Comparison between Al₂O₃ thin films grown by ALD using H₂O or O₃ as oxidant source

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Abstract—Alumina (Al₂O₃) thin films have been deposited on silicon substrates by atomic layer deposition at 200°C using TMA as Al precursor and H₂O or O₃ as oxygen precursor. The growth rate has been found to be lower for ozone-based processes as compared to H₂O. The electrical characterization of the deposited layers has shown that when using O₃ the films exhibit larger defect densities as compared to those grown using H₂O, although these show larger trapping. A post deposition anneal process at 650°C has been shown to lower the defect densities, being this annealing more efficient for O₃-grown layers. The effect of post-metallization annealing in forming gas is also investigated.

Keywords: Al₂O₃; ALD; Ozone

I. INTRODUCTION

The continuous miniaturization of complementary metal-oxide-semiconductor (CMOS) technologies has lead to unacceptable tunneling current leakage levels for conventional thermally grown SiO₂ gate dielectrics. As a consequence, there is a need to replace this oxide by a dielectric material that has to fulfil several requirements among them: higher dielectric constant (high-k) than that of SiO₂, so that a thicker layer gives rise to higher gate capacitance, low leakage current, high breakdown field, prevention of dopant diffusion and good thermodynamic stability [1,2].

In addition to the above constraints, the technology used to deposit these layers has to be compatible with CMOS technologies and has to provide excellent thickness control. To this respect, atomic layer deposition (ALD) has been shown to meet most of these demands. This technique relies on a self-limiting film growth process based on sequential saturative surface reactions. An ALD process consists in pulsing first the appropriate precursor gas into the reaction chamber, followed by a purge step with an inert gas so that the excess of precursor and the reaction products are pumped away; next, the second precursor gas is pulsed and finally another purge step is done. This constitutes one cycle of the process and the number of cycles is adjusted to the required film thickness.

Alumina (Al₂O₃) is one of the most extensively studied high-k materials due to its relatively high dielectric constant, high thermal stability and good adhesion to many surfaces. In addition to the use of Al₂O₃ as gate dielectric in MOSFETs [3],

it is also of interest for a wide range of microelectronics applications, such as dynamic random access memories (DRAM) [4], organic light emitting devices [5], silicon solar cells [6], or microelectromechanical systems [7].

The ALD deposition of alumina is usually carried out at low temperatures (<300°C) by means of Trimethylaluminium (TMA) as Al precursor and H₂O as oxygen precursor [8]. The electrical characteristics of the as-deposited layers exhibit large negative fixed charge and interface state densities and charge trapping, although these characteristics can be improved by including an intermediate oxide between the high-k layer and the silicon substrate or by high-temperature post-deposition processes. Since OH radicals give rise to interface states and defects in the films, the use of an oxygen source such as O₃ has been shown to improve the characteristics of as-deposited layers [9, 10]. In addition, graphene devices with a gate dielectric of Al₂O₃, deposited with TMA and O₃, have been reported [11], since this precursor makes the deposition on graphene conformal, i.e., there is not a selective deposition of Al₂O₃ along the steps edges obtained when using H₂O.

In this work we report on the growth of thin layers of Al₂O₃ deposited by ALD on silicon substrates, using H₂O and O₃ as oxygen source. Comparison of the electrical characteristics of the layers is carried out through MIS capacitor test structures and the effect of post-deposition thermal treatments is studied.

II. EXPERIMENTAL

A. Atomic Layer Deposition Process

The studied Al₂O₃ layers were grown by Atomic Layer Deposition in a Cambridge NanoTech Savannah 200 system, equipped with TMA, H₂O and O₃ as oxygen precursors, and N₂ as carrier and purge gas. The ALD process was done at 200°C with a base pressure of 300 mTorr. The ALD cycle consisted of: (1) oxygen precursor injection (15 ms for H₂O and 200 ms for O₃); (2) N₂ purge (5 s for H₂O and 9 s for O₃); (3) TMA injection (50 ms); and (4) N₂ purge (5 s).

The deposition of Al₂O₃ has been carried out on p-type (100) silicon with 0.1-1.4 Ω·cm resistivity. Prior to deposition, the silicon samples were cleaned in a H₂SO₄ + H₂O₂ solution, followed by an HF dip, deionized water rinse and nitrogen blow dry.

Figure 1. Thickness of Al_2O_3 grown on silicon v. number of ALD cycles for processes with H_2O or O_3 as oxygen precursor.

This cleaning sequence was done just before transferring the samples into the ALD reactor; therefore the deposition was performed on a hydrogen-terminated silicon surface.

