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Dielectric Properties of Thermal and Plasma-Assisted Atomic Layer Deposited Al_2O_3 Thin Films

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A comparative electrical characterization study of aluminum oxide (Al_2O_3) deposited by thermal and plasma-assisted atomic layer depositions (ALDs) in a single reactor is presented. Capacitance and leakage current measurements show that the Al_2O_3 deposited by the plasma-assisted ALD shows excellent dielectric properties, such as better interfaces with silicon, lower oxide trap charges, higher tunnel barrier with aluminum electrode, and better dielectric permittivity ($k = 8.8$), than the thermal ALD Al_2O_3 . Remarkably, the plasma-assisted ALD Al_2O_3 films exhibit more negative fixed oxide charge density than the thermal ALD Al_2O_3 layers. In addition, it is shown that plasma-assisted ALD Al_2O_3 exhibits negligible trap-assisted (Poole-Frenkel) conduction unlike the thermal ALD Al_2O_3 films, resulting in higher breakdown electric fields than the thermal ALD prepared films.

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Among various metal oxides with medium dielectric permittivity, Al_2O_3 has been proposed as a promising and reliable candidate as an initial replacement for the conventional silicon oxide (SiO_2) as a gate oxide material in metal-oxide-semiconductor transistors because of its higher dielectric permittivity of ~ 8 – 9 , low leakage current level, and high breakdown electric fields due to its large bandgap (8.8 eV).^{1–3} Al_2O_3 is known for its large band-offset with silicon, which is crucial for achieving low leakage currents through the devices.⁴ Moreover, Al_2O_3 has an excellent thermal and chemical stabilities, for instance, it remains amorphous until temperatures above 800°C.⁵ Upon using atomic layer deposition (ALD), reactive chemistries can be used which ensure very good chemisorption and growth behavior on various substrates at low deposition temperatures.³ It has been reported that Al_2O_3 can be deposited on silicon with very small interfacial oxide layer thickness compared to other high- k oxides,⁶ which makes it useful as an oxidation-barrier for the ALD processing of other high- k layers as well.⁷ More than as a gate oxide, Al_2O_3 is an important material for numerous application domains, for instance, to enhance the quantum efficiency of silicon in metal-insulator-semiconductor devices,^{8,9} to encapsulate materials and devices that are sensitive to environments such as humidity, to enhance the Q -factor of silicon cantilevers,^{10,11} to enable functionalization on hydrophobic graphene and carbon nanotube surfaces for the applications in nanoelectronics,^{12,13} and to passivate surfaces of silicon solar cells.¹⁴ Remarkable about ALD processed Al_2O_3 is that the oxide can contain intrinsic negative fixed oxide charges¹⁴ that are beneficial for the applications in charge-trap flash memory devices¹⁵ and, in particular, high-efficiency silicon solar cells.^{16,17} With the added value of ALD achieving good conformality in the high aspect-ratio features, high capacitance density metal-insulator-metal (MIM) capacitors have been realized for the integration of passive elements.^{18,19}

In this paper, we compare the dielectric properties of Al_2O_3 deposited with the thermal and plasma-assisted ALD techniques in a single reactor chamber by fabricating metal-insulator-silicon (MIS) devices. This allows us to compare between the thermal and plasma-assisted Al_2O_3 films independent of the possible variations in the deposition conditions of different reactors. The major difference in the processing of the films with these techniques is that in the thermal ALD, H_2O is employed as the oxidizing agent, while in plasma-

assisted ALD, a remote O_2 plasma is used. In such a remote plasma, O_2 is decomposed into oxygen radicals, which are known to be very efficient in oxidizing the aluminum atoms and the organic ligands of the chemisorbed precursor molecules.²⁰ Here we report that this results in unique electrical properties of the plasma-assisted ALD Al_2O_3 over the thermal ALD Al_2O_3 , such as enhanced tunnel barrier heights and correspondingly low leakage currents and very low trap densities, as revealed in capacitance–voltage (C – V) and current–voltage (I – V) measurements. It is also remarkable that the plasma-assisted ALD Al_2O_3 films exhibit a higher negative fixed oxide charge density than the thermal ALD Al_2O_3 layers.

