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Remote Plasma and Thermal ALD of Al₂O₃ for Trench Capacitor Applications

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Abstract

The remote plasma ALD process of Al₂O₃ from Al(CH₃)₃ and O₂ plasma was characterized and compared to the well established thermal ALD process of Al₂O₃ employing H₂O as the oxidant. The growth per cycle, saturation of the surface reactions and material properties were investigated for substrate temperatures between 25 and 300 °C. It was demonstrated that high-quality films can be obtained for substrate temperatures above 100 °C. For these temperatures the mass densities of the remote plasma ALD films are slightly higher than those of the thermally deposited films. Remote plasma ALD also yields fair material properties below 100 °C at a relatively high growth per cycle and short cycle times. With remote plasma ALD conformal films were achieved in high-aspect ratio structures. Together with the first results on electrical characterization, it was shown that the Al₂O₃ deposited is promising for the application in metal-oxide-semiconductor “trench” capacitors.

Introduction

Al₂O₃ is of interest for a wide range of applications because of its unique material properties. The most commonly investigated application is as a dielectric, for example as a gate oxide in CMOS (1) or a capacitor dielectric in DRAM (2). Al₂O₃ is an interesting material for these applications as it combines a high dielectric constant ($k \sim 8$ -9) with a high band gap (~ 9 eV). These properties make Al₂O₃ also an interesting material as dielectric in high density trench capacitors, e.g., for rf decoupling capacitors integrated in silicon (3,4,5). Additionally, Al₂O₃ attracts interest in emerging research involving organic electrical devices and photovoltaics, e.g., as transparent, high-density moisture permeation barrier for organic light emitting devices (OLEDs) (6,7,8) and as a surface passivation layer on high-efficiency crystalline silicon solar cells (9). Furthermore, Al₂O₃ has excellent mechanical properties and can be used as a wear resistive coating on for example microelectromechanical systems (MEMS) (10).

Critical to all these applications is a deposition technique that is capable of producing high-quality films with low pinhole density and good conformality on substrates with

demanding topology, and which offers precise thickness control even over large-area substrates. Atomic layer deposition (ALD) of Al_2O_3 is a method that has shown great potential to meet these demands. This chemical vapor deposition (CVD) like method is cyclic and based on two separately executed self-limiting half reactions: *i*) chemisorption of the metal precursor and *ii*) oxidation of the metal and removal of the organic surface groups. Thermal ALD of Al_2O_3 using trimethylaluminum ($\text{Al}(\text{CH}_3)_3$) as the metal precursor and H_2O as the oxidant has already been widely investigated and can be considered as a model system for ALD (11). In this process, $\text{Al}(\text{CH}_3)_3$ chemisorbs to surface hydroxyl groups by splitting off gaseous CH_4 . Residual $\text{Al}(\text{CH}_3)_3$ and reaction products are removed by purging and/or pumping and subsequently the $-\text{CH}_3$ ligands of the chemisorbed $\text{Al}(\text{CH}_3)_3$ species are removed by a reaction with H_2O regenerating the surface $-\text{OH}$ groups. To widen the ALD process window, O_2 plasmas and O_3 have recently been considered as alternative oxidants. O_2 plasmas are very effective oxidants that can easily remove organic ligands by O-radical driven combustion-like surface reactions (12). Therefore, the plasma-based process generally yields more process flexibility (13) including the potential of depositing higher quality materials at lower substrate temperatures while also avoiding the use of the difficult to pump H_2O .

In this contribution the remote plasma ALD process of Al_2O_3 is discussed and compared with the thermal process. In remote plasma ALD a plasma source is employed that generates plasma species remotely from the substrate. This prevents severe ion bombardment and therefore the plasma damage that has been reported for direct plasma ALD (14,15). The new Oxford Instruments FlexAL™ ALD tool is used for both the remote plasma and thermal process and the Al_2O_3 is investigated for a wide substrate temperature range. The growth per cycle, material atomic composition, uniformity, conformality, and the electrical properties of the Al_2O_3 are reported. The latter two aspects are important for the envisioned application of the remote plasma ALD Al_2O_3 in metal-oxide-semiconductor (MOS) “trench” capacitors.

