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Two-step interfacial reaction of HfO_2 high-*k* gate dielectric thin films on Si

P.F. Lee, J.Y. Dai*, H.L.W. Chan, C.L. Choy

Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, PR China

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Abstract

HfO_2 thin films have been deposited on p-type (1 0 0) Si substrates by pulsed laser deposition. Transmission electron microscopy observation illustrated that the HfO_2 films are in polycrystalline structure and the interface with Si substrate is free from amorphous layer. The rough feature of the film/Si interface suggested interfacial reaction and diffusion. Depth profile X-ray photoelectron spectroscopy (XPS) analysis results revealed the formation of Hf silicate and Hf silicide at the interface. A two-step reaction model was proposed to interpret the interfacial reaction. At initial stage of film growth, insufficient oxidation of Hf atoms on bare Si surface resulted in reaction of Hf with Si leading to silicidation of Hf, at least Hf–Si bonds formation. During the following film growth, the preformed Hf silicide was further oxidized leading to Hf silicate formation. This two-step reaction model suggests a gradient distribution of the film stack, that is, HfO_2/Hf silicate/Hf silicide/Si. It was found that with sufficient oxygen during film growth, the Hf silicide formation was suppressed.

Keywords: A. Films; B. Interfaces; C. Dielectric properties; HfO_2

1. Introduction

Due to the limitation of physical thickness of SiO_2 gate dielectric film, a new gate dielectric material with dielectric constant higher than that of SiO_2 is required to meet the next generation complimentary metal-oxide-semiconductor (CMOS) technology requirement. There are many candidates of high-*k* dielectrics such as Ta_2O_5, ZrO_2, Al_2O_3, and among them, HfO_2 is one of the most attractive candidates due to its relatively higher stability on Si substrate and better reliability [1–3]. However, it is well known that due to the presence of oxygen during the film growth, Hf silicate or SiO_2 interfacial layer is unavoidable and many studies have been devoted to the reaction mechanism and its effect to dielectric properties [3–6].

In order to reduce the equivalent oxide thickness, the Si oxide-riched interfacial layer, that is responsible for the decrease of dielectric constant, has to be reduced by reducing the oxygen during film deposition. This can lead to SiO_2 layer free HfO_2/Si interface, but may result in oxygen deficient in the HfO_2 films and also at the film/Si interfaces. The oxygen deficiency, as we have found during HfO_2 film deposition by pulsed laser deposition (PLD), results in Hf silicidation at the interfacial area which is detrimental to the MOS device performance. However, the reaction mechanism under an oxygen deficient condition between HfO_2 and Si is not well understood yet. In this paper, we propose a two-step reaction mechanism to interpret the interfacial reaction during HfO_2 thin film deposition by PLD on p-type (1 0 0) Si substrates.

2. Experimental details

The HfO_2 thin films on p-type (1 0 0) Si with resistance of 5–25 Ω cm were deposited by PLD with base vacuum of 7×10^{-5} Pa. The wave length of the Excimer laser is 284 nm and the energy density is 6 J/cm^2 with frequency of 5 Hz. In order to prevent the formation of SiO_2 interfacial layer during the film deposition, the HfO_2 films were deposited in high vacuum without introducing any oxygen gas. The deposition temperature is 550 °C and last for 2 min. After deposition, the HfO_2 thin film was subjected to a rapid thermal annealing at 650 °C for 15 s in order to reduce the oxygen

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* Corresponding author.
E-mail address: apdaijy@inet.polyu.edu.hk (J.Y. Dai).

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vacancies in the film. The formed MOS capacitor was evaluated by high frequency capacitance–voltage (*C*–*V*) measurement at 1 MHz using HP 4194A impedance analyzer. The leakage current of the MOS capacitor was characterized by current–voltage (*I*–*V*) measurement. The film thickness and interfacial property were studied by high-resolution transmission electron microscope (TEM) with JEOL 2010 microscope.

3. Results

Fig. 1 shows high-resolution TEM images of HfO_2 thin films on the Si substrate deposited at high vacuum condition with and without oxygen gas introduced. It can be seen that with oxygen gas introduced, the interface presents a thin amorphous layer (SiO_2 or Hf silicate) and the HfO_2 thin film is polycrystalline structure. For the HfO_2 thin film deposited without oxygen gas introduced, however, the interface is rough in atomic scale. One reason of this atomic scale surface roughness is the presence of large amount of misfit dislocations due to the lattice mismatch (∼5%) between HfO_2 and Si. Another possible reason is due to interfacial reaction, even though the image does not show any evidence of interfacial phase. We believe that atomic scale interfacial reaction and diffusion, for example, the formation of Hf–Si or Hf–O–Si bonds, can cause the interface roughness. It is worth noting that polycrystalline HfO_2 film on bare Si grown by PLD has also been reported earlier by Ikeda et al. [7]. However, due to the large stress at the interface and the possible phase transformation from cubic to tetragonal and monoclinic structures in the films, it is difficult to grow HfO_2 epitaxial films on Si.

