Journal of the Korean Physical Society, Vol. 50, No. 3, March 2007, pp. 666∼669

Study of the Characteristics of HfO_2/Hf Films Prepared by Atomic Layer Deposition on Silicon

Seung-Woo Do and Yong-Hyun Lee
School of Electrical Engineering and Computer Science, Kyungpook National University, Deagu 702-701

Jae-Sung Lee*
Division of Information & Communication Engineering, Uiduk University, Gyeongju 780-713

(Received 3 September 2006)

Hafnium-oxide (HfO_2) thin films were deposited on p-type (100) silicon wafers by using atomic layer deposition (ALD) with tetrakis (ethylmthylamino)-hafnium [TEMAH] and ozone. Prior to the deposition of the HfO_2 thin films, a thin Hf (10 Å) metal layer was deposited. The deposition temperature of the HfO_2/Hf thin film was 350 °C and, its total thickness was 150 Å. The deposited samples were annealed in a furnace under nitrogen ambient. Round-type MOS capacitors were fabricated with Pt electrodes prepared by using an e-beam evaporator. We observed the formation of Hf-O-Si bonds, instead of Si-O bonds, at the interface. The HfSiO layer was grown between the HfO_2 and Si; therefore, the Hf metal layer sandwiched in the HfO_2/Si structure was effectively suppressed to grow interfacial SiO_x. The MOS capacitance of the HfO_2/Hf/Si structure was larger than that of the HfO_2/Si structure. The dielectric constant of the HfO_2/Hf layer was ∼18.96, and the interface state density at the silicon interface was 2.2×10^{-12} $cm^{-2}eV^{-1}$.

PACS numbers: 77.55.+f
Keywords: Hafnium oxide (HfO_2), Atomic layer deposition (ALD), Hafnium (Hf), Interfacial SiO_x

I. INTRODUCTION

SiO_2 is a good gate dielectric material which has a low leakage current, good thermal stability, and good reliability. As the scaling down of metal oxide semiconductor (MOS) devices continues, the physical thickness of SiO_2 is approaching 1 nm, and the decrease of gate oxide thickness is the cause of serious problems, such as a high gate leakage current and oxide reliability [1,2]. If the gate leakage current is to be reduced, SiO_2 must be replaced by a high-k material, such as HfO_2 [3–6], ZrO_2 [5,6], Al_2O_3 [7], Ta_2O_5 [8], Y_2O_3 [9]. These high-k materials increase the capacitance for the same thickness as that of SiO_2 and reduce the gate leakage current.

Among the many high-k materials, HfO_2 has attracted much attention due to its high dielectric constant and compatibility with complementary metal oxide semiconductor (CMOS) processes. However, HfO_2 thin films may react with the underlying silicon substrates during deposition or annealing. The increase in an interfacial Si-O_x containing layer, such as SiO_2, is a current issue. HfO_2 thin films, however, have very poor barrier characteristics with respect to oxygen [3].

HfO_2 thin films have been deposited using many deposition techniques, such as atomic layer deposition (ALD) [10], metal organic chemical vapor deposition (MOCVD) [10], and sputtering [11]. Among the many deposition methods, ALD is extensively used for HfO_2 thin film deposition. The ALD is a novel semiconductor thin film deposition technology, which controls the surface reaction of the precursor on the substrate. The ALD process can find its advantages in accurate thickness control and excellent step coverage because the growth rate only depends on the number of growth cycles and the lattice parameters of materials.

In this study, we deposited HfO_2/Hf thin films on p-type silicon by using the ALD method. The role of the Hf layer is to prevent growth of the interfacial SiO_2 layer between HfO_2 and Si and to obtain better interface properties.

II. EXPERIMENT

The HfO_2 thin films were deposited on 4 inch p-type Si(100) wafers with a resistivity in the range of $5 - 10$ Ωcm. After the Si wafer had been cleaned using a standard RCA cleaning process, the wafer was placed in the ALD chamber. The precursors used for the HfO_2 thin film deposition were TEMAH [tetrakis