Experimental details

ALD reactor and film synthesis

Both the remote plasma and thermal ALD processes of the Al_2O_3 films were carried out in the FlexAL™ ALD tool recently developed by Oxford Instruments Plasma Technology. The system is an advanced research and development reactor equipped with a loadlock and capable of handling wafers up to 200 mm in diameter (16). For remote plasma ALD the system is equipped with an inductively coupled plasma source located above the wafer, that can be isolated from the reactor by a gate valve. The plasma source can be operated with different gases and multiple precursor pods can be connected and used simultaneously. The temperature of the precursor pods, the precursor lines, reactor walls and substrate holder can be individually controlled. Furthermore, the system is equipped with optical viewports that can be used for *in-situ* monitoring of film growth by techniques such as spectroscopic ellipsometry (SE).

For Al_2O_3 ALD, trimethylaluminum [TMA, $\text{Al}(\text{CH}_3)_3$] (Akzo-Nobel, SSG grade) was vaporized at 25 °C and a saturated dose was obtained by 20 ms vapor injection using fast switching ALD valves (Swagelok). For the plasma process, the oxidation step took place via a 400 W O_2 plasma at a pressure of 15 mTorr and ignited for typically 2 s. O_2 also

served as a purge gas because O_2 does not react with $Al(CH_3)_3$; O_2 flow was kept constant at 60 sccm during the entire cycle. A cycle time of 4 s was obtained by employing an $Al(CH_3)_3$ purge of 1.5 s and a post plasma purge of 0.5 s. For thermal ALD, H_2O was vaporized at 25 °C and dosed in steps of at maximum 120 ms. If higher doses were required the 120 ms step was repeated with 0.5 intermediate delays. A 110 sccm Ar flow at a pressure of 15 mTorr was used as purge gas and a pump-purge step (7 s evacuation and 5 s purging) was found most effective in removing residual H_2O from the reactor. Typical cycle times for the thermal ALD process were 16 s although it should be noted that no efforts were undertaken to fully optimize this cycle time. The substrate temperature was varied between 25 and 300 °C. The reactor wall temperature was kept constant at 120 °C, apart from the 25 °C deposition where the wall was kept at 25 °C.

Film analysis and characterization

Si p-type wafers with a diameter up to 200 mm were used as substrates for characterization of the ALD processes and film composition. The center thickness and refractive index of the Al_2O_3 films was monitored *in-situ* by spectroscopic ellipsometry (SE, J.A. Woollam M-2000D, 193 – 1000 nm wavelength range) made in between the ALD cycles. *Ex-situ* measurements with the same ellipsometer were performed to measure the film thickness on any position on the wafer to obtain the non-uniformity of the films as defined by:

$$\text{nonuniformity} = \frac{d_{\max} - d_{\min}}{2d_{\text{average}}}, \quad [1]$$

where $d_{\max}$, $d_{\min}$, and d_{average} are the maximum, minimum, and average thickness respectively. The Al, O, and C-content of the film were determined by Rutherford backscattering spectrometry (RBS). Elastic recoil detection (ERD) was used to determine the H-content. A 2 MeV $^4\text{He}^+$ beam was applied in these measurements. The conformality of the remote plasma ALD process was examined for a 80 nm thick Al_2O_3 film deposited in 2-2.5 μm wide and ~ 20 μm deep silicon macropore structures. After sputtering a 2 nm platinum conductive layer, high-resolution SEM images using a FEI Nova NanoSEM 600 electron microscope revealed the conformality. For electrical characterization of the Al_2O_3 films, the Si substrates were HF-dipped (1% HF solution) prior to deposition to remove the native oxide. Next aluminum electrodes (areas ranging from 0.02 mm^2 to 1.2 mm^2) were sputtered on the Al_2O_3 films using a shadow mask. Both as-deposited and forming gas annealed films (30 min 425 °C, 10% H_2 - 90% N_2) were characterized electrically. The dielectric constant and breakdown voltage of these test structures were determined by 10 kHz *C-V* and *I-V* measurements with an HP4275A multifrequency LCR meter and an Agilent 4155B parameter analyzer.

