

Nondestructive depth profile of the chemical state of ultrathin $\text{Al}_2\text{O}_3/\text{Si}$ interface

Jong Cheol Lee^{a)} and S.-J. Oh^{b)}

School of Physics and Center for Strongly Correlated Materials Research, Seoul National University, Seoul 151-742, Korea

(Received 3 September 2003; accepted 3 March 2004; published online 20 April 2004)

We investigated a depth profile of the chemical states of an $\text{Al}_2\text{O}_3/\text{Si}$ interface using nondestructive photon energy-dependent high-resolution x-ray photoelectron spectroscopy (HRXPS). The Si $2p$ binding energy, attributed to the oxide interfacial layer (OIL), was found to shift from 102.1 eV to 102.9 eV as the OIL region closer to Al_2O_3 layer was sampled, while the Al $2p$ binding energy remains the same. This fact strongly suggests that the chemical state of the interfacial layer is not Al silicate as previously believed. We instead propose from the HRXPS of Al $2p$ and Si $2p$ depth-profile studies that the chemical states of the $\text{Al}_2\text{O}_3/\text{Si}$ interface mainly consist of SiO_2 and Si_2O_3 . © 2004 American Institute of Physics. [DOI: 10.1063/1.1734684]

As the complementary metal–oxide–semiconductor field effect transistor device is scaled down to 0.1 μm , corresponding scaling of the channel length to sub-70 nm must be accompanied by the decrease of SiO_2 thickness to 10–15 Å. However, this scaling results in unacceptable high leakage current from direct tunneling through SiO_2 . Thus, physically thicker high dielectric (high- κ) oxide thin film, which has the capacitance equivalent to the SiO_2 oxide of 10–15 Å thickness, has been attracting great interest and extensively studied as a replacement for the nitrated SiO_2 gate oxide film.^{1,2} Among many candidate materials, Al_2O_3 has been recently highlighted due to its relatively higher dielectric constant ($\kappa=9$), thermodynamic compatibility of the interface with Si, and similar band gap and band offset with silica.^{3,4} Specifically, Al_2O_3 blocks oxygen or boron penetrations into the Si well.⁵ Thus, Al_2O_3 has been often used as a diffusion barrier between a high- κ dielectric layer and Si. So, a fundamental understanding of the $\text{Al}_2\text{O}_3/\text{Si}$ interface is important. Moreover, many other issues, such as thermal and chemical stability, electrical performance, and interface charge density are related to the Si/dielectrics interface chemical state.⁶ Several studies for the $\text{Al}_2\text{O}_3/\text{Si}$ interface have been performed. While some^{7,8} reported that as-grown $\text{Al}_2\text{O}_3/\text{Si}$ film had an abrupt interface or SiO_2 layer at the interface, others^{4,6} suggested that Al silicate was formed at the interface judging from the Si $2p$ binding energy which is located at 102 eV, about ~ 1 eV lower than that for SiO_2 .^{9,10} In this regard, we note Wagner *et al.*⁹ and Wannaparhun *et al.*¹⁰ reported that the Si $2p$ binding energy was located at 101.5–102.8 eV in various Al silicates. Misra *et al.*⁶ proposed that aluminum hydroxides, produced on using trimethylaluminum (TMA) and H_2O as a precursor or oxidant, reacted with Si, and formed aluminum hydroxy silicate by the following reaction:

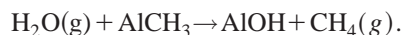


^{a)}Process Development Team, Memory Division, DS Network, Samsung Electronics Co. Ltd., Giheung-Eup, Yongin-City, Gyeonggi-Do 449-711, Korea.

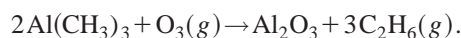
^{b)}Electronic mail: sjoh@plaza.snu.ac.kr

This situation obviously calls for a more sophisticated experimental study on the chemical state of the $\text{Al}_2\text{O}_3/\text{Si}$ interface.

