

Atomic Layer Deposition of Al₂O₃ Thin Films Using Trimethylaluminum and Isopropyl Alcohol

Woo-Seok Jeon,^a Sung Yang, Choon-soo Lee,^{b,*} and Sang-Won Kang^{a,z}

^aDepartment of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea ^bGenitech, Incorporated, Taejon 306-230, Korea

Al₂O₃ thin films were deposited on Si substrates by atomic layer deposition (ALD) using Al(CH₃)₃ (trimethylaluminum, TMA) as a metal source and (CH₃)₂CHOH (isopropyl alcohol, IPA) as an oxygen source at 250°C. The film growth rate is saturated at 0.8 Å/cycle, and it is slightly lower than that for the procedure which uses water vapor instead of IPA. The as-deposited film has a stoichiometry close to Al₂O₃ (Al/O ratio ~2:3.1) and the residual carbon content of the films is below the detection limit of secondary ion mass spectroscopy. An interface oxide between the Al₂O₃ film and Si-substrate was not detectable on the as-deposited film by transmission electron microscopy. However, after annealing at 800°C for 5 min, an interface oxide is newly formed even under the neutral ambient of Ar, and it grows thicker under the oxidizing ambient of O₂. That is, oxygen, which is oxygen in the films. Thus, although the loss of dielectric constant is inevitable during the annealing process, it can be minimized by using IPA in Al₂O₃ ALD.

© 2002 The Electrochemical Society. [DOI: 10.1149/1.1470659] All rights reserved.

Manuscript submitted May 16, 2001; revised manuscript received December 11, 2001. Available electronically April 12, 2002.

As the size of microelectronic devices is scaled down, oxide films with high dielectric constants are required for gate and capacitor dielectrics. Even though SiO₂ is an excellent dielectric material in many features, the preparation of reliable SiO₂ films thinner than 30 Å is difficult, because of the quantum mechanical tunneling of electrons, which generates a large leakage current across the films.¹ Thus, an alternative oxide film with higher dielectric constant than SiO₂ is needed.² In this respect, Al₂O₃ has been considered as a possible candidate for gate oxides as well as Ta₂O₅, HfO₂, and ZrO₂.³⁻⁵ Also, Al₂O₃ is considered as a promising capacitor dielectric, which can replace silicon oxynitride (SiON) in future dynamic random access memories (DRAM).⁶ In addition, Al₂O₃ has been recently regarded as a good passivation layer, which can prevent hydrogen penetration into the active region of semiconductor devices.⁷

In preparing high-dielectric metal oxides with a thickness in the subhundred angstrom range, atomic layer deposition (ALD) attracts considerable interest owing to its inherent merits in thin film depositions, such as a digital controllability of film thickness on an atomic scale, a superior conformal deposition on three-dimensional structures, and no particle generation, etc.⁸⁻¹⁰ In typical ALD of metal oxide thin films, H_2O has been most widely used as the oxygen source.¹¹⁻¹⁶

However, by using H_2O an unwanted interface oxide may be formed between the metal oxides and Si substrates, and it is thought that the interface oxide is composed mainly of SiO_x, as the result of the reaction between H_2O and the Si substrates during the initial stage of the ALD. Hence, the interfusion of the interface oxide would be expected to reduce the dielectric constant of the deposited thin films.¹⁷⁻¹⁹ Therefore, the suppression of the formation of the interface oxide is required in order to retain the dielectric constant of the metal oxide itself. Although Gusev *et al.* reported that no interface oxide was present between H-terminated Si and Al_2O_3 ,²⁰ Fujinami *et al.* reported that rinsing in pure water for 30 min or more after HF treatment initiated oxidation of the Si surface even at room temperature.²¹

In this study, isopropyl alcohol (IPA) was used instead of H_2O in Al_2O_3 ALD in order to prevent the interface oxide from being formed during the film deposition. Moreover, the use of IPA avoids problems caused by the condensation of H_2O vapor onto the reactor

wall and gas delivery line, which would generate particles and elongate the pulse time of inert gas to purge out H_2O vapor from the reactor. It has been clearly shown that IPA is an efficient reactant for trimethylaluminum (TMA) in forming aluminum oxide, and it should also be useful in ALD of other metal oxides.