Results and Discussion

Growth per cycle and saturation

Figure 1 shows an *in-situ* SE measurement of the Al_2O_3 film thickness as a function of the completed number of ALD cycles for both the remote plasma and the thermal ALD process. The substrate temperature was 200 °C. As expected, the thickness increases linearly with completed ALD cycles for both the remote plasma and the thermal ALD process. From these *in-situ* thickness measurements the growth per cycle (GPC) can be determined from a linear fit of the data. Clearly, the growth per cycle is higher for remote plasma ALD than for thermal ALD. The saturation behavior of the oxidation step was investigated for the remote plasma and thermal ALD by considering the GPC as a function of the O_2 plasma exposure time and H_2O dosing time. For remote plasma ALD, the results are shown in Fig. 2 for a substrate temperature of 200 °C. The corresponding non-uniformity of the film thickness over a 150 mm wafer is also given. Figure 2 reveals that surface reactions saturate during the oxidation step when the O_2 plasma exposure time is greater than 1.0 s, with a saturated value of the GPC of 1.2 Å/cycle. For shorter plasma exposure times, the GPC is not saturated and the plasma step becomes a source of film non-uniformity. This can be explained by a shortage of oxidizing plasma species at these short plasma exposure times. The plasma species will be mostly consumed in the center of the substrate where they first hit the substrate surface. If the saturation of the GPC was dominated by slow surface reaction kinetics a good uniformity would also be achieved at plasma exposure times shorter than required for saturation, i.e. gas phase species would have more time to diffuse. A 2 s plasma exposure time was found to yield saturated growth over the whole substrate area for all substrate temperatures investigated between 25 and 300 °C. The non-uniformity determined over 200 mm wafers decreased from 1.2 % at 25 °C to 0.5 % at 300 °C for this setting.

Figure 1. Al_2O_3 film thickness as a function of the number of cycles for both remote plasma ALD and thermal ALD. The thickness was determined by *in-situ* spectroscopic ellipsometry and the growth per cycle was obtained from the linear fits. The substrate temperature was 200 °C.

Figure 3 shows the GPC for the thermal process as a function of water dosing time for substrate temperatures of 100 °C and 200 °C. Different pump and purge steps have been used for the different data points shown in Fig. 3, which can explain the scatter between data points.

Figure 2. The growth per cycle (GPC) and non-uniformity for remote plasma ALD Al_2O_3 as a function of plasma exposure time. The non-uniformity (in %) was determined over a 150 mm wafer. The substrate temperature was 200 °C and a 400 W plasma power was used. The lines serve as a guide to the eye.

Note that the H_2O dosing time required to obtain saturation is significantly larger than the $\text{Al}(\text{CH}_3)_3$ dosing time of 20 ms, even though the delivery details and vapor pressure are similar for both H_2O and $\text{Al}(\text{CH}_3)_3$ (saturated vapor pressure of H_2O and $\text{Al}(\text{CH}_3)_3$ are ~24 Torr and ~16 Torr at 25 °C, respectively). The relatively long time required to achieve saturation of the surface reactions is probably due to slow kinetics of the H_2O half reaction (17), which also explains the high uniformity of the thermal ALD process under all conditions studied. The non-uniformities were <1 % as determined over 200 mm wafers. Another observation was that for shorter cycle times with reduced purging (and pumping) and for high H_2O dosing times (>240 ms), the GPC decreased slightly using the same $\text{Al}(\text{CH}_3)_3$ dose. Usually one expects an increase in growth per cycle due to parasitic chemical vapor deposition (CVD) reactions when there is residual H_2O during $\text{Al}(\text{CH}_3)_3$ dosing. Yet, it can also be that some $\text{Al}(\text{CH}_3)_3$ is consumed by parasitic CVD, at spots within the reactor that are difficult to purge. In the remainder of this work a typical H_2O dosing time of 240 ms was used in the thermal ALD process of Al_2O_3 .

Figure 3. The growth per cycle (GPC) of thermal ALD Al_2O_3 as a function of water dosing time. Data is given for substrate temperatures of 100 °C and 200 °C. The lines serve as a guide to the eye.

Under this condition the GPC appears to be saturated while it also prevents the need for the very long purge times required when using longer H_2O dosing times.