Experimental

Al_2O_3 thin films of thicknesses ranging from 5 to 80 nm were deposited on HF-last (hydrogen fluoride) p-type 150 mm silicon wafers (with resistivity 3–10 Ω cm) in a FlexAl ALD reactor from Oxford Instruments (Oxfordshire, UK) in the remote plasma and thermal mode. The precursor used for the Al_2O_3 deposition was trimethylaluminum [TMA, $\text{Al}(\text{CH}_3)_3$, Akzo-Nobel (Amersfoort, Netherlands), selective semiconductor grade] which was vapor-drawn at room temperature. Using fast switching ALD valves, a saturated precursor dose was obtained by a 20 ms vapor injection. For the plasma process, the oxidation step took place using a 400 W O_2 plasma at 15 mTorr ignited for a duration of typically 2 s. The O_2 also served as a purge gas because there was no indication that the O_2 does react with $\text{Al}(\text{CH}_3)_3$ under the specific operation conditions used in the current work. The O_2 flow was kept constant at 60 sccm during the entire cycle. A cycle time of 4 s was obtained by employing a TMA purge of 1.5 s and a postplasma-purge of 0.5 s. For the thermal ALD, H_2O was vapor-drawn at room temperature and dosed in steps of at maximum 120 ms. A 110 sccm Ar flow (at 15 mTorr) was used as a purge gas and a pump–purge step (7 s evacuation and 5 s purging) was found most effective in removing the residual H_2O from the reactor. Typical cycle times for the thermal ALD process were 16 s. The substrate temperature was kept constant at 300°C for both the remote plasma ALD and the thermal ALD. During the ALD growth, film thickness measurements were carried out by in situ spectroscopic ellipsometry, employing a model-based analysis in which the standard Cauchy relationship is used to describe the dispersion of the refractive index of Al_2O_3 .²¹ A detailed description of the material properties of the deposited films has been reported elsewhere.²² Furthermore, we want to note that the O_2 plasma properties and the plasma-assisted ALD process of Al_2O_3 have extensively been characterized in previous work.²³

Annealing of the Al_2O_3 films was done at 450°C in forming gas (10% H_2 and 90% N_2) for 30 min prior to the metal electrode depo-

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Figure 1. (Color online) C - V characteristics of $\text{Al}/\text{Al}_2\text{O}_3/\text{Si}$ devices with (a) an as-deposited thermal ALD film, (b) an annealed thermal ALD film, (c) an as-deposited plasma-assisted ALD film, and (d) an annealed plasma-assisted ALD film.

sition. A 500 nm thick aluminum layer was sputter deposited on top of these thin films as an electrode material through a shadow mask to form $\text{Al}/\text{Al}_2\text{O}_3/\text{Si}$ MIS capacitor test devices. Primarily two techniques were used for the electrical characterization of the capacitors, namely C - V measurements using an HP (Houston, Texas) multifrequency LCR meter and I - V measurements with an Agilent 4155C (Lexington, USA) semiconductor parameter analyzer. Capacitance measurements were done at 10 kHz (50 mV) ac modulation. The devices used for the electrical measurements had an electrode area of $100\ \mu\text{m} \times 100\ \mu\text{m}$.

