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Growth and characterization of UHV sputtering HfO_2 film by plasma oxidation and low temperature annealing

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Abstract Ultra-thin (∼4.0 nm) HfO_2 films were fabricated by plasma oxidation of sputtered metallic Hf films with post low temperature annealing. Advantage of this fabrication process is that the pre-deposition of Hf metal can suppress the formation of interfacial layer between HfO_2 film and Si substrate. The as-deposited HfO_2 films were subsequently treated by rapid thermal annealing at different temperatures in N_2 to investigate the effects of thermal annealing on the physical and electrical properties of HfO_2 film. A SiO_2-rich interface layer was observed after higher temperature rapid thermal annealing and the phase change of HfO_2 film from amorphous into crystalline occurred at about 700°C. As a result of higher temperature annealing, effective dielectric constant and leakage current were significantly influenced by the formation of interface layer and the crystallization of HfO_2 film.

Keywords High-*k* dielectric thin films · Metal-oxide-semiconductor · UHV Sputtering · Rapid thermal annealing

High-*k* gate dielectrics have attracted much attention for replacing conventional SiO_2 for future generation of complementary metal-oxide-semiconductor (CMOS) device. Several metal oxides with higher dielectric constant (k) in the range of 10–25, such as Al_2O_3 (∼10) and La_2O_3 (∼20), have been proposed as potential candidates for SiO_2 gate replacement. However, Hafnium Dioxide (HfO_2) is attractive due to its high dielectric constant (22–25), relatively large band gap (5.8 eV) and thermodynamic stability in direct contact with silicon [1, 2]. HfO_2 films prepared by sputtering, atomic layer deposition, pulse laser deposition, and electron beam evaporation had been widely studied [3–6]. However, the formation of interfacial layer, due to the oxidation of Si substrate during film fabrication and subsequent annealing, and the crystallization of HfO_2 films are still serious issues [7–9]. Recently, remote plasma oxidation has been performed to form the stoichiometric HfO_2 film, in which the oxygen radicals oxidize the Hf metal selectively other than Si substrate [10]. In comparison to rapid thermal annealing (RTA), plasma oxidation technique has advantages of suppressing the interfacial diffusion at the interface between HfO_2 film and Si substrate [11]. Plasma oxidation, using oxygen radicals to oxidize Hf metal at low temperatures, can maintain HfO_2 film in an amorphous phase with silicate interface, but it leads to both reduction of equivalent oxide thickness (EOT) and leakage current density (J_g) [12]. Rapid thermal annealing at elevated temperature can be used to densify the deposited oxide film and improve the properties of the films. However, uncontrolled formation of an interfacial oxide layer during annealing is undesirable and will increase the EOT.

In this paper, we investigated the effects of post-deposition annealing of HfO_2 film (∼4 nm) on their interfacial, microstructural and electrical characteristics. As a result of higher temperature annealing, a SiO_2-rich interface layer was observed. The phase transition of HfO_2 film from amorphous into crystalline occurred at about 700°C. The formation of

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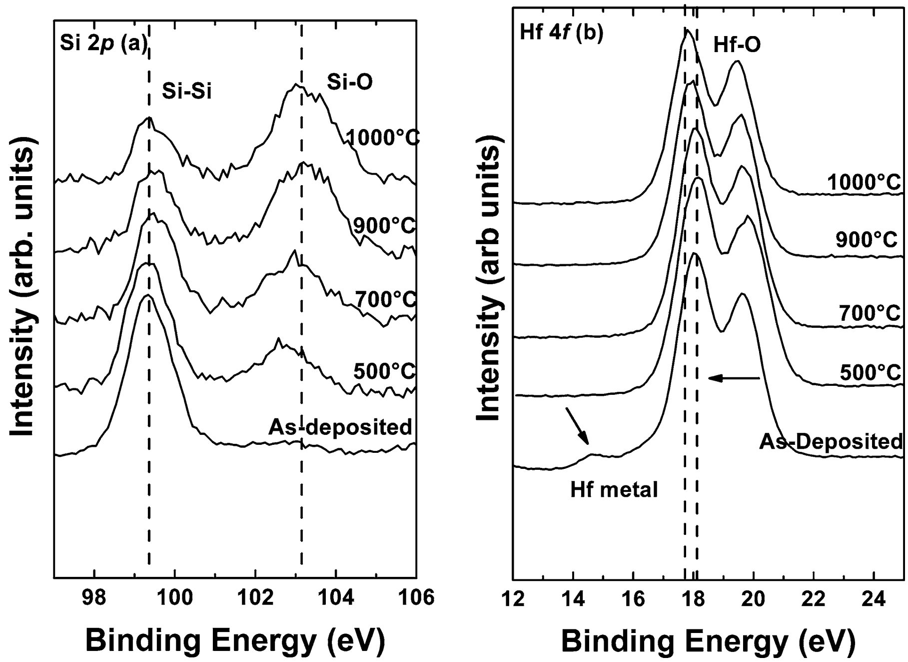

Fig. 1 (a) Si 2p (b) Hf 4f core-level spectra of ∼4 nm as-deposited HfO_2 film and films with rapid thermal annealing at different temperatures

interface layer and the crystallization of HfO_2 film significantly influenced the effective dielectric constant and the leakage current.