Figure 4 shows the GPC of the remote plasma ALD process measured as a function of substrate temperature between 25 °C and 300 °C. Data are also given for thermal ALD for substrate temperatures of 100, 200, and 300 °C. For remote plasma ALD, the GPC decreases monotonically with increasing substrate temperature from 1.7 Å/cycle at 25 °C to 1.0 Å/cycle at 300 °C. For thermal ALD, a maximum in GPC is observed for 200 °C. At 200 °C the GPC is 1.0 Å/cycle while it is 0.9 Å/cycle and 0.8 Å/cycle at 300 and 100 °C, respectively. Although not apparent from Fig. 3, we found that it was more difficult to reach saturation for the H_2O dose at 100 °C. This can be one of the reasons why the GPC for thermal ALD decreases at lower substrate temperatures. The decrease of the GPC of Al_2O_3 , at increasing substrate temperature for remote plasma and thermal ALD (for substrate temperatures > 200 °C) is in line with observations reported in the literature for thermal ALD (18,11,17) and plasma assisted ALD (19,14,20). This decrease is generally attributed to thermally activated recombination reactions of surface hydroxyl groups (-OH), the so-called dehydroxylation (11,21). Assuming that the reactive Al_2O_3 surface sites created during O_2 plasma exposure are also hydroxyl groups (12), these dehydroxylation reactions can also explain the decrease of the GPC for the remote plasma ALD case. Furthermore, it is important to note that the GPC for the remote plasma ALD process exceeded in all cases that for thermal ALD. Especially at lower temperatures, this effect becomes very apparent. A similar result was reported by Lim *et al.* (19), who compared direct plasma ALD with thermal ALD of Al_2O_3 . It appears that the O_2 plasma is more effective as oxidant than H_2O , especially at low substrate temperatures. At higher temperatures the discrepancy becomes relatively small. This suggests that the GPC becomes dictated by the stability of the hydroxyl groups at the surface at these temperatures.

Figure 4. The growth per cycle (GPC) of Al_2O_3 as a function of substrate temperature for remote plasma and thermal ALD.

Film composition

Figure 5 shows the RBS and ERD results for the remote plasma and thermal ALD films. The mass density, depicted in Fig. 5(a) was calculated from the atomic areal densities and the film thickness determined by SE. The mass density increases from $2.6 \pm 0.1 \text{ g}\cdot\text{cm}^{-3}$ at 25°C to $3.0 \pm 0.1 \text{ g}\cdot\text{cm}^{-3}$ for temperatures higher than 200°C .

The densities obtained with thermal ALD were comparable but always slightly lower than the remote plasma ALD values. Figure 5(b) shows that the ratio of oxygen to aluminum $[\text{O}]/[\text{Al}]$ in the Al_2O_3 films were very similar for the remote plasma ALD and thermal ALD processes. Films deposited at temperatures of 200°C and higher were stoichiometric ($[\text{O}]/[\text{Al}] = 1.5$) whereas the films were oxygen rich at lower temperatures. At 25°C the $[\text{O}]/[\text{Al}]$ ratio was even ~ 2.15 . Figure 5(c) shows that the H-content in the film also increased at lower substrate temperatures. At 300°C the H-content was $\sim 1.4 \text{ at.}\%$ while a value over $15 \text{ at.}\%$ was reached at 25°C . Although within the accuracy of the data, the H-content appears to be slightly higher in the thermal ALD Al_2O_3 films, which is consistent with the slightly lower mass density of these films. The fact that the films increase in O and H-content at low temperatures suggests that a significant amount of hydroxyl groups are incorporated into the film at these temperatures (21). This is observed by the $-\text{OH}$ stretch vibrations observed by infrared transmission spectroscopy in films deposited at 25°C (16). The C-content was below the RBS detection limit of $\sim 1 \text{ at.}\%$ in all cases, with the exception of the film deposited by remote plasma ALD at 25°C which contained $5 \text{ at.}\%$ carbon. Upon doubling the plasma exposure time from 2 s to 4 s for this temperature, the C-content decreased below the detection limit and the film became more stoichiometric and slightly denser (see Fig. 5).

Figure 5. Material composition as a function of substrate temperature. (a) Mass density as determined from Rutherford backscattering spectrometry and ellipsometry; (b) [O]/[Al] ratio as determined from Rutherford backscattering spectrometry; and (c) H-content as determined by elastic recoil detection. For the deposition at 25 °C data is given for both the standard recipe (4 s cycle time, 2 s plasma exposure) and for extended plasma exposure (6 s cycle time, 4 s plasma exposure).

From the aforementioned results, it can be concluded that the material properties of remote plasma and thermal ALD are very similar for substrate temperatures over 100 °C although the remote plasma process yields higher growth per cycle values at reduced cycle times. For low substrate temperatures the discrepancy between remote plasma ALD and thermal ALD becomes more apparent with remote plasma ALD providing the option to deposit Al₂O₃ with fair properties at high growth rates (high growth per cycle with short cycle times).

