



Nucleation Behavior of Atomic Layer Deposited SiO₂ for Hf-Silicate Films

Kwun-Bum Chung,^a W. J. Lee,^b C. Y. Kim,^b Mann-Ho Cho,^{b,z} and Dae Won Moon^c

^aDepartment of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202, USA

^bInstitute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea

^cDivision of Advanced Technology, Korea Research Institute of Standards and Science, Daejeon 305-340, Korea

The nucleation and growth of SiO₂, as a function of surface condition, was investigated using in situ medium-energy ion-scattering analysis. The amount of SiO₂ required for saturation on the thermal oxide and on the chemical oxide was found to be 0.75 and 3.84×10^{14} Si/cm², respectively. The growth of SiO₂ on the initial HfO₂ surface increased as a function of HfO₂ coverage and growth when the HfO₂ coverage over 1 monolayer (ML) becomes saturated when the coverage of SiO₂ is $\sim 7 \times 10^{14}$ Si/cm², which corresponds to a coverage of 1 ML SiO₂. The nucleation of SiO₂ greatly depends on the initial surface conditions. In addition, the nucleation of SiO₂ has a tendency to become saturated, regardless of the initial surface conditions.
© 2009 The Electrochemical Society. [DOI: 10.1149/1.3098496] All rights reserved.

Manuscript submitted December 9, 2008; revised manuscript received February 9, 2009. Published March 23, 2009.

The aggressive scaling of complementary metal-oxide-semiconductors has led to the situation where the fundamental thickness of the Si-based oxide, when used as a gate oxide, has reached the limit.¹ High dielectric oxides are considered to be attractive alternatives to Si-based oxides due to their inherent increased thickness and lower leakage current.² Among the candidates currently under consideration, HfO₂ was thought to be a promising material for replacing Si-based oxides due to its high dielectric constant (~ 25) and thermodynamic stability when in direct contact with Si. However, HfO₂ films have a tendency to readily crystallize, and channel mobility is relatively low because of its high interfacial trap charge compared to SiO₂.^{3,4} In order to increase the crystallization temperature and improve the thermal stability of this material when it is in contact with Si, recent studies have focused on the Hf-silicate gate stack, which shows a channel mobility close to the universal value of SiO₂ and superior interfacial stability.^{5,6}

The atomic layer deposition (ALD) technique has recently been applied to the growth of several high-dielectric oxides because of its various merits as a more promising technique compared to conventional deposition methods. In the ALD technique, cycles comprised of alternating source pulses and purge sequences are applied repeatedly. Each source precursor also undergoes a self-limiting reaction on the surface.⁷ Therefore, it is possible to deposit films with excellent properties, which allow highly conformal growth with accurate thickness and uniform coverage at the atomic level.⁸ A number of studies have attempted to develop an understanding of the mechanism by which high dielectric oxides such as HfO₂ and Al₂O₃ occurs, including the initial growth stage when the ALD is used.⁹⁻¹² However, analyses of the growth behavior of ternary-oxide-like Hf-silicate films (Hf_xSi_yO_{1-x-y}) is a difficult task due to the complex reaction combinations of ternary systems and the lack of appropriate characterization tools. In a previous study we reported on the growth kinetics of ALD Hf-silicate films using Hf[N(CH₃)(C₂H₅)₄] and SiH[N(CH₃)₂]₃ precursors. We concluded that the nucleation of HfO₂ is dependent on the remnant Si-H bonds after the growth of ALD SiO₂.¹³ Even if the previous report could have investigated the growth kinetics of ALD Hf-silicate films as a function of the ratio of alternate deposition cycles between HfO₂ and SiO₂, the nucleation and growth behavior of SiO₂ for Hf-silicate films still remain the main parameters in terms of our understanding of the growth mechanism of Hf-silicate films. This is primarily because the ALD growth of Hf-silicate films involves the alternating deposition of HfO₂ and SiO₂. In addition, a systematic approach to the ALD growth mechanism for Hf-silicate films is a very important issue in terms of the

development of alternatives to SiO₂, because the initial growth of the dielectric layer determines the qualities of a film and the interface.

The focus of the present study was on the nucleation behavior of ALD SiO₂ as a function of various initial surface conditions. The nucleation characteristics of SiO₂ were investigated using in situ medium energy ion scattering (MEIS) analysis as a function of the number of deposition cycles of SiO₂.

