Electronic Materials Letters, Vol. 5, No. 4 (2009), pp. 187-190
DOI: 10.3365/eml.2009.12.187

Effects of Initial Growth Mode on the Electrical Properties of Atomic-Layer-deposited HfO_2 Films

Hyo Sik Chang*

Energy and Semiconductor Center, Korea Institute of Ceramic Engineering and Technology,
30 Gyeongchung Rd., Sindun-myeon, Icheon-si, Gyeonggi 467-843, Korea

The effects of the initial growth mode on the electrical properties of atomic layer deposition-grown HfO_2/SiO_2/Si metal-oxide-semiconductor devices were investigated using in-situ medium energy ion scattering (MEIS). MEIS results clearly showed that wet chemical oxide has a more layer-like growth at an initial growth stage than a thermal oxide starting surface. On the high OH group surface, less shifting of the flat band voltage and mininal hysteresis in the C-V curve was observed primarily due to structural uniformity in the HfO_2 dielectric. The method of surface preparation directly influenced the growth morphologies. These morphologies at the initial growth stage strongly affected C-V quality and charge trapping.

Keywords: atomic layer deposition, medium-energy ion scattering, initial growth, $HfCl_4$, HfO_2

1. INTRODUCTION

With aggressive downscaling of critical dimensions in complementary metal oxide semiconductor (CMOS) devices, high dielectric constant dielectrics are required for sub-100 nm metal-oxide-semiconductor (MOS) structures because conventional SiO_2 film is too thin to minimize the tunneling current. Replacements by thicker high-k layers to reduce direct tunneling have been investigated as alternative gate dielectric materials. Among the various materials to be considered, HfO_2 and its silicates appear to be the most promising candidates because they meet not only the dielectric constant but are also expected to provide thermal stability.[1-4]

Initial growth of HfO_2 is critical for the development of alternatives for SiO_2 because dielectric layer properties depend on initial growth and interface controllability. Therefore, it is important to understand the initial growth stage during the atomic layer deposition (ALD) process of hafnium oxide. In our previous study, we showed that island-like growth occurred at initial HfO_2 growth and that these islands merged into a continuous atomic layer with increasing ALD cycles.[5]

In the current study, we examined the effects of the initial growth mode on the electrical properties of atomic-layer deposited HfO_2 and the role of the starting surface using in situ medium energy ion scattering (MEIS), which is a high resolution version of Rutherford backscattering spectroscopy, RBS, with a depth resolution of ~ 3Å.[6,7]

*Corresponding author: hschang@kicet.re.kr

2. EXPERIMENTS

HfO_2 films were deposited on various Si surfaces by a showerhead-type ALD at a temperature of 300. After standard cleaning, samples were prepared with various starting surfaces: (1) radical oxygen treated Si with low-temperature treatment (thermal oxide); (2) HF-treated Si (H-terminated Si); and (3) wet chemical oxide grown by SC 1 solution (chemical oxide) prior to HfO_2 deposition. The precursors used for the Hf source and the O source were $HfCl_4$ and H_2O respectively. The source temperatures were 170°C for $HfCl_4$ and 14.5°C for H_2O. One cycle of ALD- HfO_2 growth consisted of an 800 ms pulse of $HfCl_4$, followed by a 200 ms pulse of H_2O, each carried by a flow of nitrogen and separated by 100 seconds. We extended the purge time to eliminate CVD type of growth. The gas line of the final dose was separated in order to prevent interference among the two gases and the process pressure was 250 mTorr.

In order to investigate the ALD growth mechanism of HfO_2 film at the initial growth stage, the sample could be transferred in situ from the deposition chamber to the MEIS chamber using a transfer rod after HfO_2 growth. The MEIS analysis was accomplished with a 100 keV proton beam in the double alignment condition. This reduces contributions from the crystalline Si substrates, allowing the deconvolution of spectra into contributions from interfacial Si signals. The incident ions were along [111] in the (011) plane and the scattered ions were along $[00\bar{1}]$ with a scattering angle of 125°.[6] During the MEIS experiments, the specimen was moved and the H^+ dose was maintained below 2×10^{15} cm^{-2} in order to prevent damage.