---

*E-mail: dsw95@ee.knu.ac.kr

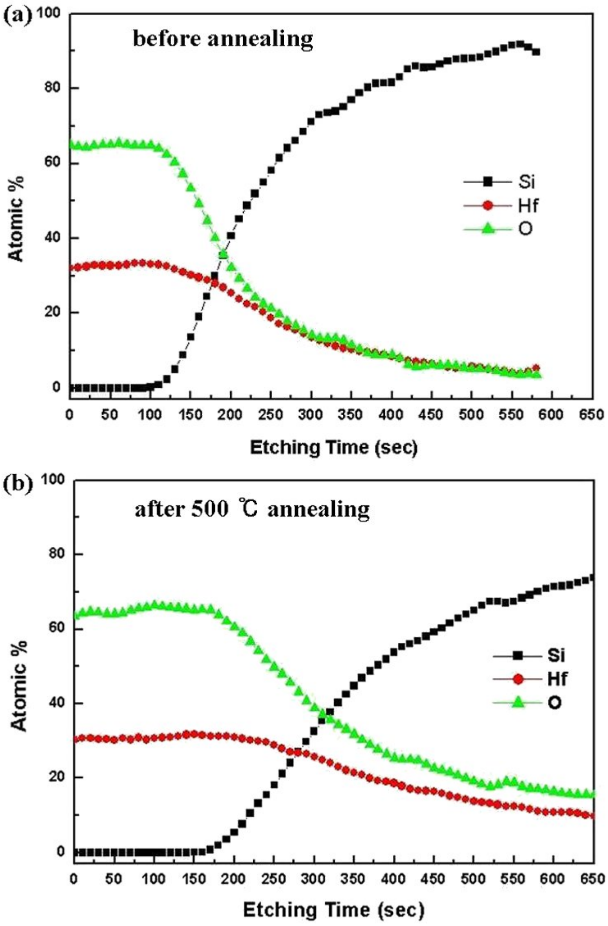

Fig. 1. AES depth profiles of (a) an as-deposited HfO_2/Hf thin film and (b) a 500 °C annealed HfO_2/Hf thin film.

(ethylmthylamino)-hafnium] and ozone. In order to prevent the formation of a SiO_2 interfacial layer, a thin Hf (10 Å) metal layer was deposited by using ALD. The HfO_2 thin film was deposited by alternating pulses of TEMAH and ozone. A deposition cycle is defined as a pulse of TEMAH, an argon purge to remove the unreacted precursor, an ozone pulse, and a final argon purge. The HfO_2 thin film's thickness was controlled by using the number of cycles. The deposition temperature of the HfO_2/Hf thin film was 350 °C, and its total thickness was 150 Å. After deposition, the films were annealed in a nitrogen ambient in a thermal furnace.

The thickness of the HfO_2 thin film was measured using ellipsometry. The chemical compositions of the HfO_2/Hf thin films were investigated using AES (auger electron spectroscopy). The analysis of interfacial region of HfO_2/Si was done using XPS (X-ray photoelectron spectrometry) and TEM (transmission electron microscopy). The C-V analysis of the MOS capacitors was based upon conventional MOS C-V theory. High-frequency (1 MHz) and low-frequency (100 kHz) C-V measurements were achieved by using 1 MHz C meter / C-V plotter (HP4280A). The I-V measurements were performed using semiconductor parameter analyzer (HP4155).

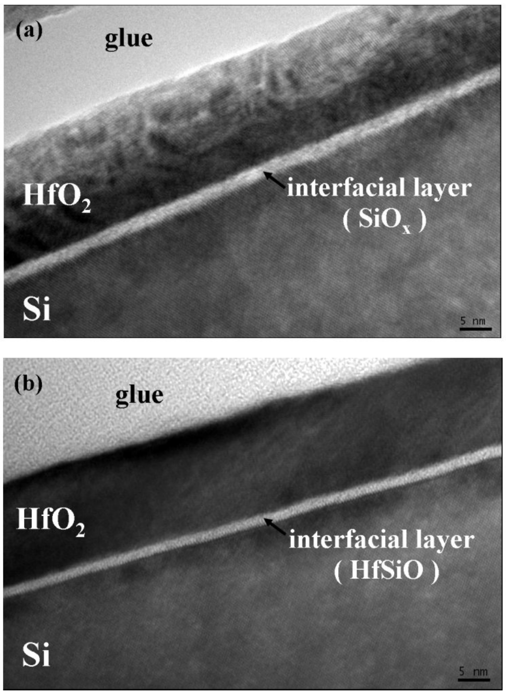

Fig. 2. TEM images of (a) the HfO_2/Si structure and (b) the HfO_2/Hf/Si structure. Both structures were annealed at 500 °C.

III. RESULTS AND DISCUSSION

Figure 1 shows the chemical composition of the HfO_2/Hf thin films on Si. As Figure 1(a) shows, the ratio of O/Hf is about 2, indicating the film is stoichiometric. For samples annealed at 500 °C, the film maintained in stoichiometry. Thickness, measured using ellipsometry, of the annealed sample was the same as the thickness of the sample before annealing. As the pre-sputtering time for removing carbon from the surface was different for each film during AES analysis, the etching time in each figure is rather different.