Results and Discussion

Figure 1 shows the C - V characteristics of the capacitors with 10 nm thick films of (Fig. 1a) as-deposited thermal ALD Al_2O_3 , (Fig. 1b) annealed thermal ALD Al_2O_3 , (Fig. 1c) as-deposited plasma-assisted ALD Al_2O_3 , and (Fig. 1d) annealed plasma-assisted ALD Al_2O_3 . In both the thermal ALD and plasma-assisted ALD cases, forming gas annealing (FGA) appears to have a considerable influence on the device properties. The as-deposited thermal ALD Al_2O_3 films exhibit poor C - V curves with shoulders that correspond to interface states due to the defects such as Si dangling bonds at the $\text{Al}_2\text{O}_3/\text{Si}$ interface.²⁴ These characteristic bumps are seen both in forward and reverse sweeps, indicating that the trap density is comparatively larger in these films. The curves exhibit a hysteresis of ~ 0.3 V and a large flatband voltage shift, indicating that the oxide contains a significant number of mobile charges (such as oxygen vacancies and ions diffused into the oxide layer from the ambient). Upon FGA, the flatband shift and hysteresis are reduced (< 0.2 V) and the capacitance at accumulation condition has been enhanced by 23%. The reverse characteristic shows a smoother behavior as well, although the stretch out is still very significant. This indicates that the traps are still present but could be partially filled in the forward sweep and captured there, resulting in a smaller hysteresis.

The as-deposited plasma-assisted ALD films show better C - V characteristics compared with the thermal ALD films. These films also exhibit interface states, but unlike the thermal ALD films, they do not show characteristic bumps due to the trap levels in depletion, indicating that the oxide-silicon interface does not trap a significant number of charges. Upon FGA, the C - V curves become much smoother and no interface states are observed anymore. Upon FGA, two competing processes can occur in terms of the thickness of the

Figure 2. (Color online) EOT vs physical thickness of Al_2O_3 films deposited by (a) thermal ALD and (b) plasma-assisted ALD.

films: a slight reduction in the thickness due to further densification and a slight increase in the thickness due to passivation of the defect by the incorporation of nitrogen or hydrogen atoms. The saturation capacitance of the thermal ALD films increases by approximately 4%, which could be due to a slight densification of the film during FGA. Conversely, the as-deposited plasma-assisted ALD films are already denser than the thermal ALD films, as has been reported before.^{22,25} Therefore, the dominating effect should be a minor swelling of the films, resulting in a slight reduction in the saturation capacitance upon FGA, as shown in Fig. 1.

Figure 2 depicts the equivalent oxide thickness (EOT) calculated for films with different thicknesses deposited with (Fig. 2a) the thermal ALD and (Fig. 2b) the plasma-assisted ALD techniques. To estimate the EOT, the expression $\text{EOT} = \epsilon_0 \times k_{\text{SiO}_2} / (C/A)$ was employed, assuming that the interfacial SiO_x layer has a dielectric constant of $k_{\text{SiO}_2} = 3.9$. From the slope of these plots, the k -values of the stacks can be estimated from the expression $k = k_{\text{SiO}_2} \times (d/\text{EOT})$. A k -value of 6.7 was estimated for the as-deposited thermal ALD films, remaining practically the same (at 6.5) upon FGA. As evident from Fig. 2a, FGA does not have any significant influence on the dielectric properties, but it improves the interface quality with the electrodes. In contrast, the as-deposited plasma-assisted ALD films

Figure 3. (Color online) Flatband voltage V_{FB} as a function of EOT of the (a) as-deposited and (b) annealed films deposited with thermal ALD and plasma-assisted ALD. The solid and open squares are flatband voltages of the devices with the plasma-assisted ALD Al_2O_3 measured from forward and reverse C - V curves, and the solid and open circles are that of the thermal ALD Al_2O_3 layers. The error-bars are smaller than the size of the symbols.

give a k -value of 7.8 ± 0.3 , which improves to 8.8 ± 0.2 after FGA, as shown in Fig. 2b. Groner et al. have reported the k -values of the thermal ALD Al_2O_3 layers ranging from 4 to 7.6 for film thicknesses ranging from 30 to 120 nm.²⁶ From a linear extrapolation of the plots to the EOT axis, the thickness of the native silicon oxide layer was estimated to be 2.2 nm for both the as-deposited and annealed thermal ALD films and 2.1 nm for both the as-deposited and annealed plasma-assisted ALD films. For the plasma-assisted ALD films, these values are somewhat thicker than those obtained by transmission electron microscopy (TEM) inspection revealing 1.2 nm prior to anneal and 1.4–1.5 nm after anneal.^{19,22}