XPS technique has been widely used in the study of thin film chemical structure and interfacial reactions in the systems of HfO_2/Si and Hf silicate/Si [8–15]. In order to study the interfacial reaction and diffusion that may occur at the interface of the HfO_2 film on Si, the as-grown films were subjected to XPS analysis. Fig. 2 shows the depth profile XPS binding energy of Hf 4f and Si 2p peaks as the film was progressively milled by Ar^+ in-situ sputtering. One can see from Fig. 2(a) that with increasing depth, the peak position of Hf 4f shifted from HfO_2 (17.6 eV) to elemental Hf (∼14.6 eV). The presence of elemental Hf peak inside the film illustrates the existence of oxygen vacancies. The dominated elemental Hf peak at the interfacial area suggests more oxygen deficiencies during the early stage of film growth. It may also evidence Hf silicide formation at the interface since the Hf–Si binding energy is very close to that of the elemental Hf peak [8–10]. In fact, as shown in Fig. 2(b), when approaching the film/Si interfacial area, the appearance of a shoulder in the Si 2p peak toward higher energy is an indication of Hf–Si bond formation [12]. This fact and the appearance of elemental Hf 4f peak when approaching the film/Si interface suggest that Hf silicide or Hf–Si bonds was formed at the interfacial area, even though there is no evidence from TEM observation. It may be argued that sputtering process used for depth profile changed the chemical state at the interfacial region [2]. However, the XPS spectra of Hf 4f and O 2p at the surface support our explanation. Since the film is only about 30 Å, the XPS spectra from surface also contain information from the interfacial area due to the penetration effect.

The depth profile XPS study also revealed Hf–silicate formation at the interfacial area. The Si 2p peak at ∼102.8 eV in the spectrum as indicated by an arrow as shown in Fig. 2(b) corresponds to Hf–silicate bonding energy [8]. The shifting to a higher binding energy of Hf 4f peak from spectrum (i) to (ii) as can be clearly seen in Fig. 2(a) also evidences the presence of Hf–silicate at the interfacial area [8,10].

The formation of Hf silicide or Hf–Si bonds at the HfO_2/Si interface can be understood by considering the fact of insufficient oxidation of Hf adatoms at the beginning of film growth on bare Si surface which leading to the reaction of Hf with Si. The Hf silicate formation is believed to be due to the further oxidation of Hf silicide that has been formed at the

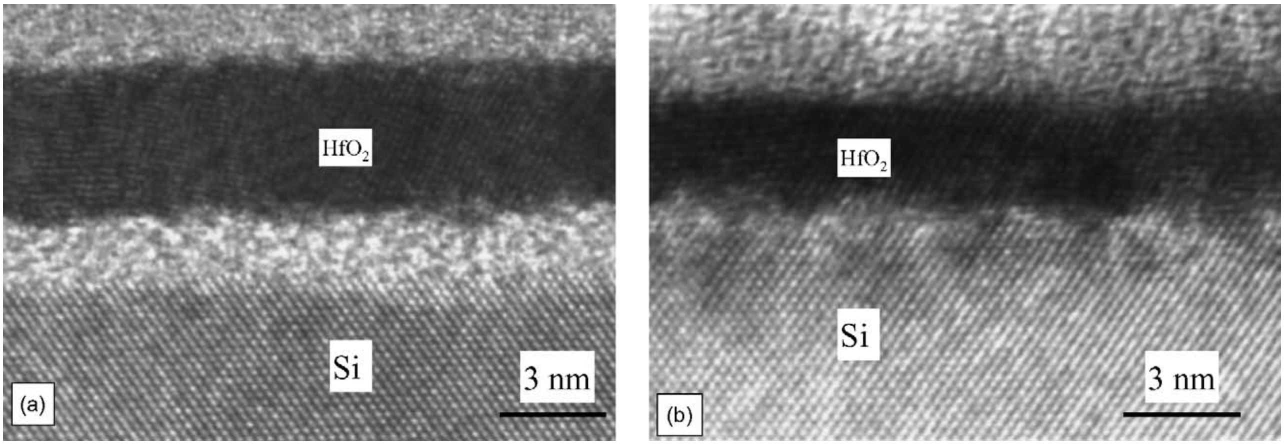

Fig. 1. Cross-sectional HRTEM pictures of HfO_2 films on Si substrates observed along Si [1 1 0] direction: (a) with SiO_2-riched amorphous layer, and (b) without amorphous layer.

