HF-dip, the wafers were loaded into the TFS 500

ALD reactor (Beneq) where $Al_2O_3$ film was deposited on both sides of the wafers. The ozone generator used in the experiments was Modular 4 HC (WEDECO GmbH) with an ozone peak concentration at 168 g/Nm$^3$. The Al precursor, dimethylaluminum chloride $(CH_3)_2AlCl$ (CAS number: 1184-58-3), was purchased from Sigma-Aldrich and it was pulsed into the ALD reactor by its own vapor pressure at 25 °C. The ALD cycle was performed using the following sequence: DMACl (0.2 s) – $N_2$ purge (3 s) – $O_3$ (2-40 s) – $N_2$ purge (5 s). The substrate deposition temperature varied from 150 to 350 °C. In the passivation study 100 ALD cycles were made, which resulted in film thickness of 7 – 8 nm.

In order to study the tolerance of the thin films against the high temperature processes or to activate the passivation, some wafers were annealed in nitrogen ambient at 400 °C for 30 min in a tube furnace. Such relatively low anneal is referred as LT throughout the paper. Some of the wafers were further annealed at high temperature in a Rapid Thermal Anneal (RTA) furnace with a peak temperature of 800 °C for 3 s in nitrogen, where a contact thermocouple was used to monitor the wafer temperature. Such high-temperature process is referred as HT in the paper. The anneal time-temperature profiles were selected to simulate the PECVD $SiN_x$ capping or the contact sintering (400 °C) or the rapid contact firing process through $SiN_x$ (800 °C).

To monitor the surface passivation quality, Quasi-Steady-State Photoconductance Decay (QSSPC) method with a generalized mode was used to measure the effective minority carrier lifetimes ($\tau_{eff}$).[52] The reported values are taken at the injection level of $1\cdot10^{15}$ cm$^{-3}$. It is well known that a high quality surface passivation requires both good chemical and field-effect passivation.[10] These two passivation aspects were characterized quantitatively by so-called interface defect density ($D_{it}$) and interface charge density ($Q_f$), respectively. Such parameters were measured with a corona capacitance-voltage (C-V) measurements by PV-2000 (Semilab).[53] The $D_{it}$ and $Q_f$ values were averaged over five measuring points on one wafer.

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The film thickness was measured by an ellipsometer (Philips Plasmos SD 2300) with 632 nm wavelength. ALD films prepared with different temperatures were measured by X-ray reflectivity (XRR) (Philips X'Pert) method to determine the film mass density. Elemental composition of the films was determined by means of Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) method using 10.2 MeV $^{63}$Cu ion beam from the 1.7 MV Pelletron accelerator of the Accelerator Laboratory of the University of Jyväskylä.[38] This method requires a film thickness greater than 10 nm for obtaining reliable depth profiles. Thus, 400 ALD cycles (~30 nm) were deposited on samples used for elemental analysis. This also has been justified as the film thickness did not influence the passivation quality nor the CV results. Similar thickness independency has been reported earlier for TMA-based ALD processes.

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