Figure 2(a) and 2(b) show TEM images of the HfO_2/Si and the HfO_2/Hf/Si structures. Both samples were annealed at 500 °C. The thickness of the thick HfO_2 film is about 15 nm while the thin film at the interface is about 2 nm thick in the HfO_2/Si structure. The thickness of the interfacial layer, SiO_x, has been reported not to depend on the HfO_2 thickness, but to depend on the oxygen pressure [3]. In our HfO_2/Hf/Si structures, the thickness of the interfacial layer depends on the as-deposited Hf thickness. In Figure 2(b), interfacial layer thickness is less than about 2 nm, which is thinner than SiO_x film shown in Figure 2(a).

Figure 3 shows the Hf 4f and Si 2p XPS spec-

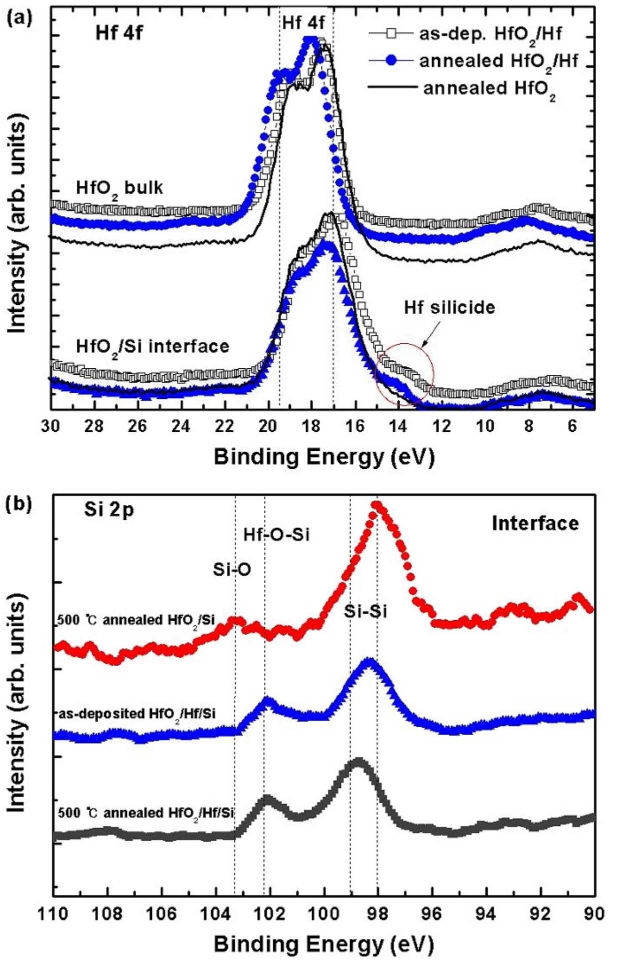

Fig. 3. (a) Hf 4f and (b) Si 2p XPS spectra for the HfO_2/Si structure and the HfO_2/Hf/Si structure.

tra obtained from both the HfO_2/Si structure and the HfO_2/Hf/Si structure. For the HfO_2 bulk in both structures, the Hf 4f peak is observed in range of 17 $\sim$ 20 eV. This peak represents the formation of Hf-O bonds [5, 11]. The binding energy signal of Si 2p was not observed in the HfO_2 bulk. In the HfO_2/Hf thin film, the formation of the Hf-Si bond was observed at the interface, as shown in Figure 3(a). The binding energy of Hf-Si bonds was measured to be 14.3 eV. However, the Hf-Si bond was not observed in the HfO_2/Si structures because the interfacial layer was usually composed of Si and O atoms, as shown in Figure 3(b). The Si 2p peak can be divided into three components: the binding energies of Si-Si bonds (99.3 eV), Hf-O-Si bonds (around 102.7 eV), and O-Si-O bonds (103.3 eV) [4,12,13]. In our HfO_2/Hf films, the peak at 98 $\sim$ 99 eV in the Si 2p spectra represented the silicon substrate component. The high-energy 102.3 eV and 103.3 eV features in the Si 2p spectra represent Hf-O-Si bonds and Si-O bond, respectively. Thus, our film structure achieved the HfO_2/HfSiO/Si structure after annealing, without the creation of a SiO_x layer.