A p-type Si(100) substrate was chemically cleaned by the RCA method and a dilute HF solution to remove surface contamination and native oxides. In order to investigate the nucleation and growth of SiO₂ as a function of surface conditions, a thermal oxide surface, a chemical oxide surface, and the former surfaces that had been treated for different cycles (1–5 cycles) of HfO₂ on the thermal oxide were prepared after chemically cleaning the surface. The thermal SiO₂ with a thickness of ~ 1 nm was grown using rapid thermal oxidation with the assistance of an oxygen plasma. The chemical SiO₂ was formed by the RCA method after the complete removal of native oxides through RCA cleaning and immersion in an HF solution. HfO₂ layers, treated using different cycles (1–5 cycles), were grown using an ALD system which has a vertical warm-wall reactor with a showerhead and a heat susceptor. The HfO₂ layers were deposited at a temperature of 280°C using tetrakis(ethylmethylamino)hafnium {Hf[N(CH₃)(C₂H₅)₄]} and H₂O, respectively, as the reacting sources for Hf and O. The sequential deposition of SiO₂ using tris(dimethylamino)silane {SiH[N(CH₃)₂]₃} as a function of the

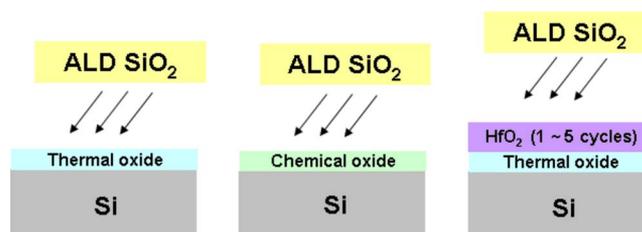
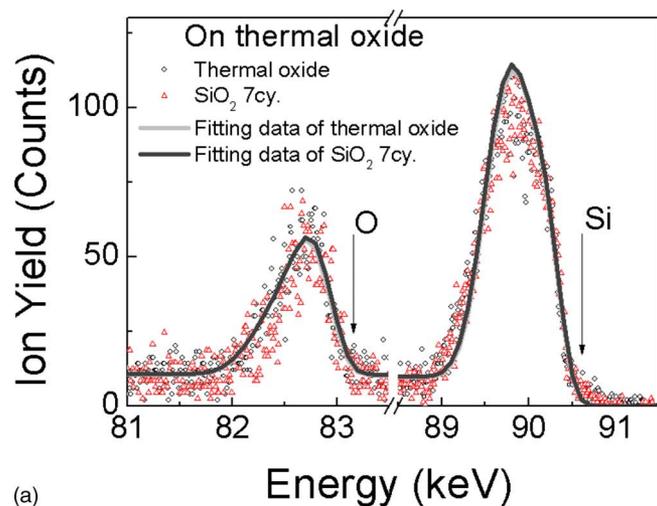
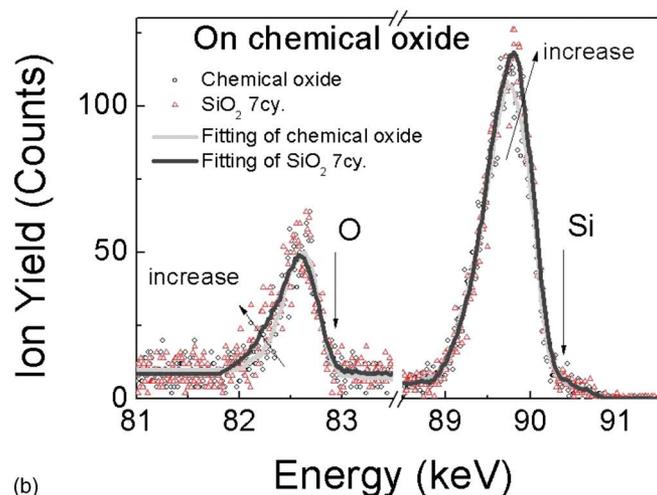


Figure 1. (Color online) Schematics for experimentally investigating the nucleation of SiO₂ for various surface conditions: The following surface conditions were considered: thermal oxide, chemical oxide, and the initial HfO₂ surface as a function of HfO₂ coverage. The ALD deposition of SiO₂ as a function of SiO₂ cycles (1–7 cycles) was immediately performed for the different surface conditions. Immediately after the deposition of sequential SiO₂ (1–7 cycles), the samples were analyzed by in situ MEIS measurements. MEIS spectra of the thermal oxide were used as a reference for comparison to the differences between the initial surface conditions after the sequential deposition of SiO₂.

