Thermal stability of HfO_2/Si (001) films prepared by electron beam evaporation in ultrahigh vacuum using atomic oxygen*

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HfO_2 films on silicon substrates have been prepared by electron beam evaporation in ultrahigh vacuum using atomic oxygen. Synchrotron radiation photon–electron spectroscopy was used to investigate the thermal stability of HfO_2 films under an ultrahigh vacuum environment. At the temperature of 750 °C, HfO_2 films begin to decompose. After being further annealed at 850 °C for 3 min, HfO_2 films decomposes completely, partially to form Hf-silicide and partially to form gaseous HfO. Two chemical reactions are responsible for this decomposition process. A small amount of Hf-silicide, which is formed at the very beginning of growth, may result in the films grown subsequently to be loosened, and thereby leads to a relatively low decomposition temperature.

Keywords: surface and interface, high-k oxides, photon–electron spectroscopy

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HfO_2 is one of the most promising alternative dielectrics for the next generation complimentary metal–oxide semiconductor devices due to the advantages such as a relatively wide band gap, a proper conduction band offset and good thermal stability on Si.[1] In the past decade, different kinds of methods had been used to prepare the HfO_2 films. Many of them focused on chemical vapour depositions (CVD, e.g. ALD and MOCVD) since the high quality HfO_2 films can be obtained by CVD in contrast to generally a poor quality HfO_2 films obtained by physical vapour depositions (PVD), especially for the films prepared under the condition of the low oxygen partial pressure.[2−5]

Ultrahigh vacuum e-beam evaporation is a powerful PVD technique, often used to grow epitaxial films. It can precisely control the thickness and impurity concentration of ultra-thin films, and obtain uniform films on a large area. Thus, several groups have tried to grow the HfO_2 films by this method with molecular oxygen and metallic Hf as reactant source.[4,5] However, the quality of the films obtained is often poor due to the formation of a large amount of Hf-silicide at the HfO_2/Si interface, leading to voids in the HfO_2 films. Recently, we reported that high quality HfO_2 films have been achieved by using atomic rather than molecular oxygen as reactant source, and their structure and electrical properties have been characterized.[6,7]

However, as an alternative gate dielectrics to replace SiO_2, the thermal stability of HfO_2 films on Si is of great concern. The previous experimental studies on the stability of HfO_2/Si interface show diverse results, strongly depending on the deposition methods adopted, and most studies focusing on CVD prepared HfO_2 films.[8−12] It was reported that HfO_2 films prepared by ALCVD are unstable at the temperature of about 920–1000 °C under ultrahigh vacuum (UHV) and decomposed to form Hf silicide.[8] In addition, Zeman *et al.* reported that the HfO_2 films grown by plasma enhanced CVD are stable up to 1000 °C under UHV.[11] In this paper, the thermal stability of the HfO_2 films grown by ultrahigh vacuum e-beam evaporation is investigated with Synchrotron Radiation Photon–Electron Spectroscopy (SRPES). The de-

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composition of the HfO_2 films is studied at elevated temperatures under UHV. Two chemical reactions are responsible for this decomposition process. The difference in thermal stability between HfO_2 films prepared by this method and those by CVD is discussed. A small amount of Hf-silicide at the interface, which is formed at the very beginning of the film growth by this method, may slightly loosen the films grown subsequently, and thereby is responsible for a relatively low decomposition temperature.

The substrate used was 1.5-inch p-type Si(001) wafer with a resistivity of about 0.05 Ω·cm. A typical heating process was adopted to get a clean Si surface in molecular beam epitaxy (MBE) system. Then, the substrate was cooled down to around 350 °C. The HfO_2 film was grown by reaction of Hf flux and atomic oxygen flux on the substrate surface. Hf flux was produced by heating the metallic Hf source with the purity of 99.95% placed in a water-cooled copper crucible of the electron beam evapourator of riber Si-MBE system. The atomic oxygen beam was generated by an RF plasma atom source (Oxford, HD-25R) with inlet of high purity (99.999%) oxygen. The partial pressure of oxygen in the growth chamber was 2×10^{-6} Torr (1 Torr=133 Pa). The growth rate was around 0.1–0.2 nm/min. The growth was reported in detail elsewhere.[6]

The thermal stability of the HfO_2 film on Si under an ultrahigh vacuum was analysed with SRPES on the SGM1 Scienta beamline at the synchrotron radiation source at Institute for Storage Ring Facilities, Aarhus University, Denmark. The thickness of film was about 5 nm, which is thin enough to avoid the charge effect during PES measurement. Ar^+-etching was adopted to remove carbon contamination on the surface and to thin the film as well. The energies of excitation photons were set at 128 eV and 230 eV for the measurement of core level, and at 53 eV for the measurement of valence band, respectively. The pass energy was fixed at 20 eV, corresponding to an energy resolution of 56 meV. The substrate Si 2p 3/2 peak is located at binding energy (BE) of 99.20 eV, which was used as a reference energy for spectrum analysis.[13] Annealing was performed in the UHV by applying a direct electrical current across the samples. The refractive indexes of the HfO_2 films were measured by ellipsometric methods.