In this letter, we prepared $\text{Al}_2\text{O}_3/\text{Si}$ films by atomic-layer deposition (ALD) using TMA and H_2O or O_3 as the precursor and oxidant, respectively. In H_2O -based $\text{Al}_2\text{O}_3/\text{Si}$ film (HA), AlOH species are produced through the following chemical exchange.¹¹



However, when O_3 is used as the oxidant to grow O_3 -based $\text{Al}_2\text{O}_3/\text{Si}$ film (OA), AlOH species are not produced since the following reaction takes place:¹²



The comparison of the chemical states of both interfacial layers would reveal whether AlOH and OH species play an important role or not in the formation of oxide interfacial layer (OIL): SiO_2 or Al-silicate layer. We investigated this issue by the nondestructive depth profile of Si and Al metal interface states using high-resolution synchrotron x-ray photoelectron spectroscopy (HRXPS) with various photon energies, and propose an identification of the chemical states of the $\text{Al}_2\text{O}_3/\text{Si}$ (100) interface. The depth profile clearly shows that there is no Al-silicate formation in the interface, which naturally leads us to identify the $\text{Al}_2\text{O}_3/\text{Si}$ (100) interface as mainly consisting of Si_2O_3 and SiO_2 .

~ 4 -nm-thick Al_2O_3 films were grown by an ALD process using TMA and H_2O or O_3 as the precursor and oxidant respectively, at a wafer temperature of 300 °C on B-doped p -type 8-in.-diameter (100) Si wafers (doping concentration of $1 \times 10^{15} \text{ cm}^{-3}$). The native oxide on the Si wafer surface was removed by Radio Corporation of America cleaning immediately prior to the Al_2O_3 film growth. The film thickness was determined by ellipsometry. X-ray photoelectron spectroscopy (XPS) measurements were performed on the soft x-ray beamline (8A1) connected to an undulator (U7) at the Pohang Accelerator Laboratory in Korea. The end station

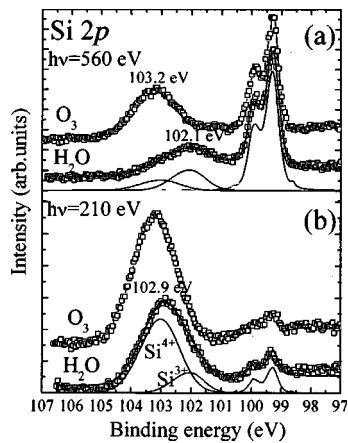


FIG. 1. Si 2p core-level spectra taken at (a) $h\nu=560$ and (b) $h\nu=210$ eV for HA and OA films, respectively. The open squares are experimental data points, and the solid lines are the results of the curve fittings with the decompositions: Si^{1+} , Si^{3+} , Si^{3+} , and Si^{4+} shifted from the bulk Si 2p binding energy of 99.3 eV by 1.0, 1.8, 2.62, and 3.7 eV, respectively.

was composed of a high performance electron analyzer (SCIENTA-200) with an energy and angular resolution of 5 meV and 0.5° , respectively.

In order to investigate the interfacial chemical state, the depth profiles of the interface Si, and Al metal states were performed nondestructively using HRXPS taken at various incident photon energies $h\nu$. The sputtering process commonly used in a depth profile study of secondary ion mass spectroscopy or Auger electron spectroscopy usually changes the chemical states at the interfacial region due to the sputtering damage. On the other hand, our method makes use of the variation of the probing depth depending on the kinetic energy, and keeps intact the interfacial region to be investigated. First, the Si 2p core-level spectra were taken at $h\nu=560$ for both the O_3 -based $\text{Al}_2\text{O}_3/\text{Si}$ film (OA) and the H_2O -based $\text{Al}_2\text{O}_3/\text{Si}$ film (HA), and shown in Fig. 1(a). The binding energy was calibrated using the Fermi edge spectrum of the *in situ* evaporated Ru-metal film. Si 2p spectra taken at $h\nu=560$ consist of two peaks: A sharp and strong peak at 99.3 eV for both the HA and the OA, and a broad peak at a higher binding energy of 102.1 eV and 103.2 eV for the HA and the OA, respectively. The area of this peak of the OA is larger than that of the HA. This means that oxygen reacts with Si in the OA more actively than HA. The former peak in the lower binding energy is obviously from the pure Si in the substrate. Although it is clear that the high binding energy component is related to the OIL, it is not obvious what they are. They can be explained by two possibilities. One possible interpretation is that this component is due to the Si—O—Al bonds formed by Si diffusion into the Al_2O_3 layer under excess oxygen (i.e., hydroxide).⁶ On the other hand, it can also be explained as the contribution of a Si^{4+} component for SiO_2 along with three intermediate components for the suboxide species of Si^{1+} — Si^{3+} at the interface without invoking the possibility of the silicate formation. Considering that Si 2p binding energy for SiO_2 is usually located between 103 eV and 103.9 eV, it is clear that the OIL of the OA consists of mainly SiO_2 instead of the Al silicate. The formation of SiO_2 at the interface is due to the sufficient supply of oxygen from dissociation of O_3 . Excess oxygen reacts with Si and forms the SiO_2 layer. This is contrary to the