Experimental

 Al_2O_3 films were grown on Si(100) substrates at 250°C using TMA and IPA under a deposition pressure of 133 Pa. The growth experiments were carried out using a hot-wall-type ALD reactor. The initial Si(100) wafer surface was treated in 50% HF solution for 3 min, rinsed in deionized (DI) water, and blown with a nitrogen gun. TMA and IPA were alternately supplied into the reaction chamber by the sequential injection of a TMA pulse, an Ar pulse, an IPA pulse, and then another Ar pulse. This sequential injection is one deposition cycle, and the growth of films is accomplished by repeating a cycle. The Ar pulse isolates the reactants from each other. During ALD, the partial pressure and the pulse time of TMA were controlled in the range of 1.33-13.3 Pa and 0.3-5.0 s, respectively. In case of IPA, the pulse time was also changed from 0.3 to 5 s, but the partial pressure was fixed at 13.3 Pa.

An annealing process was performed on the as-deposited films by a rapid thermal process (RTP) at 800°C for 5 min at 40,000 Pa under the neutral ambient of Ar or the oxidizing ambient of O2. Before and after the annealing, the surface smoothness, stoichiometry, and crystallinity of the films were evaluated with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD), respectively. A single-crystal sapphire was used as a standard sample to correct the relative atomic sensitivity factor (RASF) of XPS for aluminum and oxygen. Carbon incorporation in the films was investigated with SIMS and the film thickness was measured with an ellipsometer (Rudolph AutoEL-II). In addtion, the interface between the deposited Al₂O₃ films and the Si substrate was investigated by TEM analysis. The current-voltage (I-V) and the capacitance-voltage (C-V at 1 MHz) characteristics of the films were measured on metal oxide semiconductor (MOS) capacitors of Pt/Al2O3/p-type Si(100) structure, in which 1000 Å thick Pt dots with a diameter of 160 µm were sputtered on the Al₂O₃ films.

Results and Discussion

^z E-mail: swkang@kaist.ac.kr

Figure 1 shows the growth kinetics of Al_2O_3 ALD depending on the pulse time and partial pressure of TMA and IPA at a deposition temperature of 250°C. The deposition of Al_2O_3 shows typical char-

^{*} Electrochemical Society Active Member.



Figure 1. Thickness/cycle of deposited Al_2O_3 films on Si(100) vs. reactant pulse times at 250°C. (a) The dependence of growth thickness/cycle of Al_2O_3 film on TMA pulse time, the partial pressure of TMA was 1.33 Pa, the pulse time of IPA was 3 s. (b) The dependence of growth thickness/cycle of Al_2O_3 film on TMA pulse time, the partial pressure of TMA was 13.3 Pa, the pulse time of IPA was 3 s. (c) The dependence of growth thickness/cycle of Al_2O_3 film on TMA pulse time, the partial pressure of TMA was 1.33 Pa, the pulse time of IPA was 3 s. (c) The dependence of growth thickness/cycle of Al_2O_3 film on IPA pulse time, the partial pressure of TMA was 1.33 Pa, the pulse time of TMA was 3 s.