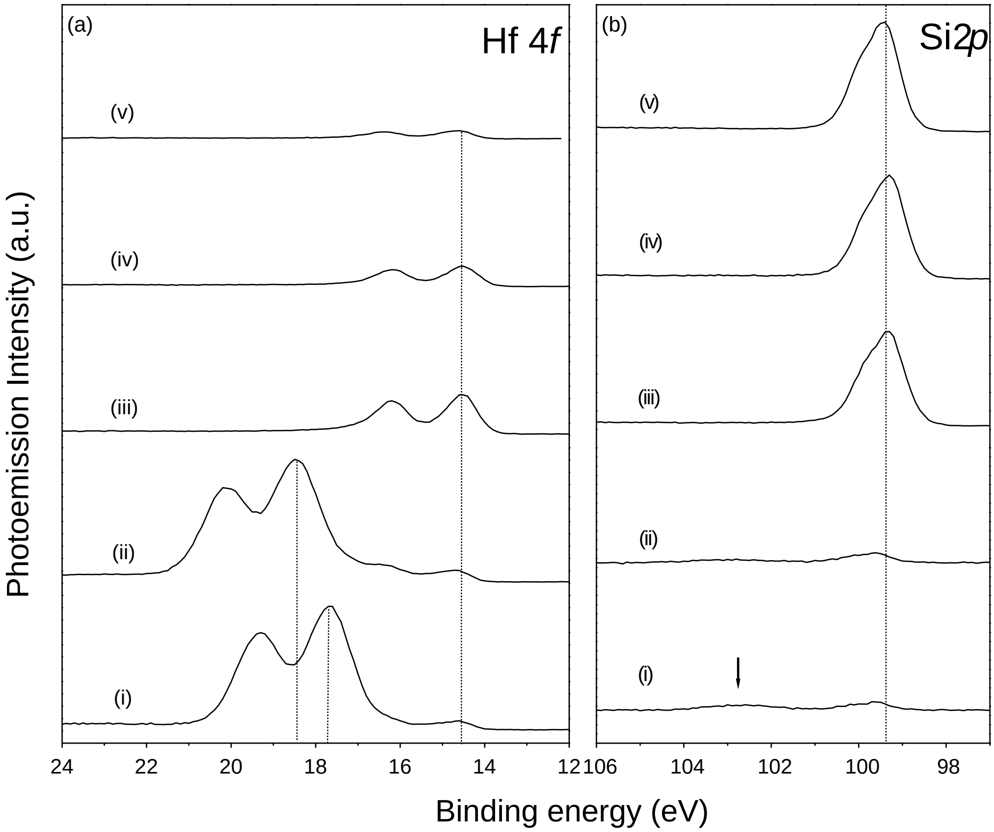

Fig. 2. XPS depth profile of HfO_2 film on Si: (a) Hf 4f peak, (b) Si 2p peak. The sequence of the spectra are as follow: (i) film surface, (ii) after a 30 s sputtering, (iii) after a 630 s sputtering, (iv) after a 870 s sputtering, and (v) after a 1350 s sputtering.

interface. A model was proposed to interpret this two-step interfacial reaction mechanism as illustrated in Fig. 3. The first few layers of Hf atoms arrive at Si surface when the system is in a high vacuum condition, thus, the lack of oxygen atoms at the initial stage of film growth leads to Hf silicide formation. After a few laser pulses ablation on the target, the pressure in the vacuum chamber was noticed to increase in one order due to the generation of plume. There will be more oxygen atoms arrive on the sample surface together with Hf atoms and result in oxidation of the preformed Hf silicide into Hf silicate. It is reasonable to expect that with optimized oxygen partial pressure during film growth, the Hf silicide formation can be suppressed at the early stage of film growth or can be eliminated during subsequent growth.

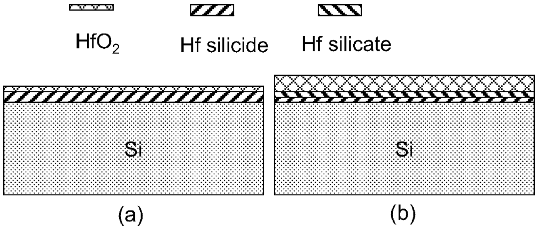

Fig. 3. Schematic diagram of a two-step interfacial reaction model: (a) interfacial reaction forming Hf silicide at initial stage of film growth, and (b) oxidation of Hf silicide leading to Hf silicate formation at the interface.