^z E-mail: mh.cho@yonsei.ac.kr



(a)



(b)

Figure 2. (Color online) MEIS energy spectra for the nucleation of SiO_2 (a) on the thermal oxide and (b) on the chemical oxide as a function of SiO_2 cycles. The dots are raw experimental results and the lines are fitting data using the Kido program. The arrows in Fig. 2b represent the increases in the coverage of Si and O after seven cycles of SiO_2 deposition.

number of SiO_2 cycles (1–7 cycles) was immediately performed for the different surface conditions. Details of the conditions used for the ALD process have been described in a previous report as well.¹³ Immediately after the completion of the sequential SiO_2 (1–7 cycles), the samples were transferred to a MEIS analysis chamber using an in situ transfer system. The pressure of the MEIS chamber and the transfer system were maintained below $\sim 5 \times 10^{-10}$ and $\sim 5 \times 10^{-8}$ Torr, respectively. Due to maintaining the ultrahigh-vacuum conditions during the MEIS measurements and in the transfer system after each ALD SiO_2 deposition cycle, the presence of undesirable surface contaminants and modifications cannot be completely excluded. The experimental schematics for investigating the nucleation of SiO_2 for various surface conditions are depicted in Fig. 1.

The extent of coverage after each ALD cycle of SiO_2 was measured using in situ MEIS. This analysis is capable of providing a quantitative measurement and good depth resolution because the MEIS measurement, which uses a medium-energy ion beam (~ 100 keV), permits thin films to be quantitatively examined with a high-depth resolution of ~ 3 Å.¹⁴ The MEIS measurement was carried out using the double-alignment condition, which eliminates contributions from crystalline Si substrates. The incident beams were aligned in the [111] direction and the scattered beams were

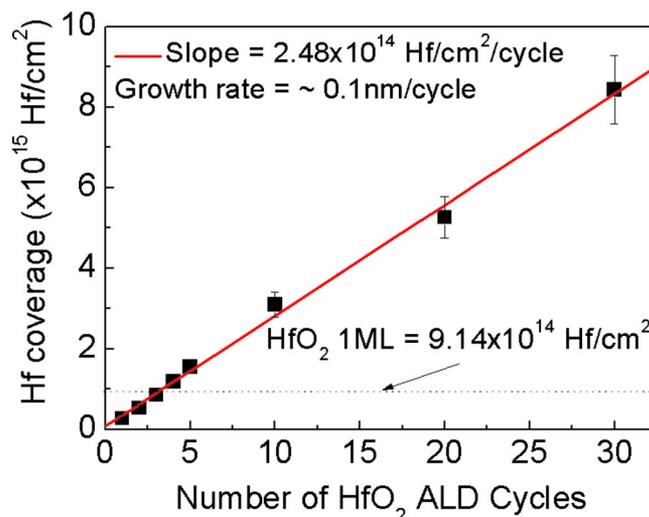


Figure 3. (Color online) Hf coverage on the thermal oxide according to the number of HfO_2 cycles used. The slope with 2.48×10^{14} $\text{Hf}/\text{cm}^2/\text{cycle}$ denotes the growth rate of HfO_2 , which can be converted into ~ 1 Å/cycle.

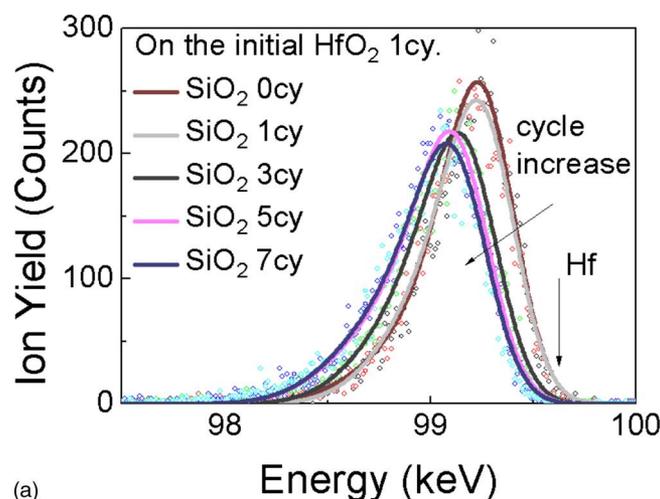
aligned along the [001] direction with a scattering angle of 125° . During the MEIS measurement, an ion beam with a small area of 5×10^{-3} cm^2 was used to scan the wide sample surface and the dose of the proton beam was maintained below $\sim 10^{15}$ cm^{-2} to minimize damage caused by the concentrated impact of the ion beam.