acteristics of ALD, in which the film thickness deposited during one cycle (thickness/cycle) is self-limited. From the deposition characteristics, it is clear that IPA reacts with TMA and forms aluminum oxides at 250°C. When the pulse time of IPA exceeds 1 s, the thickness/cycle is saturated at 0.8 Å/cycle. In addition, the saturated pulse time of TMA is shortened from 2 s to 1 s as the partial pressure of TMA increases from 1.33 Pa to 13.3 Pa. However, the thickness/cycle at the saturated condition is not affected by the partial pressure of TMA. This implies that, under the saturated condition, the amount of TMA* (the asterisk denotes all possible surface species remaining after the TMA pulse) adsorbed on the film surface is limited by its molecular size owing to steric hindrance. The saturated thickness/cycle of 0.8 Å/cycle, which corresponds to 0.37 monolayer/cycle (ML/cycle), is lower than that of 1.0 Å/cycle reported by George et al., in which H₂O was used instead of IPA at the same deposition temperature of 250°C.¹² The difference in the saturated thickness/cycle between two Al2O3 ALDs can be understood by adopting the concept of secondary adsorption, which has been proposed in our previous papers to explain the saturated thickness/cycle exceeding 1 ML/cycle in ALD.^{22,23} During IPA or H₂O pulse, the oxygen sources will react with TMA* adsorbed on the film surface and form Al₂O₃. The oxygen sources are then likely to adsorb on both of the outermost surfaces of the newly formed Al₂O₃ and the newly exposed surface, which had been screened with TMA* before. This is referred to as the secondary adsorption. As a result, the surface of the film will be covered with IPA* or H₂O* after the pulse of the oxygen sources, and then these secondary adsorbed oxygen sources will also react with TMA during the following TMA pulse. However, at the saturation conditions in the two Al₂O₃ ALDs, where the adsorption and desorption rates are at the steady-state condition, the quantity of the secondary adsorbed chemical groups would be much less in case of IPA* than H₂O*, because IPA* has a much larger molecular size. As a result, the total amount of TMA that will be involved in Al₂O₃ formation during a cycle will be reduced. Thus, when IPA is used as an oxygen source in Al2O3 ALD, the saturated thickness/cycle will be reduced as compared to the situation, where H₂O is used as an oxygen source.



Figure 2. XPS depth profile through 110 Å Al_2O_3 films on Si(100), comparing (a) no anneal *vs.* (b) Ar, (c) O_2 anneal. The atomic percents of Al and O were (a) 37.39 and 58.33%, (b) 37.35 and 58.58%, and (c) 37.34 and 58.58%. The extent of carbon impurities were minimal.

Before and after annealing at 800°C for 5 min under Ar or O₂ ambient, the chemical composition of the films was analyzed by XPS using a single-crystal sapphire as a reference. Figure 2 illustrates the XPS depth profiles for aluminum, oxygen, and carbon in the films. The chemical composition of the films remains unchanged before and after annealing and, regardless of the annealing ambient, it is slightly oxygen-rich with the composition ratio of Al:O = 1:1.56. The XPS analysis also shows that carbon impurities are negligible in the bulk of Al2O3 film as well as at the Al2O3/Si interface. In order to confirm the carbon impurities in the films, SIMS depth profiles of carbon were measured, and are shown in Fig. 3. Except at the film surface, the carbon impurities in the films were about 10^2 counts/s, almost the detection limit of SIMS, before and after the annealing, and are independent of the annealing conditions. That is, Al₂O₃ films deposited by ALD using IPA are nearly carbonfree. This extremely low carbon incorporation is significant, when compared to results previously reported in other ALD²⁴ and metallorganic chemical vapor depositions (MOCVD) of Al₂O₃.^{18,25,26} In their work, the carbon impurities were incorporated into the films up



Figure 3. SIMS depth profiles of carbon in Al_2O_3 films. Except at the films surface, the films were nearly carbon-free before and after annealing.