The flatband voltages (V_{FB}) of the as-deposited thermal ALD and plasma-assisted ALD devices as a function of EOT are shown in Fig. 3a and those of the annealed devices are shown in Fig. 3b. The capacitors fabricated from the films deposited with thermal ALD do not show any clear variation of V_{FB} with EOT, whereas the plasma-assisted ALD films exhibit a linear increase with EOT. Generally, for a capacitor with an oxide of dielectric constant k and thickness d , the flatband shift can be expressed as²⁴

$$V_{FB} = \phi_{MS} - (Q_f + Q_{it}) \frac{d}{\epsilon_0 k} - \frac{1}{\epsilon_0 k} \int_0^d [\rho_m(x) + \rho_{ot}(x)] x dx \quad [1]$$

where ϕ_{MS} is the work-function difference between the metal electrode and the silicon substrate. The second term represents the contribution to the mirror charge in the semiconductor conduction band from the sum of the fixed oxide charge (Q_f) and the oxide trap charges at the interface (Q_{it}). The third term represents the mobile charges and the oxide trap charges in the oxide, which are responsible for the hysteresis in the C - V curves (here $\rho_m(x)$ and $\rho_{ot}(x)$ represent the mobile and oxide trap charge densities, respectively). The positive flatband shift in all C - V curves of the plasma-assisted ALD samples indicates that the fixed oxide charges and the interface trap charges are negatively charged. This is in line with what has been reported by Wilk et al.² and what Hoex et al. have demonstrated for the plasma-assisted ALD Al_2O_3 films earlier.¹⁴ The thermal ALD films do not show a gradual flatband shift with the oxide thickness, which might indicate that the mobile charges and the sum of the fixed oxide charges and the oxide trap charges at the interface have opposite signs and their effect cancel out eventually. Conversely, the plasma-assisted ALD films exhibit a gradual linear increase in V_{FB} . In these samples, the mobile and oxide trap charges are significantly less because the C - V curves do not show considerable hysteresis. Therefore, it can be safely assumed that the integral part of Eq. 1 is negligibly small for the plasma-assisted ALD films. Thus, from the slope of the data in Fig. 3a and b, the total of the fixed oxide and interface trap charges Q can be estimated using²⁴

$$Q = \frac{V_{FB}}{EOT} \frac{\epsilon_0 k_{\text{SiO}_2}}{e} \quad [2]$$

with e being the elementary charge.

For the as-deposited plasma-assisted ALD Al_2O_3 devices this estimation yields a negative charge density of $\sim 9.5 \times 10^{12} \text{ cm}^{-2}$, which reduces to $\sim 5.0 \times 10^{12} \text{ cm}^{-2}$ after FGA. In comparison, this density is within the range of the negative fixed charge densities of 5×10^{12} – $1 \times 10^{13} \text{ cm}^{-2}$ observed earlier for the plasma-assisted ALD Al_2O_3 films deposited at 200°C and annealed at 425°C in N_2 atmosphere¹⁴ and for the plasma-assisted $\text{Al}_2\text{O}_3/\text{TiN}$ stacks deposited at 400°C.¹⁹ The negative fixed charge density is two times smaller than the fixed oxide charge density of $1.15 \times 10^{13} \text{ cm}^{-2}$ reported for the thermal Al_2O_3 after postdeposition annealing at a much higher temperatures such as 700°C.²⁰

Figure 4a shows the comparison of the (I - V) characteristics of the as-deposited and annealed samples, represented as the current density versus electric field (J - E) plots of 10 nm Al_2O_3 deposited using thermal ALD. The electric field was defined as the applied voltage across the electrodes divided by the total film thickness measured using in situ spectroscopic ellipsometry and X-ray reflectometry. It is seen that by forming gas annealing, the electrical properties such as the leakage current and the tunneling behavior of the films have improved appreciably.