Figure 2a shows MEIS spectra of SiO_2 nucleated on the thermal oxide as a function of sequential SiO_2 cycles. Even after seven ALD SiO_2 cycles, the coverage of the deposited SiO_2 is similar to that of initially thermally oxidized SiO_2 because the area of the Si peak and width of the O peak after seven cycles are almost the same as that for the thermal oxide. This means that the increase in coverage by the deposited SiO_2 on the thermal oxide is a very small amount. The calculated amount of SiO_2 deposited on the thermal oxide is $\sim 0.75 \times 10^{14}$ Si/cm^2 , as calculated using the Kido fitting program.¹⁵ The changes in the coverage of the deposited SiO_2 on the chemical oxide after seven cycles is higher than that on the thermal oxide, as shown by the increases in the Si and O peaks in Fig. 2b. The calculated coverage of the deposited SiO_2 on the chemical oxide is 3.84×10^{14} Si/cm^2 , which is much higher than the coverage of SiO_2 on the thermal oxide. We can thus conclude that the initial surface conditions, such as the thermal oxide and the chemical oxide, affect the nucleation of SiO_2 on those surfaces.

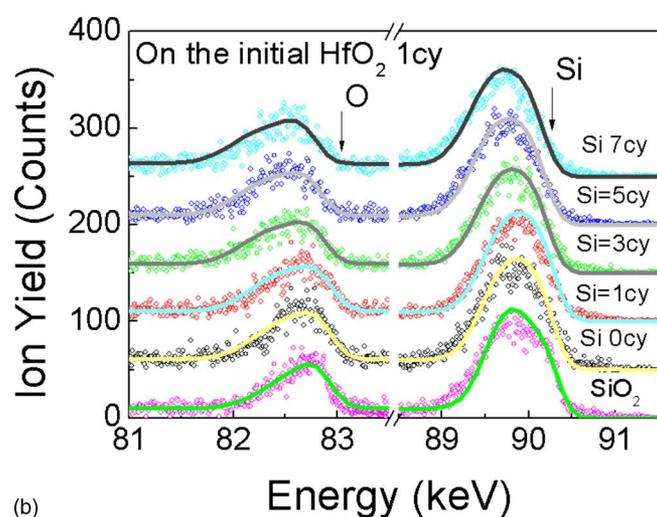
In order to investigate the nucleation of SiO_2 as a function of initial HfO_2 coverage, HfO_2 layers were prepared on the thermal oxide using different cycles (1–5 cycles). The coverage of HfO_2 using 1–2 cycles is less than 1 monolayer (ML), and for those prepared using more than three cycles of HfO_2 show a coverage of over 1 ML of HfO_2 , as evidenced by MEIS measurement, as shown in Fig. 3. From the slope of a plot of HfO_2 coverage vs the number of ALD HfO_2 cycles, the growth rate can be calculated to be ~ 1 Å/cycle, in good agreement with previously reported results.^{12,d}

The MEIS energy spectra after each ALD cycle of SiO_2 on the initial coverage of HfO_2 using one cycle are shown in Fig. 4. As the cycles of deposited SiO_2 are increased, the leading edge of the Hf peak moves backward after three cycles of SiO_2 , as shown in Fig. 4a. Moreover, the shape and movement of the Hf peak are saturated after five cycles of SiO_2 . The width of the O peak is also saturated as

^d The growth rate of HfO_2 was calculated by the slope of Hf coverage. The $\sim 90\%$ density (2.49×10^{15} Hf atoms/ cm^2 nm) of the theoretical crystalline HfO_2 molecular density (2.77×10^{15} Hf atoms/ cm^2 nm) was used because the deposited HfO_2 films with an amorphous structure have a lower density than those with a crystalline structure.