Figure 1 shows Hf 4f core level spectra of HfO_2 films before and after annealing with an excitation phonon energy of 128 eV. For the as-deposited film, as shown in Fig. 1(a), only a doublet peak, corresponding to the Hf^{4+} 4f core level of HfO_2, appears at a binding energy (BE) of 18.15 eV. Note that with this excitation phonon energy no significant signal corresponding to Hf-silicide is observed as shown in Fig. 1(a). For the sample annealed at the temperature lower than 750 °C, the spectra look unchanged (not shown here). After annealing at 750 °C for 3 min, a small additional doublet peak denoted by arrow A in Fig. 1(b) appears at a binding energy of about 3.6 eV lower than that of HfO_2, which can be attributed to Hf-silicide.[8] So, the film is believed to be unstable and decomposed at a annealing temperature over 750 °C. After further annealing at 850 °C for 3 min, the Hf 4f peak of HfO_2 completely disappears and only the Hf 4f doublet peak of Hf-silicide can be observed, as shown in Fig. 1(c). Moreover, the intensity of the Hf 4f signal in Fig. 1(c) is reduced by a factor of four, compared with that of the as-deposited film. This indicates that when HfO_2 film is completely decomposed, only a small portion of product is Hf-silicide and most part of product may be gaseous and desorbed, which results in the intensity of the Hf 4f signal to be reduced by a factor of four.

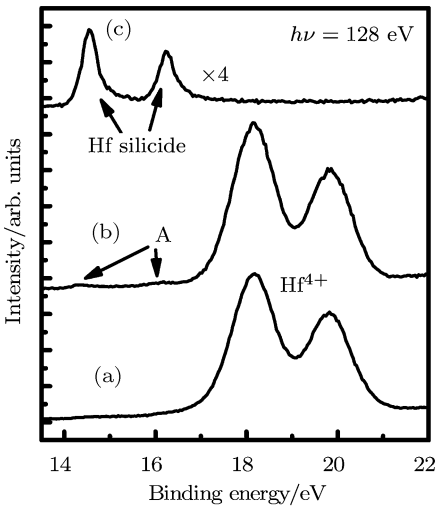


Fig. 1. Hf 4f core level PES spectra of HfO_2 films on Si. The excitation photon energy is 128 eV. (a) The as-deposited films, (b) annealed at 750 °C under the UHV conditions, and (c) further annealed at 850 °C under the UHV conditions.

Figure 2 shows Si 2p core level spectra of HfO_2 films grown on Si substrates. For the as-deposited film, the Si 2p signal from the substrate, denoted by Si^0, is located at a binding energy of 99.20 eV. An oxidized Si 2p signal is centred at 102.65 eV, about 3.45 eV higher than that of Si^0 2p, which is attributed to Hf-silicate rather than SiO_2 at the interface, since

the binding energy of the Si 2p peak for SiO_2 is 3.9∼4.2 eV higher than that of Si^0 peak.[14] Likewise, for the sample annealed at a temperature lower than 750 °C, the Si 2p signal shows little change compared with that for the as-deposited film. After annealing at 750 °C for 3 min, the oxidized Si 2p signal disappears and Si^0 signal becomes dominant, as shown in Fig. 2(b). The evolution of Si 2p core level spectra confirms the above conclusion that the film begins to decompose at the temperature over 750 °C. Moreover, since the Si 2p signal of Hf-silicate at interface disappears, as shown in Fig. 2(b), whereas Hf 4f signal of HfO_2 film does not change significantly, as shown in Fig. 1(b), this decomposition reaction at this temperature is suggested to occur only at the interface layer rather than in the whole film. For the sample annealed at 850 °C for 3 min, the intensity of the Si 2p peak is increased by a factor of eight, as shown in Fig. 2(c). In addition, a small hump at the left shoulder of the Si 2p peak appears, which could be ascribed to Hf-silicide. So, both Si 2p and Hf 4f spectra reach the same conclusion that the HfO_2 film become unstable at the temperature of 750 °C and is fully decomposed at the temperature of 850 °C.