In order to obtain the growth characteristics of the deposition, a set of ALD processes has been carried out varying the number of ALD cycles from 10 to 400. The deposited Al_2O_3 layer thickness was measured by means of a Rudolph Research Auto EL ellipsometer.

B. MIS capacitors fabrication

The fabrication process of the MIS capacitors started with standard wafer cleaning followed by a wet thermal oxidation process at 1100°C leading to a 400 nm-thick SiO_2 layer. This field oxide was patterned by photolithography and wet etching. Immediately after cleaning in $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ and a dip in $\text{HF}(5\%)$, the deposition of the Al_2O_3 layer by an ALD process of 100 cycles at 200°C was carried out. After growth of the dielectric film, some samples underwent a post-deposition anneal (PDA) at 650°C in N_2 atmosphere for 30 min. Next a 500 nm-thick $\text{Al}/0.5\%\text{Cu}$ layer was deposited that constitutes the metal gate of the MIS structure. After patterning the metal layer by photolithography and wet etching, the back of the wafers was also metalized with aluminum for electrically contacting the silicon substrate. Finally the wafers underwent a post-metallization annealing (PMA) in forming gas ($\text{N}_2/(10\%)\text{H}_2$) at 350°C for 20 min. The fabricated MIS structures are square-shaped with four different surface areas ranging from $2.304 \times 10^{-3} \text{ cm}^2$ to $6.4 \times 10^{-5} \text{ cm}^2$.

C. Electrical Characterization

The study of the electrical characteristics of the different MIS structures has been carried out through the measurement of high-frequency capacitance-voltage (C-V) performed at room temperature in a light-proof, electrically shielded probe station. C-V curves of MIS capacitors with a surface area of $2.304 \times 10^{-3} \text{ cm}^2$ were measured at a frequency of 100 kHz using a HP4192-A Impedance Analyzer in the parallel configuration. The stair sweep voltage was 0.05 V and the a.c signal voltage was 0.03 V. In order to evaluate the hysteresis

Figure 2. ToF-SIMS data corresponding to negative ions of AlO , Si , SiO_2 and C . The results for two samples of ALD Al_2O_3 grown on silicon are compared: H_2O (dashed line) and O_3 (solid line) as oxygen precursor.

the voltage was swept from inversion to accumulation and then back from accumulation to inversion.

III. RESULTS AND DISCUSSION

A. ALD growth

The experimental data of the thickness of Al_2O_3 layers grown by ALD at 200°C are shown in Fig. 1. A linear dependence of the layer thickness on the number of ALD cycles is obtained for both oxidant sources. From the slope of the linear fitting of the experimental data the growth-per-cycle (GPC) is obtained, resulting in GPC values of 0.11 nm/cy for H_2O and 0.08 nm/cy when using O_3 . This indicates a faster Al_2O_3 deposition for H_2O than for O_3 , in accordance to previously reported ALD results [11, 12]. It should be noted that if there exist an interfacial layer of SiO_2 between the Al_2O_3 film and the silicon substrate, ellipsometry measurements will yield the total dielectric thickness since both materials in their amorphous phase have a similar optical constant. An estimate of the thickness of the interfacial layer can be obtained from the linear fitting of the experimental data in Fig. 1, which results in 0.5 and 1.5 nm for H_2O and O_3 samples, respectively.

In order to analyze the composition of the as-deposited films, time-of-flight secondary-ion-mass spectroscopy (ToF-SIMS) was carried out with an Ion-ToF IV on two samples of as-deposited Al_2O_3 on silicon for an ALD process of 100 cycles, using either H_2O or O_3 as oxygen source. Depth profiling was obtained by sputtering with a Cs beam, starting on the Al_2O_3 surface. Since ToF-SIMS signals were taken under identical system conditions for both samples, the results for the same element on each sample are comparable. The obtained negative ions signals of interest are shown in Fig. 2, indicating that at the interface no significant differences exist between processes made by means of H_2O or O_3 . Contrary to the reported analysis for annealed ALD Al_2O_3 layers [13], in our case as-deposited layers grown using O_3 exhibit a higher C concentration than those grown with H_2O as oxygen source.