previous proposal that the excess oxygen (such as —OH species) reacts with Si to finally form a silicate.⁶ In case of the HA, considering that oxygen reacts with Si in the HA less actively than OA in this study, the possibility of the formation of silicate in the OIL is weak, but it is not possible to distinguish unambiguously between these two possibilities from this spectrum alone.

To clarify and identify the interfacial chemical state more clearly, the Si 2p core-level spectra were taken at $h\nu=210$ eV and shown in Fig. 1(b). Inelastic mean-free path (IMFP) of photoelectrons from the Si 2p core level when the incident photon energy is 210 and 560 eV is 8 and 16 Å, respectively.¹³ As $h\nu$ decreases, the probing depth becomes shallow and the region closer to AlO_2 layer is sampled. A broad peak attributed to OIL of the OA is located at 103.2 eV in Fig. 1(b). This is consistent with the results in Si 2p core-level spectra taken at $h\nu=560$ eV. However, a broad peak attributed to OIL of the HA is located at 102.9 eV in Fig. 1(b). This binding energy is 0.8 eV higher than that in Si 2p core-level spectra taken at $h\nu=560$ eV [Fig. 1(a)]; that is, as the probing depth becomes shallow, Si 2p peak attributed to OIL in the HA is shifted to the high binding energy side. In this regard, we might remember Kato *et al.*¹⁴ and Opila *et al.*¹⁵ reported that as Hf concentration increases in $\text{Hf}_x\text{Si}_{1-x}\text{O}_2$ compounds, the Si 2p core-level shifts to the lower binding energy side. This shift can be explained by the higher ionicity of Hf—O bonding compared to Si—O bonding. In the present case, the Si—O bond is about 50% ionic, whereas the Al—O bond is 60%–70% ionic.¹⁶ Hence, we expect that if the OIL in the HA is Al silicate, the Si 2p peak must shift to the lower binding energy side as $h\nu$ decreases because we are probing closer to AlO_2 layer and Al concentration in the silicate should increase. However, the Si 2p peak in the HA was found to shift to the higher-energy side close to that in SiO_2 as the probing depth became shallow. This result proves that the OIL in the HA is not Al silicate. Instead, this Si 2p peak shifts toward the higher binding energy side can be explained by the formation of SiO_2 and SiO_x suboxide layer in the $\text{Al}_2\text{O}_3/\text{Si}$ (100) interface. In fact, the existence of Si suboxides at the SiO_2/Si interface has long been established by the Si 2p core-level XPS study.¹⁷

For quantitative analyses of the oxidation chemical states of the HA interface (we focused on the analysis of HA, because it is clear that the OIL of OA consists of mainly SiO_2 as mentioned above), Si 2p spectra were fitted with four higher binding energy components in addition to the bulk Si contribution, that is, the Si^{4+} component for SiO_2 and three intermediate components for the suboxide species of Si^{1+} — Si^{3+} . These oxidation states were found to show chemical shifts of 1.0, 1.8, 2.62, and 3.7 eV for Si^{1+} — Si^{3+} and Si^{4+} , respectively, from the bulk Si 2p binding energy of 99.3 eV. These values are in agreement with those reported for a thermally grown SiO_2/Si interface.^{17,18} From the relative intensity of each Si 2p oxidation state, we can also conclude that the oxidation chemical state consists mainly of Si_2O_3 and SiO_2 . In addition, by comparing Figs. 1(a) and 1(b), we can see that the Si^{4+} component is enhanced at a more surface-sensitive measurement condition of the photon energy ($h\nu=210$ eV). This means that the SiO_2 layer is on top of Si_2O_3 suboxide layers. Closer to Al_2O_3 layer, more