Conformality and electrical properties

For the application of the Al_2O_3 films in metal-oxide-semiconductor (MOS) “trench” capacitors both the electrical properties and the conformality of the films deposited in high-aspect ratio structures are important. Figure 6 shows a high resolution SEM image of a remote plasma Al_2O_3 -film deposited in 700 cycles at a substrate temperature of 200 °C in a macropore structure with an aspect ratio of ~ 8:1. Arrays of such macropores are used as rf decoupling capacitors integrated in silicon (3). The thickness of the film measured with spectroscopic ellipsometry on the top surface of the wafer was 83 nm. The thicknesses measured with high-resolution SEM at the bottom and sidewall of the macropores was 80 ± 3 nm. The remote plasma is therefore able to deposit conformal films in these high aspect ratio structures. Recombination losses of reactive oxygen species such as O-radicals are apparently not significant which can be understood from a low surface recombination coefficient for these species on oxides.

Preliminary results of the electrical characterization of Al_2O_3 films deposited on planar substrates at a substrate temperature of 200 °C are shown in Fig. 7. In this figure, the equivalent oxide thickness (EOT) values calculated from the C - V measurements are shown as a function of the physical Al_2O_3 film thickness. The EOT increases linearly with the Al_2O_3 -film thickness for both the as-deposited films and the films forming gas annealed at 425 °C. Using the expression

$$\text{EOT} = \frac{C/A}{\epsilon_0 k(\text{SiO}_2)} = \frac{k(\text{SiO}_2)}{k(\text{Al}_2\text{O}_3)} d(\text{Al}_2\text{O}_3) + d(\text{SiO}_2), \quad [2]$$

where C/A is the measured capacity density and ϵ_0 is the vacuum permittivity, the dielectric constant can be determined as $k = 7.8$ and $k = 8.9$ for the as-deposited and annealed Al_2O_3 , respectively. The offset of the linear fit can be most probably attributed to the presence of a ~2.3 nm interfacial SiO_x layer, similar to that found in other plasma assisted ALD studies of Al_2O_3 (9, 22). From I - V measurements, the catastrophic breakdown field was determined to be 9.7 ± 0.5 MV/cm for as-deposited films and 8.4 ± 0.5 MV/cm for the post-deposition annealed films. These electrical properties show that the remote plasma ALD films have potential for application in metal-oxide-semiconductor (MOS) capacitors.

Figure 6. High resolution scanning electron microscope (SEM) images of Al_2O_3 deposited by remote plasma ALD in macropore structures with an aspect ratio of ~8 (diameter: 2-2.5 μm , depth: 19 μm). The Al_2O_3 was deposited using 700 ALD cycles.

Figure 7. Equivalent oxide thickness (EOT) vs. physical thickness of Al₂O₃ films deposited at 200 °C by remote plasma ALD. Both the as-deposited and the annealed (425 °C, forming gas) material are shown.

Conclusions

The deposition of Al₂O₃ by remote plasma atomic layer deposition in the Oxford Instruments FlexALTM reactor was studied and compared with results from thermal ALD in the same reactor. Trimethylaluminum [Al(CH₃)₃] was used as the metal precursor and O₂ plasma and H₂O were used as oxidizing agents for the plasma and thermal process, respectively. For remote plasma ALD with a total cycle time of 4 s, the growth per cycle decreased monotonically with substrate temperature, from 1.7 Å/cycle at 25 °C to 1.0 Å/cycle at 300 °C. This growth per cycle was consistently higher than that obtained for thermal ALD. For the latter a maximum growth per cycle of ~1.0 Å/cycle was found at 200 °C. The film properties investigated were nearly independent of oxidant source for temperatures between 100 and 300 °C, with a slightly higher mass density for the remote plasma ALD Al₂O₃ films. Films deposited at 200 and 300 °C were stoichiometric with a mass density of 3.0 g/cm³ and low C (<1 at.%) and H (<3 at.%) contents. At lower substrate temperatures oxygen-rich films were obtained with a lower mass density and higher H-content. For remote plasma ALD, the Al₂O₃ films were uniform with non-uniformities of <2% over 200 mm diameter substrates. Excellent conformality was obtained for films deposited in macropores with an aspect ratio of ~8 (diameter 2.0-2.5 μm). Preliminary results on electrical properties of remote plasma deposited films showed high dielectric constants of 7.8 and 8.9 for as-deposited and forming gas annealed Al₂O₃, respectively. In combination with the high-breakdown fields obtained, this study revealed that remote plasma ALD Al₂O₃ is a promising candidate for application in metal-oxide-semiconductor (MOS) “trench” capacitors.

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