Experimental

For all depositions, n-type (100) Si substrate was last cleaned by 5% HF to remove native Silicon dioxide. Hf metal films (∼3 nm) were fabricated on Si substrate by ultra-high-vacuum (UHV) dc sputtering system at room temperature in Ar plasma with a base pressure of 5×10^{-10} Torr. Hf metal films were transferred, without breaking the vacuum, to a chamber equipped with an Oxford Plasmalab ICP65 system. After plasma oxidation for 60 sec at room temperature, HfO_2 films (∼4 nm) were annealed at 400°C in N_2 for 10 sec to densify HfO_2 films. To investigate the effects of RTA temperature on the physical and electrical properties of HfO_2 films, HfO_2 films were treated by RTA under different temperatures from 500°C to 1000°C.

All samples with and without RTA treatments were characterized by *ex situ* high-resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS) with monochromatic and standard Al source. Furthermore, in order to evaluate the electrical properties of the plasma oxidation HfO_2 films in response to post-deposition annealing processing, Al was sputtered on HfO_2 films as gate electrode patterned with a mask which has regular holes (diameter ∼0.18 mm). To form Metal-oxide-silicon (MOS) capacitor for electrical measurements, the backside of Si substrate was also sputtered with Al.

Results and discussion

Ex situ XPS measurement was performed on HfO_2 films with respect to different annealing conditions compared with the as-deposited HfO_2 film. Figure 1 shows the Si 2p (a) and Hf 4f (b) core-level XPS spectra of HfO_2 films as a function of annealing temperatures. In Fig. 1(a) for Si 2p spectra, a peak at 99.3 eV for all samples are mainly corresponds to Si–Si bond of Si substrate. For the as-deposited HfO_2 film, there is no other peak observed except the peak center at 99.3 eV, suggesting the interface free from SiO_2 and silicate. This implies that the oxygen radical oxidized Hf metal selectively other than Si substrate during the plasma oxidation process to fabricate HfO_2 film, which has been demonstrated by Yamamoto et al. [10]. In contrast with the formation of the interface layer when HfO_2 film deposited directly on Si substrate, the free of interface layer provided evidences that this fabrication process can remarkably prevent the oxygen diffusion through HfO_2 film layer into Si substrate [13]. However, with the increasing temperature of RTA, it should be noted that the peak of Si 2p at 102.8 eV shift to 103.3 eV. The shifts of Si 2p peak energy indicated that the oxidation state of Si enhanced with the elevation of RTA temperature [14]. The peak of Si 2p for samples after 900°C annealing was at 103.3 eV, which suggests the formation of SiO_2-rich interface. We assumed that the formation of interfacial layer was probably due to the diffusion of oxygen during RTA. These results well agreed with interfacial layer observed from HRTEM images, which will be discussed later.

As shown in Fig. 1(b), for all samples, Hf 4$f_{7/2}$ peak at 16.8 eV, corresponding to Hf–O bond, separated by 1.7 eV from Hf 4$f_{5/2}$ peak at 18.5 eV. However, for the as-deposited

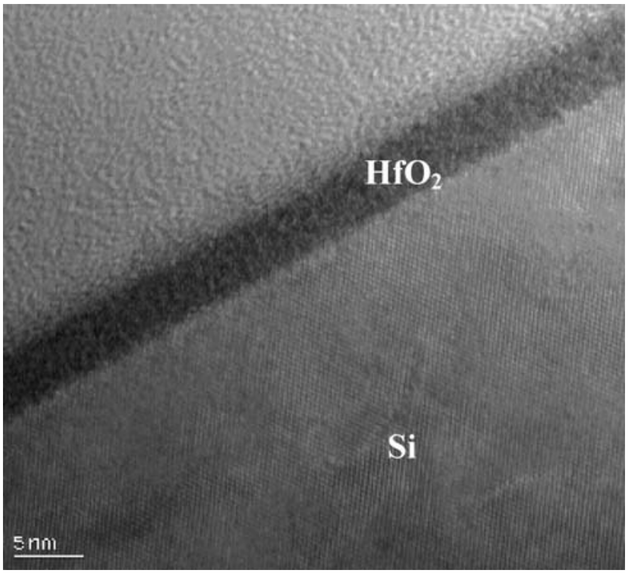

Fig. 2 Cross-sectional HRTEM image of as-deposited HfO_2 film (∼4 nm)