(a)

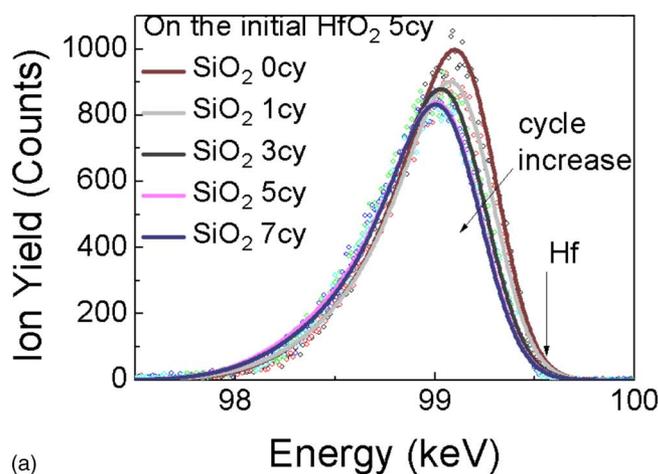


(b)

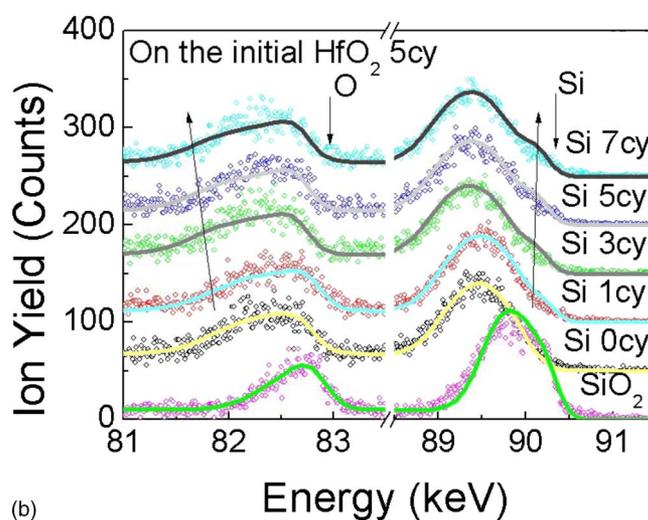
Figure 4. (Color online) MEIS energy spectra for nucleation of SiO₂ on the initial coverage of HfO₂ with one cycle in the energy regions of (a) Hf and (b) Si, O. The dots denote raw experimental results and the lines are data fitted using the Kido program. A HfO₂ layer was grown on the thermal oxide using one cycle, which resulted in coverage of HfO₂ below 1 ML. In order to compare the thermal oxide and the nucleation of SiO₂ on the initial coverage of HfO₂ using one cycle, MEIS energy spectra of the thermal oxide are plotted in the energy region of Si and O.

a function of sequential SiO₂ cycles. However, the extent of coverage of the deposited SiO₂ on the initial coverage of HfO₂ using one cycle is increased by only a small amount. The use of one cycle of HfO₂ does not cover the entire thermal oxide surface at the bottom, considering the fact that the coverage of HfO₂ is below 1 ML in Fig. 3. Therefore, these results indicate that most of the deposited SiO₂ can be grown on local grains of HfO₂, because growth of SiO₂ on the thermal oxide proceeds readily, as shown by the results in Fig. 2a and the movement of the leading edge of the Hf peak directly reflects the overlayer on the initial HfO₂ surface.

Figure 5 represents the MEIS energy spectra after each ALD cycle of SiO₂ on the initial coverage of HfO₂ using five cycles. The outstanding difference from the previous results is the changes in the Si peak. The leading edge of the Si peak prior to the additional deposition of SiO₂ moves backward due to the coverage of HfO₂ with five cycles, which corresponds to quantities of HfO₂ over 1 ML. Consequently, the thermal oxide layer at the bottom is completely passivated by the initial coverage of HfO₂ when five cycles are used. In the case of one cycle of SiO₂, a small shoulder in the Si



(a)



(b)

Figure 5. (Color online) MEIS energy spectra for the nucleation of SiO₂ on the initial coverage of HfO₂ using five cycles in the energy regions of (a) Hf and (b) Si, O. The dots denote raw experimental results and the lines are data fitted using the Kido program. The HfO₂ layer was grown on the thermal oxide using five cycles, resulting in a HfO₂ coverage of over 1 ML. In order to compare between the thermal oxide and the nucleation of SiO₂ on the initial coverage of HfO₂ using one cycle, MEIS energy spectra for the thermal oxide are plotted in the energy region of Si and O.

peak can be seen at the leading edge, around 90.2 eV. It was possible to measure a HfO₂ layer of over 1 ML because of the differences between the thermal oxide and overlayer of deposited SiO₂. The shoulder of the Si peak increases as a function of the number of SiO₂ cycles used, and the amount of SiO₂ deposited is much higher than that for the initial coverage of HfO₂ using one cycle. In addition, the deposited SiO₂ becomes saturated after five cycles of SiO₂, as evidenced by the shoulder on the Si peak. The other noteworthy finding is that the leading edge of the Hf peak no longer moves after five cycles of SiO₂, although a slight change in the Hf peak can be detected as the cycles of SiO₂ are increased. This slight variation in the Hf peak is caused by the effective blocking of the SiO₂ overlayer. The increment in the width of the O peak by the deposition of SiO₂ is also larger than that of the initial one cycle of HfO₂. Moreover, the width of the O peak becomes saturated after five cycles of SiO₂, as shown by the changes in the Hf peak.