3. RESULTS AND DISCUSSION

Figure 1 shows the proton backscattering energy of Hf atoms for HfO_2 film grown on a wet chemical oxide. HfO_2 films grown on chemical oxide showed a fast growth rate at the initial stage, compared with thermal oxide. Figure 1 clearly shows that in the early stages of growth, HfO_2 coverage per cycle was highest for the chemical oxide underlayer and HfO_2 films grown on the chemical oxide showed ~ 2 times faster growth rate compared to thermal oxide at the initial stage. As a result, the first 1 monolayer formed completely at 7 cycles (1 ML HfO_2 may be calculated simply as the HfO_2 molecular density, equal to 9.14×10^{14} Hf atoms/cm^2). The Hf coverage of ~5 cycles was equivalent to the Hf coverage of 10 cycles on thermal oxide. The shape of the Hf peak is sharp, compared with the sample grown on a thermal oxide. Therefore, chemical oxide had more layer-like growth than the other starting surfaces, as shown in Fig. 1. However, ALD growth did not occur via a monolayer-by-monolayer mode, since only a partial monolayer (~16 %, 1.5×10^{14} Hf atoms/cm^2) growth per cycle was observed. More importantly, subsequent cycles did not necessarily lead to reaction and coverage at previously unreacted Si-OH sites. Incoming $HfCl_4$ preferentially reacts with previously unreactied Si-OH sites, and growth will occur predominantly on these sites.

Hf coverage rapidly increased at the first cycle and then the HfO_2 film linearly grew in a linear fashion at a constant coverage rate, as shown in Fig. 2. The HfO_2 layer grown on the chemical oxide showed the highest nucleation site after the first cycle, 3.3×10^{15} Hf atoms/cm^2. The atomic force microscopy (AFM) data of the inset of Fig. 2, which was in each case normalized to the roughness of the starting surface, appear that the thermal oxide underlayer results in slightly more rough HfO_2 films.

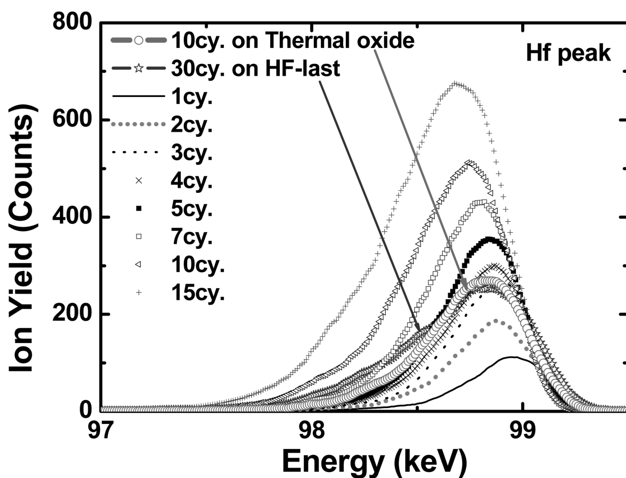

Fig. 1. MEIS spectra of Hf atoms for HfO_2 deposited on chemical oxide. The Hf coverage of ~5 cycles on chemical oxide is equivalent to the Hf coverage of a 10 cycles on thermal oxide.

In order to determine the effect of growth kinetics on the electrical characteristics of ALD-grown HfO_2 films, MOS capacitors with a Pt electrode were defined by photolithography and etching. Capacitance was measured at a frequency of 1 Mhz using HP 4284 multi-frequency LCR meter and the current-voltage characteristics with the HP 4155 pA meter/d.c. source. The measurements were carried out at room temperature.

Figure 3(a) shows the typical capacitance-voltage (C-V) characteristics with a gate area of 9×10^{-6} cm^2 for 20-70 cycles HfO_2 grown on the thermal oxide. No post-deposition annealing was performed. As the thickness of the film increased, the C-V curve shifted towards negative voltage,

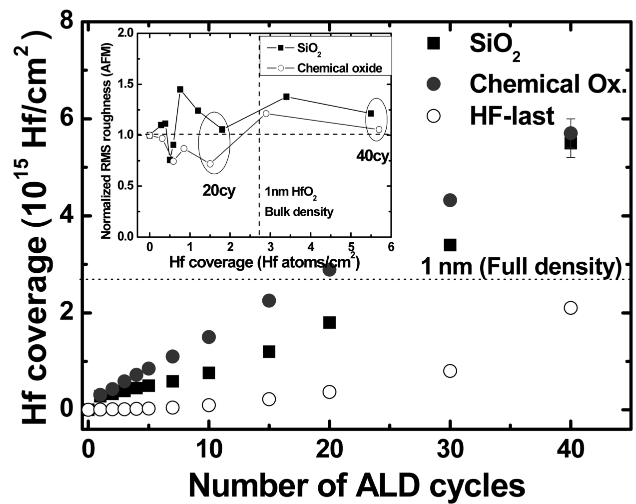

Fig. 2. Hf coverage, measured by in-situ MEIS, as a function of the number of HfO_2 deposition cycles, for samples exposed to ≤ 40 cycles. The inset shows nomalized AFM measurements of HfO_2 films grown on the different starting surfaces, as a function of Hf coverage.