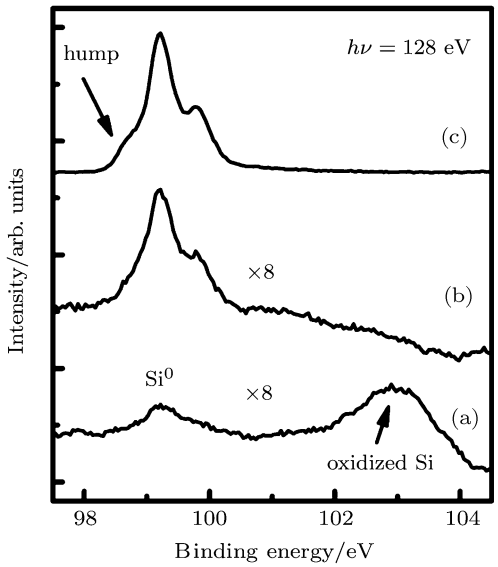


Fig. 2. Si 2p core level PES spectra of HfO_2 films on Si. The excitation photon energy is 128 eV. (a) The as-deposited films, (b) annealed at 750 °C under the UHV conditions, and (c) further annealed at 850 °C under the UHV conditions.

Likewise, this conclusion can be further confirmed by the O 2p valence band spectra at the kinetic energy range of around 43–50 eV with an excitation phonon energy of 53 eV, as shown in Fig. 3. For the as-deposited films, a small hump at a kinetic energy of about 41.40 eV in Fig. 3(a) is likely due to OH-related species, which is difficult to be removed despite the Ar^+ etching cleaning process taken.[2] As shown in Fig. 3(b), little change is observed for the O 2p signal after annealing at 750 °C for 3 min although the film begins to decompose at this temperature. It implies that at this temperature the film decomposition occurs at the interface rather than in the films since the O 2p signal with this kinetic energy range mainly originates from the surface of the HfO_2 film due to a limited escape depth of electrons. This result agrees well with the observation by both Si 2p and Hf 4f spectra. After annealing at 850 °C for 3 min, the O 2p signal almost disappears, and the features corresponding to the Si 3s and 3p emerge at the kinetic energy ranging from 48.6 eV to 53.6 eV in Fig. 3(c), indicating a complete decomposition of the HfO_2 film.

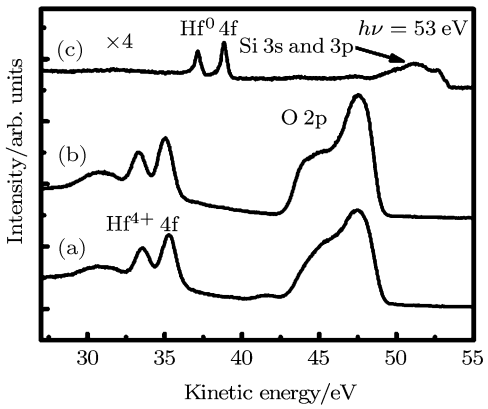


Fig. 3. Valence band spectra of HfO_2 films on Si. The excitation photon energy is 53 eV. (a) The as-deposited films, (b) annealed at 750 °C under the UHV conditions, and (c) further annealed at 850 °C under the UHV conditions.

According to the above analyses, the decomposition mechanism for HfO_2 film on Si could be revealed. Firstly, at the temperature of 750 °C, the decomposition reaction for the HfO_2 film is initiated only at the interface where the Hf-silicate is formed, while the film as a whole is hardly decomposed, based on the finding that the Si 2p peak of Hf-silicate disappears with an appearance of Hf-silicide signal, whereas the Hf^{4+} 4f peak of the HfO_2 film does not change. The following chemical reaction presumably accounts for this initial decomposition at the interface,

$$HfSi_xO_y + Si \rightarrow HfSi_x + HfO(g) + SiO(g). \quad (1)$$

After further annealing at 850 °C, the HfO_2 films completely decomposed. Another chemical reaction is

likely responsible for this decomposition of the HfO_2 films,

$$HfO_2 + Si \rightarrow HfSi_x + HfO(g) + SiO(g). \quad (2)$$

The product of gaseous HfO(g), involved in both decomposition reactions, desorbs, which leads to the remarkable reduction of the intensity of the Hf 4f signal as shown in Fig. 1(c).