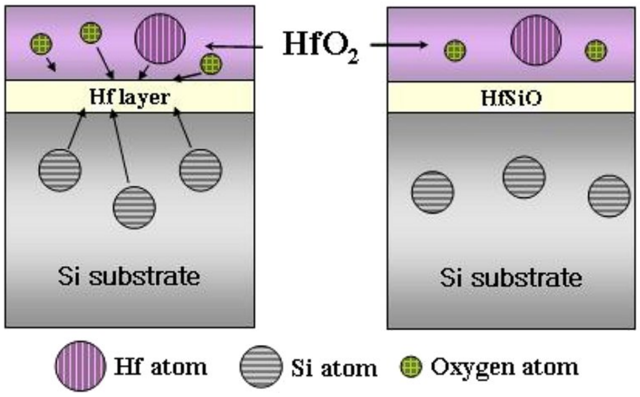

Fig. 4. Schematic explanation of the function of the Hf metal layer.

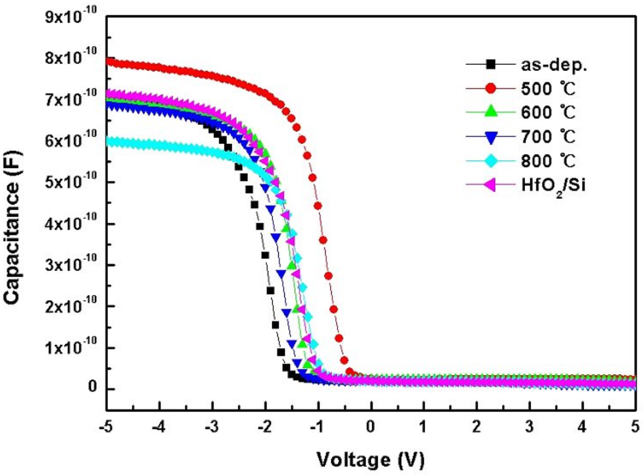

Fig. 5. C-V characteristics of Pt/HfO_2/Hf/Si structures for various of annealing temperature.

Through the results of AES and XPS, we found that the Hf layer is changed as an HfSiO film at the HfO_2/Si interface. The role of the Hf layer is illustrated in Figure 4. The Hf metal layer may combine with silicon and oxygen atoms in the sandwiched structure. Therefore, the Hf metal layer can prevent oxygen diffusion into the silicon substrate.

The C-V characteristics of the HfO_2/Hf thin films are show in Figure 5. The electrode area was 7.07×10^{-4} cm^{-2}. The capacitances show different trends, depending on the annealing temperature, because defect generation is related to the chemical reactions in the interface. The measured capacitance of the HfO_2/Hf/Si structure with 500 °C annealing was 7.91×10^{-10} F, which corresponded to $k \sim 18.96$. The dielectric constant k of the HfO_2/Si structure was $\sim$17. The flatband voltage shifted toward positive voltage in the 500 °C annealed HfO_2/Hf/Si structure, which means a decrease in the number of oxide trap charges. The capacitance of the HfO_2/Hf/Si structure was larger than that of the HfO_2/Si structure. As a result, the HfSiO layer was grown between the HfO_2 and Si, therefore, the Hf

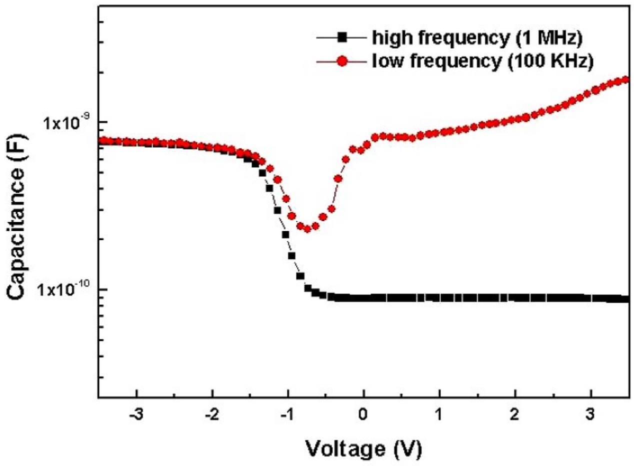

Fig. 6. C-V characteristics for two values of the bias frequency.

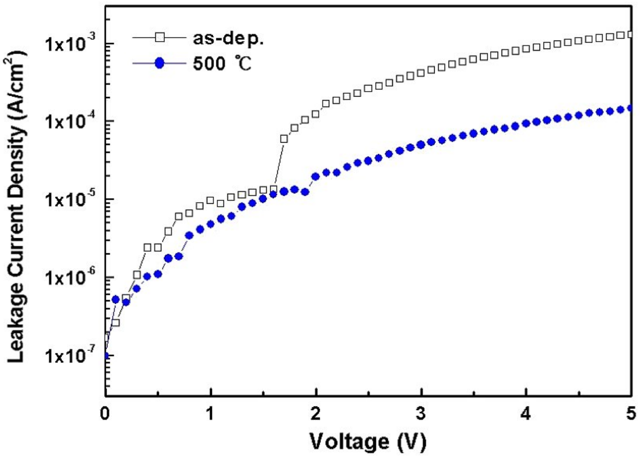

Fig. 7. Leakage current density for the HfO_2/Hf films.

metal layer sandwiched in the HfO_2/Si structure effectively suppressed the growth of interfacial SiO_x.