Figure 4. TEM cross-sectional images of Al_2O_3 films using TMA and IPA (a, top) as-deposited at 250°C, (b, center) after annealing at 800°C for 5 min in Ar, and (c, bottom) after annealing at 800°C for 5 min in O₂. Interlayers were present at the interfacial regions of Al_2O_3 /Si after annealing.

to the order of atomic percent, and were piled up especially at the Al_2O_3 /Si interface. This suggests that IPA is very efficient reactant for TMA without leaving a hydrocarbon residue. From the XRD analysis, not shown here, it is revealed that the Al_2O_3 films have an amorphous structures before and after the annealing process, while the Al_2O_3 films as-deposited by MOCVD using TMA and N₂O at 720-1050°C have γ - Al_2O_3 structure.^{26,27} This difference in crystal structure may be due to the deposition temperature. The surface



Figure 5. TEM cross-sectional images of Al_2O_3 film using TMA and H_2O as-deposited at 250°C. Interlayers were present at the interfacial regions of Al_2O_3/Si in as-deposited films.

roughness of the films analyzed by AFM is a few angstroms in root mean square values and shows no difference between before and after the annealing.

It is well known that the Al₂O₃ films formed by conventional MOCVD yield SiO₂ at the interfacial region of the Al_2O_3 /Si sub-strate before annealing.^{18,19} In order to study the formation of interface oxide in Al₂O₃ ALD, cross-sectional TEM images were investigated before and after the annealings. Figures 4a and 5 illustrate the formation of an interfacial layer on the as-deposited Al₂O₃ films depending on the oxygen sources used. When IPA is used, no interfacial layer is detectable. However, an interfacial layer with a thickness of 12 Å, as shown in Fig. 5, is generated on the as-deposited film that is grown by ALD using H₂O instead of IPA. The interfacial layer should be formed during an early stage of Al2O3 ALD, because the surface of the Si substrate will be directly exposed to H₂O until it is completely covered with an Al₂O₃ layer, and the exposed surface will almost certainly be oxidized at a temperature of 250°C, which is the deposition temperature of the film. Hence, the interfacial layer should be an oxide having a composition of $SiAl_vO_v$, even though it is not pure SiO_2 . On the other hand, the data herein show that IPA does not thermally oxidize Si at a temperature of 250°C, and thus, although the surface of the Si substrate is also exposed to IPA during an early stage of Al₂O₃ ALD, there is no chance to form silicon oxides at the interface. It would be helpful to obtain a higher effective dielectric constant in the films by suppressing the formation of SiAl_xO_y, which should have a lower dielectric constant than Al₂O₃. However, as shown in Fig. 4b and c, the interface oxide is newly generated during the annealing processes, and is inevitable, even though the annealing process is performed under the neutral ambient of Ar. The thickness of the interface oxide appears to be about 10 and 25 Å after annealing under the ambient of Ar and O_2 , respectively. This implies that the interface oxide is grown by the self-reaction between excess oxygen in the Al₂O₃ film and the Si substrate at the annealing temperature of 800°C, and further by the thermal oxidation of the Si substrate due to the diffusion of the ambient oxygen through the film. Therefore, the film annealed in O₂ ambient has a thicker interface oxide. But, surprisingly, before and after annealing the increment of the film thickness including the interface oxide, is almost negligible. From this, it would be expected that the annealing process would make the Al₂O₃ layer become dense, leading to reduction in the thickness of the Al_2O_3 layer. In order to clarify the existence of silicon oxides at the interface, XPS depth profiles were performed on the films which were deposited using IPA, and the results for Si 2p near the interface



93 96 99 102 105 108 Binding energy (eV)

Figure 6. XPS analysis for Si 2p peak near the interfacial regions of Al_2O_3/Si for (a, top) as-deposited at 250°C, (b, center) after annealing at 800°C for 5 min in Ar, and (c, bottom) after annealing at 800°C for 5 min in O_2 .

are illustrated in Fig. 6. As shown in Fig. 6a, on the as-deposited film, which has no interface oxide, there is only one Si 2p peak emitted from the Si substrate at the interfacial regions of Al_2O_3/Si . However for the film annealed in O_2 ambient, two Si 2p peaks are found at 97.2 and 101.4 eV, which correspond to peaks emitted from the Si substrate and SiO_x , respectively. This indicates that the interface oxide is partly composed of silicon oxides. From the results of TEM and XPS analyses, it is clear that the growth of the interface oxide can be prevented by the use of IPA instead of H₂O during film

deposition, and that the interface oxide which is newly generated during annealing is inevitable owing to the self-reaction between Al_2O_3 and the Si substrates.