Figure 4b shows the comparison of the J - E characteristics of the as-deposited Al_2O_3 film with annealed plasma-assisted ALD Al_2O_3 film. Apparently, there is not much change in the leakage behavior of the plasma-assisted ALD film upon annealing, except a minor reduction of the leakage current before Fowler-Nordheim (F-N) tunneling sets in close to an electric field of 6 MV/cm. The onset for Fowler-Nordheim charge conduction increases upon annealing for the thermal ALD films (3.5 MV/cm) but does not reach the onset for F-N for the plasma-assisted ALD films (6 MV/cm). From the I - V measurements of ten devices distributed on different locations of the wafer, the average breakdown field of the thermal ALD Al_2O_3 is $\sim 5 \pm 0.8 \text{ MV/cm}$, whereas that of the plasma-assisted ALD film is $\sim 9 \pm 0.5 \text{ MV/cm}$ upon electron injection from the Al top electrode.

Figure 5 shows the Arrhenius behavior of the current density J of 10 nm thick Al_2O_3 films deposited with thermal and plasma-assisted

Figure 4. (Color online) Current density J as a function of an applied electric field E as deduced from the I - V measurements on the as-deposited and annealed Al_2O_3 films deposited with (a) thermal ALD and (b) plasma-assisted ALD. Negative bias is applied to the Al top electrode.

ALDs. In order to ensure that the measurements are not influenced by the electron tunneling through the films, the leakage current measurements performed at different temperatures were at a fixed electric field of 3 MV/cm, which resorts under the space-charge limited conduction regime. The slope of the distribution is given by $e\Delta E/k$, from which the activation energy ΔE of the traps can be estimated (k is the Boltzmann constant). From Fig. 5a, the thermal activation energy of the shallow traps is estimated to be 0.53 ± 0.01 eV for the as-deposited thermal ALD films. The activation energy is reduced to 0.27 ± 0.01 eV for the thermal ALD films after FGA, as shown in Fig. 5b. In the case of the plasma-assisted ALD films, the as-deposited films have a thermal activation energy of 0.28 ± 0.02 eV, as estimated from Fig. 5c, which reduces upon FGA to 0.08 ± 0.02 eV, as shown in Fig. 5d. This reduction indicates that the trap levels originating from the imperfections of the oxide-silicon interfaces such as dangling bonds and defects are healed out upon annealing.¹¹ This shows that the plasma-assisted ALD films have a much better interface and oxide properties compared to the thermal ALD films.

Because the $\text{Al}_2\text{O}_3/\text{Si}$ conduction band-offset is 2.8 eV, the effect of Schottky emission of electrons can be ignored. From the Arrhenius behavior, we can conclude that the leakage current through the thermal ALD films is more sensitive to temperature than through the plasma-assisted ALD films and indicates that the electric conduction mechanism could be significantly influenced by the trap

Figure 5. (Color online) Arrhenius behavior of the current density of the Al_2O_3 films deposited using thermal ALD, (a) as-deposited and (b) annealed films; and plasma-assisted ALD, (c) as-deposited and (d) annealed films. Each data point is the average of 1000 current points measured over three different devices. The error-bars of the data are smaller than the symbols.

levels distributed below the conduction band of the thermally deposited oxide films. Therefore, the role of Poole-Frenkel (P-F) conduction cannot be neglected in these films. The P-F charge injection is a thermally activated and electric field-assisted thermal hopping mechanism of the charge carriers through the trap levels in the conduction band of the oxide. The current density due to the P-F charge injection is expressed as²⁷

$$J_{\text{P-F}} = CE \exp\left(-q \frac{\phi_t - \sqrt{qE/\pi\epsilon_0\epsilon_r}}{kT}\right) \quad [3]$$

where ϕ_t is the trap ionization energy, as derived from the Arrhenius behavior, and ϵ_r is the dynamic dielectric constant of the film.