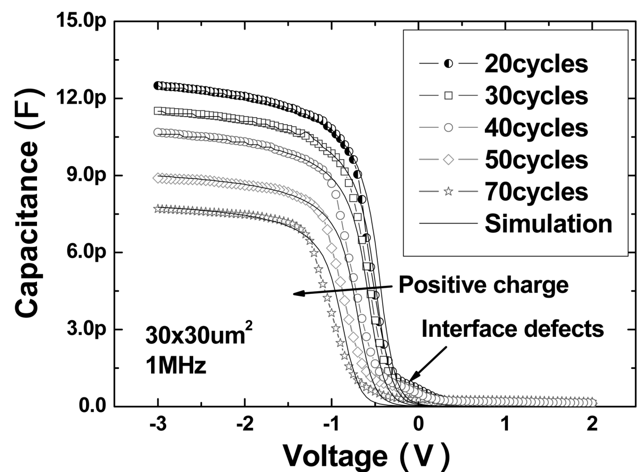

Fig. 3. (a) C-V measurements in accumulation taken at 1 Mhz on MOS capacitors with 20-70 ALD growth cycles of HfO_2 on top of SiO_2. (b) C-V curves for Pt-gated MOS capacitor with 20-70 ALD growth cycles of HfO_2 on top of chemical oxide.

implying the presence of a positive charge in the HfO_2 film. A "bump" was observed between -0.7 V and 0 V for as-grown samples, showing the interface defects. This showed the interface state density (D_{it}) which was estimated by the conductance method was found to be 8.21×10^{12} $cm^{-2}eV^{-1}$. These interface defects could be reduced by forming gas anneal (FGA).[8]

On the high OH group surface, the shift of flat band voltage (V_{FB}) was negligible. This is attributed to structural uniformity in the HfO_2 dielectric, as shown in Fig. 3(b). This is in contrast to capacitor structures grown on thermal oxide. The interface trap density D_{it} was estimated to be 2.3×10^{12} $cm^{-2}eV^{-1}$.

Figure 4 clearly shows the effect of surface preparation on the electrical characteristics and the superior electrical properties of HfO_2 grown on chemical oxide. On the H-terminated interface, the highest hysteresis value, ~150 mV was observed. This is attributed to incomplete film growth, which may be associated with non-uniform bonding at the HfO_2/Si interface or non-uniformity of the interface composition. Therefore, electrons were trapped at pre-existing defects in the HfO_2 layer. Large hysteresis, counter clockwise always, was present in all films, but hysteresis was small for film grown on chemical oxide. The small hysteresis observed in the C-V curve is considered to be due to charge trapping in HfO_2 and/or near the HfO_2/chemical oxide interface. We believe that this resulted from relatively uniform Hf-O-Si/Hf-O bonding at the interface, as shown in Fig. 5.

V_{FB} changes with increasing capacitance equivalent thickness (CET), as shown in Fig. 3(a). Other studies have observed similar V_{FB}-film thickness dependencies, suggesting that a fixed charge in high-k films was distributed throughout the film rather than existing only at the interface.[9-11] However, a positive relation between V_{FB} and film thickness has not

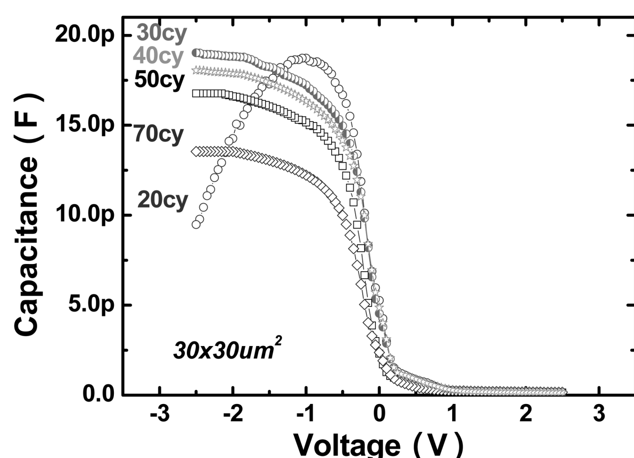

Fig. 4. Effect of surface preparation on C-V hysteresis. In chemical oxide, hysteresis was the lower value than that of other cases.