For a more detailed interpretation of the nucleation and growth of SiO₂ as a function of surface conditions, Fig. 6 shows plots of (a) Si and (b) O coverage for the SiO₂ overlayer, and Tables I and II summarize Si and O coverage depending on the initial surface con-

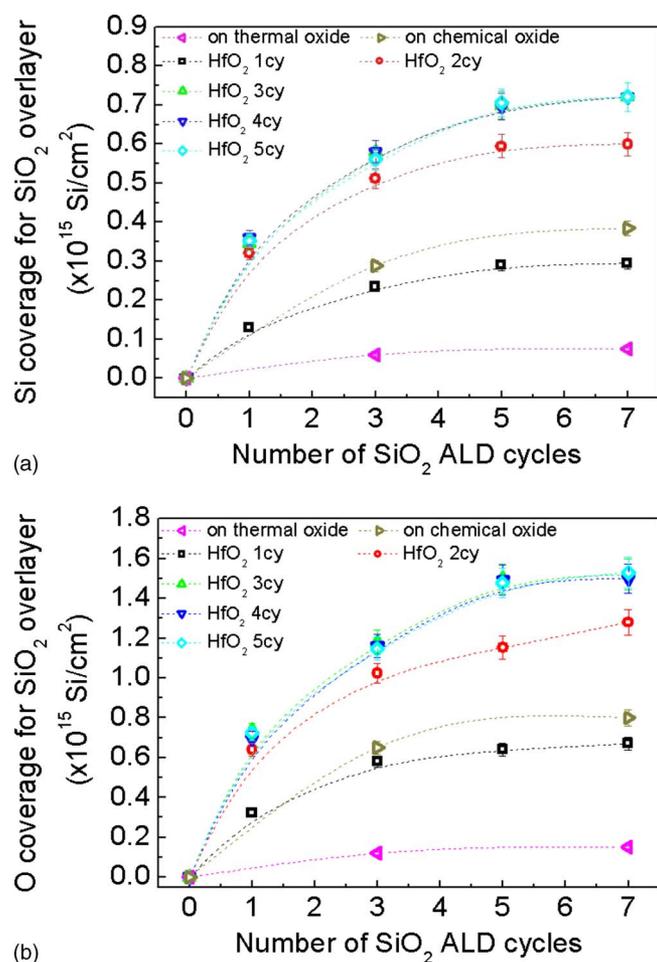


Figure 6. (Color online) (a) Si and (b) O coverage for the SiO₂ overlayer on the various surface conditions as a function of the number of SiO₂ deposition cycles. Uncertainties of 5% on the calculated coverage determined by the fits are included with error bars.

ditions as a function of the number of SiO₂ deposition cycles. Figure 6 includes uncertainties of 5% on the calculated coverage, as determined by the fits. Interestingly, the growth behavior of SiO₂ depends on both the surface conditions and the initial HfO₂ coverage. The coverage of Si and O on the deposited SiO₂ on the chemical oxide is higher than that on the thermal oxide. Up to three cycles of initial HfO₂, in which the HfO₂ coverage corresponds to 1 ML, the Si and O coverage of the deposited SiO₂ increases as a function of the number of SiO₂ deposition cycles used. However, the amounts of Si and O coverage of the deposited SiO₂ are similar over three cycles of initial HfO₂ (1 ML). Another remarkable finding is that the Si and

O coverage of the deposited SiO₂ becomes saturated after five cycles of SiO₂, regardless of the surface conditions and the initial coverage of HfO₂. The saturated Si and O coverage on the chemical oxide surface are 3.84 and 7.7×10^{14} O/cm², which are five times the values for the thermal oxide surface. Moreover, the value for O coverage is twice that for Si coverage, which are reasonable values, because the stoichiometry of SiO₂ is 1 Si atom to 2 O atoms. The saturated Si coverage on the initial coverage of HfO₂ over 1 ML is $\sim 7.21 \times 10^{14}$ Si/cm², which is an SiO₂ layer of 1 ML with a thickness of ~ 3.5 Å.^e