Figures 6a and b show the Poole-Frenkel behavior of the annealed thermal ALD and plasma-assisted ALD films, respectively. Even after annealing, the thermal ALD films are sensitive to temperature, while the plasma-assisted ALD films show no temperature sensitivity at all, again underlining the good quality of the oxide achieved by plasma-assisted ALD. From the P-F characteristics of the thermal ALD films, the dynamic dielectric constant ϵ_r was estimated to be 2.04 ± 0.15 . This corresponds to a refractive index of 1.43 ± 0.05 . This is somewhat lower than the value of ~ 1.65 for dense, amorphous Al_2O_3 films deposited by ALD reported previously²² and is considerably lower than the bulk value of a single-crystalline Al_2O_3 , which lies in the range of 1.70–1.76 depending on the crystal structure of the oxide.¹²

Figure 7 demonstrates the F-N tunneling behavior of the annealed thermal ALD and plasma-assisted ALD films. As evident from the characteristics, the thermal ALD films have an earlier onset of the F-N tunneling than the plasma-assisted ALD films. The F-N tunneling depends on the energy difference of the conduction bands of the electrode (here aluminum) and the oxide materials. Thus, a larger current at an earlier onset of the tunneling implies that the conduction band of the thermal ALD oxide is lower than that of the plasma-assisted ALD oxide with respect to the conduction band of the Al electrode. This is evidenced by the slope of the tunneling characteristics as well.

The leakage current at high electrical fields through a dielectric material as a result of F-N tunneling is given by²⁴

Figure 6. (Color online) Poole-Frenkel plots measured at different temperatures for the annealed Al_2O_3 films deposited by (a) thermal ALD and (b) plasma-assisted ALD.

$$J_{\text{F-N}} = \frac{e^3 m}{16\pi^2 \hbar m_{\text{ox}} \Phi_B} E^2 \exp\left(-\frac{4}{3} \frac{\sqrt{2m_{\text{ox}}}}{e\hbar E} \Phi_B^{3/2}\right) \quad [4]$$

where Φ_B is the barrier height for the tunneling and m_{ox} is the effective mass of electrons in the oxide. With a reported electron

Figure 7. (Color online) Fowler-Nordheim tunneling through the annealed Al_2O_3 films deposited by thermal ALD and plasma-assisted ALD.

Figure 8. (Color online) $\text{Al-Al}_2\text{O}_3$ barrier heights estimated for the thermal ALD and plasma-assisted ALD Al_2O_3 films as a function of film thickness in their as-deposited (represented by 5, 10, and 20) and annealed states (represented by 5, 10, and 20 Å). The open symbols represent the barrier heights of the as-deposited and the closed symbols represent the barrier heights of the annealed devices.

effective mass of $0.23m_0$ for Al_2O_3 (Ref. 10), the estimated $\text{Al-Al}_2\text{O}_3$ barrier height values are plotted as a function of the oxide thickness in Fig. 8 for the thermal ALD and plasma-assisted ALD films. The barrier heights generally do not depend on the thickness of the films, which means that any influence of direct tunneling is unlikely, even in the thinnest (5 nm) films investigated here. Annealing does not seem to have a significant influence on the barrier height of the films. However, a clear difference in the barrier height is observed between the thermal and plasma-assisted ALD films. The average $\text{Al-Al}_2\text{O}_3$ barrier height of the latter films is 2.47 ± 0.36 eV, while that of the thermal ALD films is 1.32 ± 0.16 eV. The theoretical $\text{Al/Al}_2\text{O}_3$ barrier height reported by Miyazaki is 2.25 eV,²⁸ and the photoemission studies by Goodman indicate an $\text{Al/Al}_2\text{O}_3$ barrier height of 2.0 eV.²⁹ The leakage current through the device, as evident from Eq. 4, increases exponentially with the reducing barrier height and thus a lower barrier height contributes to the larger power consumption of the device.