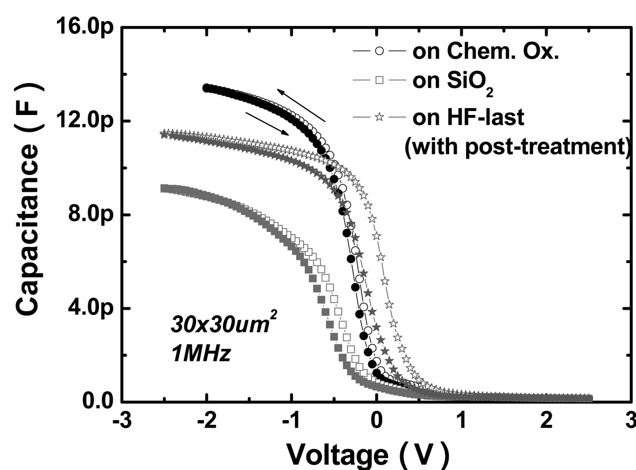

Fig. 5. The model of growth mechanism of ALD HfO_2 layer grown on the different OH- density surfaces at the initial growth stage.

been universally reported. The origin of V_{FB}-film thickness dependencies is not clear at present. One possibility is the difference in the HfO_2 structure and interface structure due to the difference in the ALD growth mode. Recently, Stesmans reported that the density of P_{b0} (Si dangling-bond-type defect) is sensitive to the deposition process and improvement of the HfO_2 nucleation site using a chemical oxide may yield a better Si/oxide interface.[12] As suggested by this research, surface preparations can affect observed V_{FB} values. Based on the results obtained here, we deduced that the morphologies of thin film resulting from differences in the initial growth affect C-V qualities.

4. CONCLUSION

We investigated the effects of the initial growth mode on the electrical properties of atomic layer deposition-grown HfO_2/SiO_2/Si. MEIS results clearly showed that wet chemical oxide yielded more layer-like growth at an initial growth stage than a thermal oxide starting surface. HfO_2 films grown on a wet chemical oxide showed negligible hysteresis and better interface state density than other surface conditions. The improvement of electrical characteristics can be explained by the uniform and smooth morphology at the HfO_2/Si interface. This showed that the surface preparation directly influences growth morphologies. This growth morphology at the initial growth stage strongly affected the C-V quality and charge trapping.

ACKNOWLEDGMENT

The author would like to thank Dr. D. W. Moon from KRISS and Dr. M.-H. Cho from Yonsei University for MEIS experiment and technical assistance.

REFERENCES

1. B. H. Lee, L. Kang, R. Nieh, W.-J, Qi, and J. C. Lee, *Appl. Phys. Lett.* **76**, 1926 (2000).
2. M. Balog, M. Schieber, M. Michiman, and S. Patai, *Thin Solid Films* **41**, 247 (1977).
3. G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys*. **87**, 484 (2000).
4. H. Kim, P. C. Mclntyre, and K. C. Saraswat, *Appl. Phys. Lett*. **82**, 106 (2003).
5. H. S. Chang, H. Hwang, M.-H. Cho, and D. W. Moon, *Appl. Phys. Lett.* **86**, 032104 (2005).
6. J. F. van der Veen, *Surf. Sci. Rep.* **5** 199 (1985).
7. E. P. Gusev, H. C. Lu, T. Gustafsson, and E. Garfunkel, *Phys. Rev. B* **52**, 1759 (1995).
8. H. Park, M. Hasan, M. Jo, and H. Hwang, *Electron. Mater. Lett.* **3**, 75 (2007).
9. R. S. Johnson, G. Lucovsky, and I. Baumvol, *J. Vac. Sci. Technol.* A **19**, 1353 (2001).
10. G. D. Wilk, M. L. Green, M.-Y. Ho, B. W. Busch, T. W. Sorch, F. P. Klemens, B. Brijs, R. B. van Dover, A. Kornblit, T. Gustafsson, E. Garfunkel, S. Hillenius, D. Monroe, J. M. Hergenrother, *VLSI Tech. Dig.*, p. 88 (2002).
11. H. Harris, K. Choi, N. Mehta, A. Chandolu, N. Biswas, G. Kipshidze, S. Nikishin, S. Gangopadhyay, and H. Temkin, *Appl. Phys. Lett.* **81**, 1065 (2002).
12. A. Stesmans and V. V. Afanas'ev, *Appl. Phys. Lett.* **82**, 4074 (2003).