TABLE I

Parameter	ALD Process: TMA+H ₂ O				ALD Process: TMA+O ₃			
	As-deposited	PMA	PDA	PDA+PMA	As-deposited	PMA	PDA	PDA+PMA
T _{ox} (nm)	11.8	-	12	-	10.7	-	11	-
EOT (nm)	6.8	6.8	7.3	7.3	6.4	6.5	6.9	6.8
V _{fb} (V)	0.273	-0.269	-0.450	0.415	0.703	0.083	-0.572	0.519
V _h (V)	0.691	0.024	0.071	-0.004	0.161	-0.004	0.061	-0.005

B. Electrical characteristics

The measured C-V curves were used to extract a set of electrical parameters characterizing the Al₂O₃ layer depending

on the processing conditions. From the capacitance of the MIS structure at the maximum gate voltage in accumulation the Equivalent Oxide Thickness (EOT) was obtained, the flat-band voltage (V_{fb}) was determined using the standard method, and the hysteresis voltage (V_h) was defined as the voltage separation at the flat-band condition between the double-sweep curves.

Fig. 3 shows an example of the normalized C-V curves obtained for as-deposited layers using H₂O and O₃, as oxygen source, for both before and after the PMA was done. The extracted values for the electrical parameters are given in Table I. When comparing the results for as-deposited layers, i.e. before the PMA was carried out, two clear differences are observed depending on the oxygen source used in the ALD process. The one with O₃ shows a hump in the C-V characteristics indicating a large density of interface states, whereas the layer grown with H₂O exhibits a larger hysteresis than the first. As indicated in Fig. 3, both types of layers exhibit counter-clockwise hysteresis which is a consequence of charge trapping [4]. Although these results cannot be used to measure the trapping since the magnitude of the voltage shift is dependent on the sweep rate relative to the trapping-detraping time constants [14], the difference in V_h does indicate that larger trapping occurs in H₂O-based layers. In Fig. 4 the results obtained after the PMA process are also given, which show how this process in a H-containing ambient anneals out the interface states in the case of O₃ samples and also the trapping in both types of Al₂O₃.

From the results of EOT and the physical dielectric thickness, T_{ox}, as measured by ellipsometry (see Table I), the extracted values for the relative dielectric constant are 6.5 and 6.8, for O₃ and H₂O, respectively.

The measured flat-band voltages indicate that a rather large negative fixed charge exists in the dielectric. In order to estimate the density of fixed charge located at the dielectric-silicon interface, the experimental values are compared to those corresponding to an ideal MIS structure. This simplified analysis gives negative charge densities larger for Al₂O₃ when grown with O₃ than when using H₂O. As shown in Fig. 5, the PMA process gives rise to a reduction in fixed charge densities for both types of layers.

With respect to the effect of the post-deposition high temperature process in N₂ atmosphere, the results obtained

from C-V measurements (Table I) indicate that, when comparing with as-deposited layers, an increase of EOT of 0.5 nm is obtained for both types of layers.

Figure 3. Normalized capacitance v. voltage characteristics for MIS at 100 kHz with as-deposited Al₂O₃ grown with ALD using H₂O or O₃ as oxygen precursor and with (w.) or without (w/o) post-metallization anneal.

The PDA process anneals out the high-density of interface states exhibited by as-deposited O₃ samples, and lowers the density of slow traps and the fixed charge density for both types of ALD processes, as indicated by the reduction in hysteresis voltage and the negative shift of flat-band voltage, although the reduction is more effective in the case of using O₃.

Figure 4. Hysteresis voltage measured from C-V characteristics at 100 kHz, depending on the oxygen precursor and on the post-deposition processes.

Figure 5. Fixed charge density obtained from C-V measurements depending on the oxygen precursor and on the post-deposition processes.

When these PDA samples undergo a post-metallization annealing in forming-gas (PMA) a different behavior is observed as compared to the effect of PMA on as-deposited layers. Although the hysteresis is also reduced to negligible values [15], the flat-band voltage shifts to positive voltages, i.e., there is an increase in fixed charge density to values similar to those of the samples when as-deposited. This effect is analogous to the one reported for ALD deposited HfO₂ layers [16] in which a forming-gas anneal after deposition led also to a positive shift of V_{fb} and was found to be due to a displacement of defects from the bulk of the dielectric layer to the interface. In the present study, however this shift is only observed after the samples undergo a PDA process. The reason for this different effect depending on the temperature and the ambient used in the post-deposition treatment is unclear.

In summary, the electrical characterization of MIS capacitors with Al₂O₃ ALD layers deposited at 200°C using TMA as Al precursor and H₂O or O₃ as oxygen source, has shown that the hysteresis present in the as-deposited layers is significantly reduced after the studied thermal treatments. However, in terms of effective trapped charges densities, the impact of a post-deposition and/or a post-metallization anneal suggests a more complex relation between these different thermal processes and the involved layers and ambients.

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