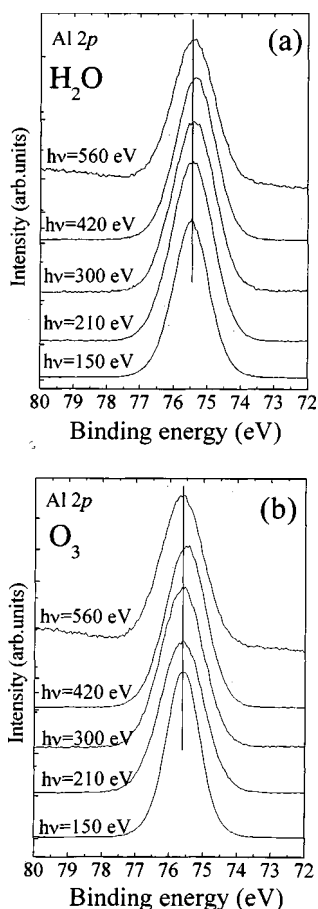


FIG. 2. Al 2*p* core-level spectra taken at $h\nu=560, 420, 300, 210,$ and 150 eV for the (a) HA and (b) OA samples.

Si—O bond is distributed. Thus, Si 2*p* peak shifts toward the higher-energy side, as $h\nu$ decreases. This result is similar to that of x-ray photoelectron spectra of thermally grown SiO₂/Si film with a transition region: A suboxide (Si¹⁺, Si²⁺, and Si³⁺) layer.^{17,18} We identify the OIL of both the OA and the HA as consisting of SiO₂ and SiO_{*x*} suboxide.

Figure 2 shows Al 2*p* core-level spectra taken at $h\nu=560, 420, 300, 210,$ and 150 eV for both the OA and the HA. The IMFP for Al 2*p* peak is 5.5 and 12.5 Å for $h\nu=210$ and 560 eV spectra, respectively.¹³ As $h\nu$ decreases, the probing depth becomes shallow and the region closer to the surface is sampled. The binding energies of Al 2*p* peaks were positioned at 17.59 ± 0.04 eV and 17.43 ± 0.04 eV for the OA and the HA, respectively, and the full width half maximum of Al 2*p* spectra for both the OA and the HA is 1.3 ± 0.1 eV without showing any shift or change with the probing depth. This result is quite significant. Wannaparhun *et al.*¹⁰ reported that the binding energy of Al 2*p* in Al silicate is located at 0.6–1.0 eV higher-energy side than that in pure Al₂O₃. Hence, our present result means that both the OA and HA have no Al—O—Si bonding states in the Al₂O₃ layer. We note Guha *et al.*¹⁹ reported the interdiffusion of Al with the Si substrate at temperatures above 900 °C. However, there was no Al 2*p* peak showing interdiffusion of Al with the Si substrate and formation of Al silicide in our present data Fig. 2. This is probably due to the relatively low deposition temperature of 300 °C in our ALD-grown sample.

Additionally, from O 1*s* x-ray photoelectron spectra of

both the HA and OA (not shown here), we confirmed that the HA surely includes much —OH species in it as reported by many groups.^{4,6,20} However, from Si 2*p* x-ray photoelectron spectra, these OH species rarely contribute to a formation of the OIL relative to O₃. More Si oxidation in OA is attributed to the higher oxidizing power of O₃ compared to that of the H₂O; $\Delta H_f^\circ(25^\circ\text{C})$ of H₂O(*g*) and O₃(*g*) is -241.82 and 142.7 kJ/mol, respectively.