The effect of interfacial silicidation to the electric properties was studied by *C*–*V* and *I*–*V* measurements. Fig. 4 is a *C*–*V* curve of the as-grown HfO_2 thin film on Si without any interfacial amorphous layer as shown in Fig. 1(b). A hump presents at the depletion region and the curve is stretched out at the end of accumulation side. This abnormal feature in the *C*–*V* curve is an indication of large leakage current and

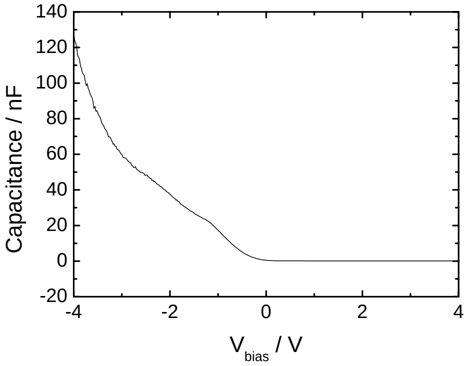

Fig. 4. High frequency (1 MHz) *C*–*V* curve of MOS capacitor with Pt dot as electrode for the HfO_2/Si systems without SiO_2-riched amorphous layer.

high density of interface states [2,3]. In fact, the *I–V* measurement resulted in a leakage current density of 0.1 A/cm^2 at 1.0 V bias voltage. The effect of thermal annealing in oxygen ambient to the improvement of the electric property of the HfO_2 films and the interface structure will be further studied.

4. Conclusion

HfO_2 thin films have been deposited on p-type (1 0 0) Si substrates by pulsed laser deposition. Transmission electron microscopy observation illustrated that the HfO_2 film is polycrystalline structure and the interface with Si substrate is free from amorphous SiO_2. Depth profile X-ray photoelectron spectroscopy (XPS) analysis results revealed the formation of Hf silicate and Hf silicide at the interface. A two-step reaction model was proposed to interpret the interfacial reaction.

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References

[1] G.D. Wilk, R.M. Wallace, J.M. Anthony, J. Appl. Phys. 89 (2001) 5243.

[2] Y.-S. Lin, R. Puthenkovilakam, J.P. Chang, Appl. Phys. Lett. 81 (2002) 2041.

[3] A. Callegari, E. Cartier, M. Gribelyuk, H.F. Okorn-Schmidt, T. Zabel, J. Appl. Phys. 90 (2001) 6466.

[4] H. Harrris, K. Choi, N. Mehta, A. Chandolu, N. Biswas, G. Kipshidze, S. Nikishin, S. Gangopadhyay, H. Temkin, Appl. Phys. Lett. 81 (2002) 1065.

[5] B.K. Park, J. Park, M. Cho, C.S. Hwang, K. Oh, Y. Han, D.Y. Yang, Appl. Phys. Lett. 80 (2002) 2368.

[6] M. Cho, J. Park, H.B. Park, C.S. Hwang, J. Jeong, K.S. Hyun, Appl. Phys. Lett. 81 (2002) 334.

[7] H. Ikeda, S. Goto, K. Honda, M. Sakashita, A. Sakai, S. Zaima, Y. Yasuda, Jpn. J. Appl. Phys. 41 (2002) 2476.

[8] P.D. Kirsch, C.S. Kang, J. Lozano, J.C. Lee, J.G. Ekerdt, J. Appl. Phys. 91 (2002) 4353.

[9] K. Yamamoto, S. Hayashi, M. Kubota, M. Niwa, Appl. Phys. Lett. 81 (2002) 2053.

[10] G.D. Wilk, R.M. Wallace, J.M. Anthony, J. Appl. Phys. 87 (2000) 484.

[11] K.P. Bastos, J. Moris, L. Miotti, R.P. Pezzi, G.V. Soares, I.J.R. Baumvol, R.I. Hegde, H.H. Tseng, P.J. Tobin, Appl. Phys. Lett. 81 (2002) 1669.

[12] M.-H. Cho, Y.S. Roh, C.N. Whang, K. Jeong, S.W. Nahm, D.-H. Ko, J.H. Lee, N.I. Lee, K. Fujihara, Appl. Phys. Lett. 81 (2002) 472.

[13] V. Cosnier, G. Theret, B. Andre, J. Vac. Sci. Technol. A 19 (2001) 2267.

[14] B.H. Lee, L. Kang, R. Nieh, W.-J. Qi, J.C. Lee, Appl. Phys. Lett. 76 (2000) 1926.

[15] S. Zaima, N. Wakai, T. Yamauchi, Y. Yasuda, J. Appl. Phys. 74 (1993) 6703.