For the HfO_2 films prepared by CVD, the decomposition temperatures are generally higher than that of the films we investigated.[8,11,12] This difference may be caused by different interface properties and/or film qualities that are also affected strongly by the former. So, the details on interface structure and chemistry are further investigated. A higher excitation photon energy of 230 eV is chosen in order to obtain more information about the HfO_2/Si interface through Hf 4f spectra, which results from a larger escape depth of Hf 4f electrons. In contrast to Fig. 1(a) of Hf 4f spectra obtained with the excitation photon energy of 128 eV, a small hump located at the binding energy of about 14.5 eV is clearly seen in the inset of Fig. 4, which corresponds to Hf-silicide at the interface. It was reported that once the silicide is formed at the interface, it will loosen the HfO_2 films or even sometimes leads to the void structure in the films, and therefore the decomposition of the HfO_2 films is likely promoted by this loose and/or void structure.[4,15] For our films, although no void structure is observed by transmission electron microscope (TEM) and scanning electron microscope (SEM) methods,[6,7] the relatively loose structure is evidenced by a lower refractive index of HfO_2 films compared with that of bulk HfO_2, as shown in Fig. 5.

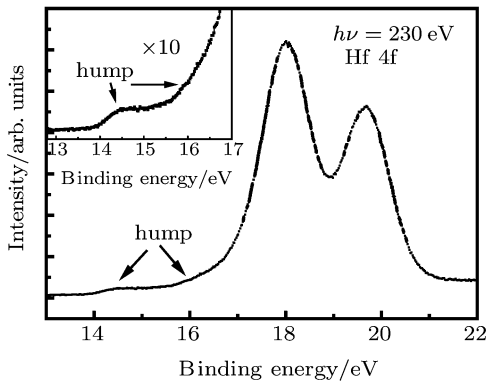


Fig. 4. Hf 4f PES spectra of HfO_2 films on Si. The excitation photon energy is 230 eV. The inset of the figure enlarges the curve in the range of binding energy 13∼17 eV.

Moreover, the Hf-silicide is likely formed at the very beginning of growth, rather than during the films growth. At the initial stage of the growth of HfO_2 films on clean Si substrate, a small portion of Hf atoms which are evapourated from the metallic Hf source presumably react directly with Si to form Hf-silicide, due to the low pressure of oxygen used, which is limited by MBE methods. Although the atomic oxygen is used in our experiments, which can only significantly reduce the Hf-silicide formation due to more oxidizations of atomic oxygen, it is still hard to completely prevent the formation of it. Contrarily, the Hf-silicide can be effectively eliminated for the HfO_2 films prepared by CVD methods due to the oxidized Hf^{4+} sources generally adopted and a high oxygen partial pressure in a typical CVD growth chamber. So, the formation of Hf-silicide at the initial growth could not completely be prevented in the MBE growth process with an Hf metallic source. It is the Hf-silicide formation that makes the subsequently grown HfO_2 films to be loosened, and thus leads to a lower decomposition temperature.

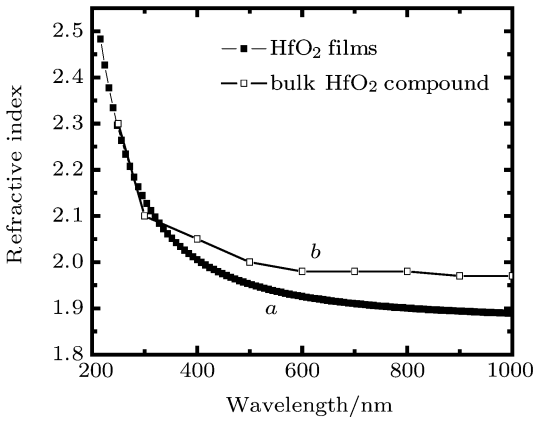


Fig. 5. Refractive index as a function of wavelength for HfO_2 film (curve *a*) grown on Si(001) and bulk HfO_2 compound (curve *b*).

In summary, thermal stability of HfO_2 films prepared by electron beam evapouration was investigated by SRPES upon UHV annealing. HfO_2 films begin to decompose at the interface at the annealing temperature of 750 °C. After annealing at 850 °C for 3 min, HfO_2 films are fully decomposed, with Hf partially forming Hf-silicide and partially forming gaseous HfO. Two chemical reactions are suggested to be responsible for the decomposition of the HfO_2 films. A small amount of Hf-silicide, which is formed at the very beginning of the growth, leads to a lower decomposition temperature compared to that of CVD-prepared HfO_2 films.

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