The I-V and C-V characteristics were measured on the MOS capacitor with Pt/80 Å thick Al₂O₃/Si substrate structure before and after annealing. The leakage current density measured at 1 MV/cm decreases from ${\sim}10^{-6}~\text{A/cm}^2$ to 5 ${\times}~10^{-8}~\text{A/cm}^2$ and 1 ${\times}~10^{-8}$ A/cm^2 after annealing under Ar and O₂ ambients, respectively. The reduction in the leakage current after annealing can be partly attributed to the densification of Al₂O₃, as previously mentioned in Fig. 4. Regardless of the annealing ambient, the time zero dielectric breakdown (TZDB) of the annealed films is \geq 7 MV/cm. However, as expected from the growth of the interface oxide, which is dependent on the annealing ambient, the film, which has a bilayer structure with the Al_2O_3 layer and the interfacial layer of $SiAl_rO_v$, shows differences in its effective dielectric constant after annealing. For the case of the Ar-annealed film, the effective dielectric constant is about 11, while that of the film annealed in O_2 ambient is about 9. The film thickness equivalent to SiO₂, t_{ox} , was 30 Å for the Ar annealed Al₂O₃ film. The trend in effective dielectric constants, as measured by the C-V method is qualitatively in good agreement with the analysis obtained from the cross-sectional TEM imagines in Fig. 4; the thicker the interface layer, the lower the effective dielectric constant. Further studies are needed to develop a quantitative approach to this issue, however.

Conclusions

Amorphous Al₂O₃ thin films were deposited by ALD using TMA and IPA at 250°C. The fully saturated deposition thickness/cycle of 0.8 Å/cycle was determined using optimum precursor pulse times. AFM images revealed exceptionally flat and conformal Al₂O₃ films with a surface roughness of only 3.5 Å (rms) after a deposition of ~80 Å film. In spite of the use of carbon-based oxygen precursor, the films were nearly carbon-free and the stoichiometry of the films was close to Al₂O₃. The t_{ox} was about 30 Å. As evidenced by TEM and XPS analyses, the SiAl_xO_y was formed at the interfacial regions of the Al₂O₃/Si after the annealing treatments. This had an effect on the t_{ox} . However, the as-deposited film has no interfacial layer at the interfacial regions. Contrary to H₂O, IPA does not thermally react with Si at a temperature of 250°C. The Al₂O₃ film prepared by ALD using TMA and IPA appears to be an excellent candidate material for sub-0.2 µm design rule applications.

Acknowledgments

This work was supported by the National Research Laboratory program of the Ministry of Science and Technology.

Korea Advanced Institute of Science and Technology assisted in meeting the publication costs of this article.