The I - V characteristics of the thermal ALD films point to a rather leaky oxide. The leakage current improves considerably after FGA. Plasma-assisted ALD films exhibit a much lower leakage current, which does not change noticeably after FGA. Thermally grown ALD films have a higher thermal activation energy compared to the plasma-assisted ALD films. This is consistent with the C - V measurements that suggest that the thermal ALD films have more trap states than the plasma-assisted ALD films. Conversely, plasma-assisted ALD has less interface-trap-levels as well, which suggests the impact of the O_2 plasma on the nucleation behavior of the film in the early stages of the growth. The chemisorption of the Al-precursor— $\text{Al}(\text{CH}_3)_3$ —in the thermal and plasma-assisted ALDs are the same, but after the reaction, the $-\text{CH}_3$ ligands are removed in the plasma-assisted ALD by a combustionlike process with the oxygen radicals rather than through a ligand exchange reaction.³⁰⁻³² Apparently, the oxygen radicals generated in the remote plasma are not only very effective in removing the $-\text{CH}_3$ groups and creating a reactive, hydroxylated surface but also create a slightly more dense film in which the density of the Si dangling bonds is drastically reduced.^{30,32} It has been demonstrated elsewhere that the actual carbon contamination is below the detection limit (i.e., <1 atom %) of Rutherford backscattering analyses for both the thermal and plasma-assisted ALD Al_2O_3 films deposited at temperatures $>200^\circ\text{C}$.²² Although very small concentrations of impurities can already give rise

to large electrical effects, the remaining carbon concentration (e.g., due to unreacted methyl groups) is considered to have a small impact on the electrical properties. This is due to the modest temperature budget during the forming gas anneal which is not able to remove the methyl groups from the films. On the contrary, the amount of hydrogen in the Al_2O_3 film could be an indication for the passivation level. Especially, the difference between the thermal and the plasma ALD processes could be explained by the ability to passivate the dangling bonds with atomic hydrogen during the FGA. Also the density of the film which is slightly higher for the plasma-assisted ALD films is an indication that already during the film growth the atoms are more closely packed, forming an amorphous and denser Al–O–Al network. The discontinuities at the Si interface (not all Si atoms are connected via an oxygen atom to aluminum) and larger density of unreacted –OH groups within a thermally grown film on Si could act as active centers for the electron trapping, thus prompting the thermal ALD films to exhibit Poole–Frenkel charge injection at lower electric fields.

Conclusions

The C – V behaviors of the as-deposited and annealed thin films of Al_2O_3 deposited by the thermal and plasma-assisted ALDs indicate that the plasma technique yields a better Al_2O_3 –Si interface from electrical perspective, though the interfacial oxide thicknesses in both cases are comparable. This is revealed by the flatband voltage shifts of the plasma-assisted ALD films which exhibit a linear relation with the thickness of the oxide. Presumably due to the dominance of mobile ions in the oxide, the thermal ALD films do not exhibit such a linear increase of the flatband voltage shift and, in addition, these films exhibit a large hysteresis in the C – V behavior. The dielectric permittivity of the annealed plasma-assisted ALD Al_2O_3 is relatively high ($k = 8.8$) and comparable to bulk Al_2O_3 , whereas thermal ALD gives a lower k -value ($k = 6.7$). In addition, the Al– Al_2O_3 barrier height of the plasma-assisted ALD oxides is almost twice larger than that of the thermal ALD oxide, which together with the low defect density explains the origin of the lower leakage currents through the plasma-assisted ALD Al_2O_3 films. The dielectric breakdown electric field of the plasma-assisted ALD Al_2O_3 is 9 MV/cm, whereas the thermal ALD Al_2O_3 breaks down at 5 MV/cm, again confirming the superior quality of the plasma-assisted ALD Al_2O_3 over the thermal ALD Al_2O_3 .

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