Figure 6 shows the C-V characteristics for two values of the bias frequency. High- and low-frequency C-V measurements were conducted using the conventional method, and we calculated the interface density of states D_{it}. When the annealing temperature was 500 °C, the interface density of states at the interface of silicon was 2.2×10^{12} $cm^{-2}eV^{-1}$. Typical SiO_2 film as gate dielectrics has a mid-gap interface density of states given by $D_{it} \sim 2 \times 10^{10}$ states/cm^2, and the reported high-k materials show $D_{it} \sim 10^{11} - 10^{12}$ states/cm^2 [14]. Our result is in the range of the published D_{it}. Figure 7 shows the leakage current density for the HfO_2/Hf films. The as-deposited thin film shows a *Fowler-Nordheim* (FN) tunneling behavior below 2 V (1.3 MV/cm). The annealed HfO_2/Hf film has a smaller leakage current than the as-deposited film, which implies that post-annealing is necessary to obtain fewer oxide traps.

IV. SUMMARY

We investigated the interfacial and the electrical characteristics of HfO_2/Hf deposited on Si by using the ALD method. The prepared film maintained its stoichiometric components. We observed both Hf-Si bonds and Hf-Si-O bonds in the HfO_2/Si interface, instead of Si-O bonds. The sandwiched Hf metal layer suppressed the growth of a SiO_x layers, instead, an HfSiO layer was grown. The Hf metal layer acts as an oxygen barrier and silicon barrier in the HfO_2/Hf/Si structure. The dielectric constant k of the annealed HfO_2/Hf film was ~18.96, and the D_{it} was 2.2×10^{12} $cm^{-2}eV^{-1}$. Our HfO_2/Hf film demonstrated a potential for use as a gate dielectric material in CMOS applications.

ACKNOWLEDGMENTS

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-041-D00487).

REFERENCES

[1] I. S. Park, T. H. Lee, D. K. Choi and J. H. Ahn, J. Korean Phys. Soc. **49**, S544 (2006).
[2] H. Jin, S. K. Oh, H. J. Kang, S. W. Lee, Y. S. Lee and K. Y. Lim, J. Korean Phys. Soc. **46**, S52 (2005).
[3] J. Lu, J. Aarik, J. Sundgvist, K. Kukli, A. Harsta and J. O. Carksson, J. Crys. Growth **273**, 510 (2005).
[4] C. C. Yeo, M. S. Joo, B. J. Cho and S. J. Whang, Thin Solid Films **462-463**, 90 (2004).
[5] G. D. Wilk, R. M. Wallace and J. M. Anthony, J. Appl. Phys. **87**, 484 (2000).
[6] H. Kato, T. Nango, T. Miyagawa, T. Katagiri, K. S. Seol and Y. Ohki, J. Appl. Phys. **92**, 1106 (2002).
[7] E. P. Gusev, M. Copel, E. Cartkier, I. J. R. Baumvol, C. Krug and M. A. Gribelyuk, Appl. Phys. Lett. **76**, 176 (2000).
[8] G. B. Alers, D. J. Werder, Y. Chabal. H. C. Lu, E. P. Gusev, E. Garfunkel, T. Gustafsson and R. Urdahl, Appl. Phys. Lett. **73**, 1517 (1998).
[9] S. Guha, E. Cartier, M. A. Gribelyuk, N. A. Bojarczuk and M. C. Copel, Appl. Phys. Lett. **77**, 2710 (2001).
[10] P. H. Triyoso, M. Ramon, R. I. Hegde, D. Roan, R. Garcia. J. Baker, X. D. Wang, P. Fejes, B. E. White. Jr. and P. J. Tobin, J. Electrochem. Soc. **152**, G203 (2005).
[11] H. Wong, N. Zhan, K. L. Ng, M. C. Poon and C. W. Kok, Thin Solid Films **462-463**, 96 (2004).
[12] K. P. Bastos, C. Driemeier, R. P. Rezzi, G. V. Soares, L. Miotti, J. Morais, I. J. R. Baumvol and R. M. Wallace, mater. Sci. Eng. B **112**, 134 (2004).
[13] J. H. Koo and H. T. Jeon, J. Korean Phys. Soc. **46**, 945 (2005).
[14] G. D. Wilk, R. M. Wallace and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).