References

- 1. A. Masaki, IEEE Circuits Devices Mag., 8, 18 (1992).
- V. Mikhaelashivili, Y. Betzer, I. Prudnikov, M. Orenstein, D. Ritter, and G. Eisenstein, J. Appl. Phys., 84, 6747 (1998).
- A. Pignolet, G. M. Rao, and S. B. Krupanidhi, *Thin Solid Films*, **258**, 230 (1995).
 J. Aarik, A. Aidla, A. A. Kiisler, T. Uustare, and V. Sammelselg, *Thin Solid Films*,
- 4. J. Aani, A. Andra, A. A. Kilsler, T. Oustare, and V. Sammerseig, *Thir Solid Fullis* 340, 110 (1999).
- 5. E. T. Kim and S. G. Yoon, Thin Solid Films, 227, 7 (1993).
- L. Manchanda, W. H. Lee, J. E. Bower, F. H. Baumann, W. L. Brown, C. J. Case, R. C. Keller, Y. O. Kim, E. J. Laskowski, M. D. Morris, R. L. Opila, P. J. Silverman, T. W. Sorsch, and G. R. Weber, *Tech. Dig. - Int. Electron Devices Meet.*, 1998, 605.
- Y. K. Kim, S. H. Lee, S. J. Choi, H. B. Park, Y. D. Seo, K. H. Chin, D. Kim, J. S. Lim, W. D. Kim, K. J. Nam, M. H. Cho, K. H. Hwang, Y. S. Kim, S. S. Kim, Y. W. Park, J. T. Moon, S. I. Lee, M. Y. Lee, *Tech. Dig. - Int. Electron Devices Meet.*, 2000, 369.
- 8. M. Ritala and M. Reskela, Nanotechnology, 10, 19 (1999).
- 9. T. Suntola, in *Handbook of Crystal Growth*, 3-part B, D. T. J. Hurle, Editor, p. 605, Elsevier, Amsterdam (1994).
- 10. T. Suntola and J. Antson, U.S. Pat. 4,058,430 (1977).
- M. Ritala, H. Saloniemi, M. Leskelä, T. Prohaska, G. Friedbacher, and M. Grasserbauer, *Thin Solid Films*, 286, 54 (1996).

- A. W. Ott, J. W. Klaus, J. M. Johnson, and S. M. George, *Thin Solid Films*, **292**, 135 (1997).
- L. Hiltunen, H. Kattelus, M. Leskela, M. Makela, L. Niinisto, E. Nykanen, P. Soininen, and M. Tiitta, *Mater. Chem. Phys.*, 28, 379 (1991).
- H. Kattelus, M. Ylilammi, J. Saarilahti, J. Antson, and S. Lindfors, *Thin Solid Films*, 225, 296 (1993).
- K. Kukli, J. Ihanus, M. Ritala, and M. Leskelä, J. Electrochem. Soc., 144, 300 (1997).
- 16. G. S. Higashi and C. G. Fleming, Appl. Phys. Lett., 55(19), 1963 (1989).
- 17. D. A. Chang, P. Lin, and T. Y. Tseng, J. Appl. Phys., 78, 7103 (1995).
- T. W. Kim, W. N. Kang, Y. S. Yoon, S. S. Yom, J. Y. Lee, C. Y. Kim, H. Lim, and H. L. Park, J. Appl. Phys., 74, 760 (1993).
- 19. T. M. Klein, D. Niu, W. S. Epling, W. Li, D. M. Maher, C. C. Hobbs, R. I. Hegde,

- I. J. R. Baumvol, and G. N. Parsons, Appl. Phys. Lett., 75(25), 4001 (1999).
- E. P. Gusev, M. Copel, E. Cartier, I. J. R. Baumvol, and M. A. Gribelyuk, *Appl. Phys. Lett.*, **76(2)**, 176 (2000).
- 21. M. Fujinami and N. B. Chilton, Appl. Phys. Lett., 63(25), 3458 (1997).
- 22. J. W. Lim, J. S. Park, and S. W. Kang, J. Appl. Phys., 87, 4632 (2000).
- 23. J. W. Lim, H. S. Park, and S. W. Kang, J. Appl. Phys., 88, 6327 (2000).
- 24. K. Kukli, M. Ritala, and M. Leskelä, J. Vac. Sci. Technol. A, 15, 2214 (1997).
- A. C. Jones, D. J. Houlton, S. A. Rushworth, and G. W. Critchlow, J. Phys. IV, 5, C5 (1995).
- M. Ishida, I. Katakabe, T. Nakamura, and N. Ohtake, *Appl. Phys. Lett.*, 52(16), 1326 (1988).
- 27. K. Sawada, M. Ishida, and T. Nakamura, Appl. Phys. Lett., 52(20), 1672 (1988).