The nucleation behavior of SiO₂ for the various surface conditions can be explained as follows: The main discrepancy in SiO₂ growth could be caused by differences in surface conditions, such as the thermal oxide, the chemical oxide, and the initial HfO₂ coverage on the thermal oxide. Green et al. reported that the growth of an atomic layer of deposited HfO₂ was dependent on the initial surface conditions.¹⁶ The growth of HfO₂ on the H-terminated surface was nonlinear, with an initially slow deposition rate, whereas that of HfO₂ on the chemical oxide was linear. Furthermore, the presence of OH species is very important to the nucleation and growth of ALD, when halide and amide-type precursors are used.¹⁷ The key point through previously reported papers was differences in OH density on the initial surface. The density of OH on the thermal oxide surface is approximately $\sim 1 \times 10^{14}$ OH/cm² and that on the chemical oxide surface is $4\text{--}7 \times 10^{14}$ OH/cm², which varied slightly, depending on the measurement conditions.¹⁸ The OH density on the HfO₂ over 1 ML, calculated based on a theoretical model, is 9.2×10^{14} OH/cm².¹⁹ These differences in OH density are consistent with our results for saturated Si and O coverages for nucleation behavior as a function of the various surface conditions used. In addition, the characteristics of saturated SiO₂ coverage, regardless of the initial surface conditions, could be due to the prevention of the nucleation of the Si precursor by remnant Si–H bonds after the ALD cycle of SiO₂, as we reported in our earlier study.¹³

Finally, a proposed model for the growth of SiO₂ for various surface conditions is shown in Fig. 7 based on the experimental results reported herein. The growth models can be classified into three representative cases, namely, HfO₂ = 0 ML (only thermal oxide), HfO₂ < 1 ML, and HfO₂ > 1 ML. The main point is that the preferred growth of SiO₂ would be expected to occur on the initial HfO₂ surface with a higher OH density, rather than on the thermal oxide.

In conclusion, the nucleation and growth of SiO₂ as a function of surface conditions were investigated using in situ MEIS analysis. The saturated coverage of SiO₂ on thermal oxide and chemical oxide was found to be 0.75 and 3.84×10^{14} Si/cm², respectively. The growth of SiO₂ on the initial HfO₂ surface increased as a function of HfO₂ coverage, and when the coverage of HfO₂ reaches coverage over 1 ML saturation occurs, and the coverage of SiO₂ is $\sim 7 \times 10^{14}$ Si/cm², which corresponds to a coverage of 1 ML SiO₂. The

^e The thickness of SiO₂ was calculated by Si or O coverage. The molecular density of SiO₂ is 2.2×10^{15} Si atoms/cm² nm.

Table I. Summary of the Si coverage depending on the initial surface conditions as a function of the number of SiO₂ deposition cycles.

Underlayer condition	Si coverage (10^{15} Si/cm ²)			
	SiO ₂ 1 cycle	SiO ₂ 3 cycles	SiO ₂ 5 cycles	SiO ₂ 7 cycles
Initial HfO ₂ = 0 cycle (thermal oxide)	—	0.06	—	0.075
Initial HfO ₂ = 1 cycle	0.13	0.23	0.29	0.29
Initial HfO ₂ = 2 cycles	0.32	0.51	0.59	0.60
Initial HfO ₂ = 3 cycles	0.35	0.58	0.70	0.72
Initial HfO ₂ = 4 cycles	0.36	0.58	0.69	0.72
Initial HfO ₂ = 5 cycles	0.35	0.56	0.71	0.72
Chemical oxide	—	0.29	—	0.38

Table II. Summary of O coverage as a function of initial surface condition with the number of SiO₂ deposition cycles used.