In summary, we investigated the depth profile of chemical states of an Al₂O₃/Si interface using nondestructive photon energy-dependent HRXPS. We found that no Al silicate was formed at the interface contrary to the model proposed previously where the excess oxygen (such as —OH species) was presumed to react with Si to finally form a silicate. We instead propose from the HRXPS of Al 2*p*, O 1*s*, and Si 2*p* core levels and their depth-profile studies that the chemical states of the HfO₂/Si interface mainly consist of SiO₂ and Si₂O₃, and these oxidation chemical states are rather dependent on the oxidant; the greater the oxidizing power of an oxidant, the greater the oxidation number of Si. These results will contribute to fully identifying the chemical states with the thermal evolution of the Al₂O₃/Si interface.

This work was supported in part by the BK-21 program of the School of Physics, Seoul National University, and the Center for Strongly Correlated Materials Research (CSCMR) through the Korean Science and Engineering Foundation (KOSEF). The support of Samsung Electronics is also gratefully acknowledged.

- ¹A. I. Kingon, J.-P. Maria, and S. K. Streiffer, *Nature (London)* **406**, 1032 (2000).
- ²G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.* **89**, 5243 (2001).
- ³R. S. Johnson, G. Lucovsky, and I. Baumvol, *J. Vac. Sci. Technol. A* **19**, 1353 (2001).
- ⁴T. M. Klein, D. Niu, W. S. Epling, W. Li, D. M. Mayer, C. C. Hobbs, R. I. Hedge, I. J. R. Baumvol, and G. N. Parsons, *Appl. Phys. Lett.* **75**, 4001 (1999).
- ⁵H. Cho, D. Park, K. Lim, J. Ko, I. Yeo, J. W. Park, and J. Roh, *Appl. Phys. Lett.* **80**, 3177 (2002).
- ⁶V. Misra, G. Lucovsky, and G. Parsons, *Mater. Res. Bull.* **27**, 212 (2002).
- ⁷M. Copel, E. Cartier, E. P. Guha, N. Bojarczuk, and M. Poppeller, *Appl. Phys. Lett.* **78**, 2671 (2001).
- ⁸M. Kundu, N. Miyata, and M. Ichikawa, *Appl. Phys. Lett.* **78**, 1517 (2001).
- ⁹C. D. Wagner, D. E. Passoja, H. F. Hillery, T. G. Kinisky, H. A. Six, W. T. Jansen, and J. A. Taylor, *J. Vac. Sci. Technol.* **21**, 933 (1982).
- ¹⁰S. Wannaparhun, S. Seal, and V. Desai, *Appl. Surf. Sci.* **185**, 183 (2002).
- ¹¹A. C. Dillon, A. W. Ott, J. D. Way, and S. M. George, *Surf. Sci.* **322**, 230 (1995).
- ¹²J. B. Kim, D. R. Kwon, K. Chakrabarti, K. Y. Oh, J. H. Lee, and C. Lee, *J. Appl. Phys.* **92**, 6739 (2002).
- ¹³S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.* **17**, 911 (1991).
- ¹⁴H. Kato, T. Nango, T. Miyagawa, T. Katagiri, K. S. Seol, and Y. Ohki, *J. Appl. Phys.* **92**, 1106 (2002).
- ¹⁵R. L. Opila, G. D. Wilk, M. A. Alam, R. B. van Dover, and B. W. Busch, *Appl. Phys. Lett.* **81**, 1788 (2002).
- ¹⁶J. Robertson, *Mater. Res. Bull.* **27**, 217 (2002).
- ¹⁷G. Hollinger and F. J. Himpsel, *Appl. Phys. Lett.* **44**, 93 (1984).
- ¹⁸J. H. Oh, H. W. Yeom, Y. Hagimoto, K. Ono, M. Oshima, N. Hirashita, M. Nywa, A. Toriumi, and A. Kakizaki, *Phys. Rev. B* **63**, 205310 (2001).
- ¹⁹S. Guha, E. P. Gusev, H. Okom-Schmidt, M. Copel, L.-Å. Ragnarsson, N. A. Bojarczuk, and P. Ronsheim, *Appl. Phys. Lett.* **81**, 2956 (2002).
- ²⁰O. Renault, L. G. Gosset, D. Rouchon, and A. Ermoliev, *J. Vac. Sci. Technol. A* **20**, 1867 (2002).