Underlayer condition	O coverage (10^{15} Si/cm ²)			
	SiO ₂ 1 cycle	SiO ₂ 3 cycles	SiO ₂ 5 cycles	SiO ₂ 7 cycles
Initial HfO ₂ = 0 cycle (thermal oxide)	—	0.12	—	0.15
Initial HfO ₂ = 1 cycle	0.32	0.58	0.64	0.67
Initial HfO ₂ = 2 cycles	0.64	1.02	1.15	1.28
Initial HfO ₂ = 3 cycles	0.74	1.18	1.50	1.52
Initial HfO ₂ = 4 cycles	0.70	1.16	1.49	1.54
Initial HfO ₂ = 5 cycles	0.72	1.15	1.48	1.53
Chemical oxide	—	0.65	—	0.77

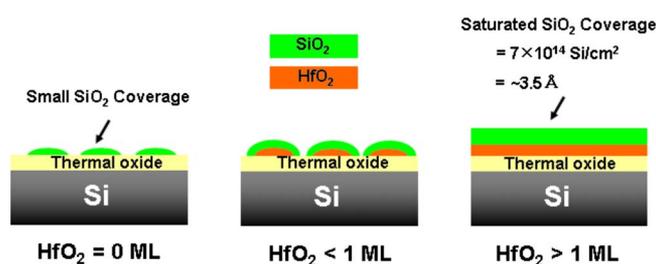


Figure 7. (Color online) Proposed models for the growth of SiO₂ on various surface conditions as a function of initial HfO₂ coverage. The growth models are divided into three representative cases: HfO₂ = 0 ML (only thermal oxide), HfO₂ < 1 ML, and HfO₂ > 1 ML.

nucleation of SiO₂ could be influenced by initial surface conditions, such as the OH density on the surface. In addition, the disturbance of nucleation by remnant Si–H bonds after the ALD growth of SiO₂ affects the saturated coverage of SiO₂ (1 ML).

Acknowledgment

This work was partially supported by the National Program for Tera-level Nanodevices of the Ministry of Education, Science, and Technology as one of the 21 Century Frontier Programs.

Yonsei University assisted in meeting the publication costs of this article.

References

1. A. I. Kingon, J. P. Maria, and S. K. Streiffer, *Nature (London)*, **406**, 1032 (2000).
2. G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.*, **89**, 5243 (2001).
3. B. H. Lee, L. Kang, R. Nieh, W.-J. Qi, and J. C. Lee, *Appl. Phys. Lett.*, **76**, 1926 (2000).
4. M.-H. Cho, Y. S. Roh, C. N. Whang, K. Jeong, H. J. Choi, S. W. Nam, D.-H. Ko, J. H. Lee, N. I. Lee, and K. Fujihara, *Appl. Phys. Lett.*, **81**, 472 (2002).
5. H. Watanabe, M. Saitoh, N. Ikarashi, and T. Tatsumi, *Appl. Phys. Lett.*, **85**, 449 (2004).
6. G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.*, **87**, 484 (2000).
7. A. W. Ott, J. W. Klaus, J. M. Johnson, and S. M. George, *Thin Solid Films*, **292**, 135 (1997).
8. M. Ritala and M. Leskela, in *Handbook of Thin Film Materials*, Vol. 1, H. S. Nalwa, Editor, Academic, New York (2002).
9. M. M. Frank, Y. J. Chabal, and G. D. Wilk, *Appl. Phys. Lett.*, **82**, 4758 (2003).
10. M.-T. Ho, Y. Wang, R. T. Brewer, L. S. Wielunski, Y. J. Chabal, N. Moumen, and M. Boleslawski, *Appl. Phys. Lett.*, **87**, 133103 (2005).
11. H. S. Chang, H. Hwang, M.-H. Cho, and D. W. Moon, *Appl. Phys. Lett.*, **86**, 031906 (2005).
12. K. B. Chung, C. N. Whang, H. S. Chang, D. W. Moon, and M.-H. Cho, *J. Vac. Sci. Technol. A*, **25**, 141 (2007).
13. K. B. Chung, M.-H. Cho, D. W. Moon, D. C. Suh, D.-H. Ko, U. Hwang, and H. J. Kang, *Electrochem. Solid-State Lett.*, **10**, G1 (2007).
14. E. P. Gusev, H. C. Lu, T. Gustafsson, and E. Garfunkel, *Phys. Rev. B*, **52**, 1759 (1995).
15. Y. Kido and T. Koshikwa, *J. Appl. Phys.*, **67**, 187 (1990).
16. M. L. Green, M.-Y. Ho, B. Busch, G. D. Wilk, T. Sorsch, T. Conard, B. Brijs, W. Vandervorst, P. I. Räisänen, D. Muller, et al., *J. Appl. Phys.*, **92**, 7168 (2002).
17. T. Suntola, *Surf. Sci.*, **100/101**, 391 (1996).
18. S. Haukka and T. Suntola, *Interface Sci.*, **5**, 119 (1985).
19. R. L. Puurunen, *J. Appl. Phys.*, **95**, 4777 (2004).