HfO_2 film, a shoulder can be clear seen at the lower binding energy at 14.4 eV. The shoulder was possibly caused by slightly amount of residual Hf metal in HfO_2 film or Hf−Si bond formed at the interface. It is worth noting that the small Hf metal peak disappeared after RTA treatments, which may caused by the fully oxidation of HfO_2 film occurred during annealing process. In addition, Hf–O peaks shifted toward elemental Hf at lower binding energy with the increasing of annealing temperatures, which may due to the dissociation of Hf−O bonds or the formation of Hf−O−Si bonds [15].

Cross-sectional HRTEM was performed to provide a direct measurement of layer thickness and yield other information including microstructure and interface quality. Figure 2 shows the cross-sectional HRTEM image of as-deposited HfO_2 film on Si substrate. The as-deposited HfO_2 film (∼ 4 nm) was in an amorphous structure without amorphous layer formed at the interface between HfO_2 film and Si substrate. This further confirms that the fabrication method used may successfully block the diffusion of oxygen through HfO_2 films into Si substrate. This may attribute to the pre-deposition of Hf metal on Si substrate, which suppressed the interfacial diffusion and reaction during the plasma oxidation process [11].

In order to study HfO_2 film in response to rapid thermal annealing, cross-sectional HRTEM was also performed on the samples with annealing treatments. Figure 3 shows images of HfO_2 film after RTA in N_2 for 10 s under temperature at (a) 500°C; (b) 700°C; (c) 900°C; and (d) 1000°C, respectively. The SiO_2-like amorphous interfacial layers were observed, which were in well agreement with XPS results. As the annealing temperature increasing, the thickness of the interfacial layer increased from 1.3 nm at 500°C to 2.5 nm at 1000°C. The thickness of interfacial layer was thicker than native silicon oxide (∼1 to 1.5 nm), indicating some catalytic oxidation effects during annealing process. The catalytic oxidation effect is proposed that the deposited metal oxide enhances oxygen dissociation which results in enhancing the oxidation rate at the interface [16]. Furthermore, it was found that HfO_2 layer slightly crystallized after 700°C RTA, which suggests that the transition temperature of HfO_2 from amorphous into crystalline phase was around 700°C. In addition, it can be predicted that the formation of interface layer will reduce the dielectric constant and increase the physics thickness of HfO_2 films.

In our experiments, another area of concern was the electrical properties of HfO_2 film in response to RTA. The formation of interfacial layer and structure transition of HfO_2 film during RTA would have significant effects on the electrical properties. The capacitances versus voltage (C-V) measurements at 100 KHz were carried out for the capacitances of Al/HfO_2/Si stacks (shown in Fig. 4). Each measurement started from inversion voltage (−3 V), then goes into accumulation region (3 V) with a bias step of 0.1 V/s. The measured capacitance density (C_{max}/A) of the as-deposited

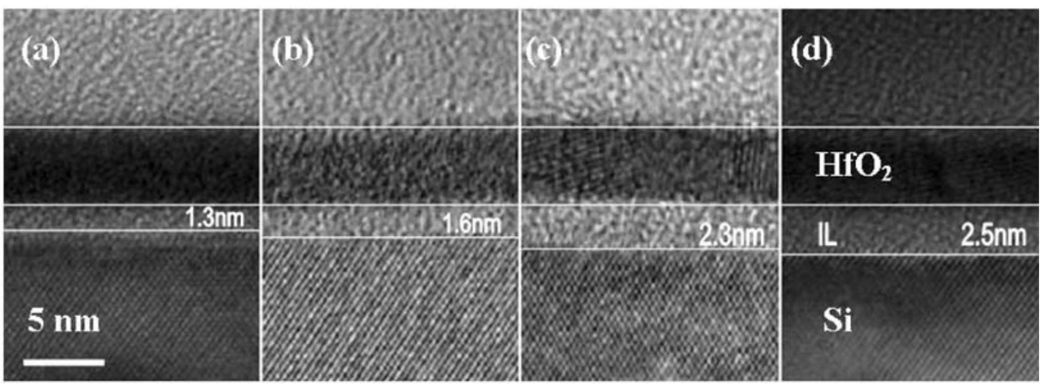

Fig. 3 Cross-sectional HRTEM images of HfO_2 film with rapid thermal annealing in N_2 for 10 s, under different temperatures at (a) 500°C; (b) 700°C; (c) 900°C; (d) 1000°C, respectively. The thicknesses of interface layers were labeled

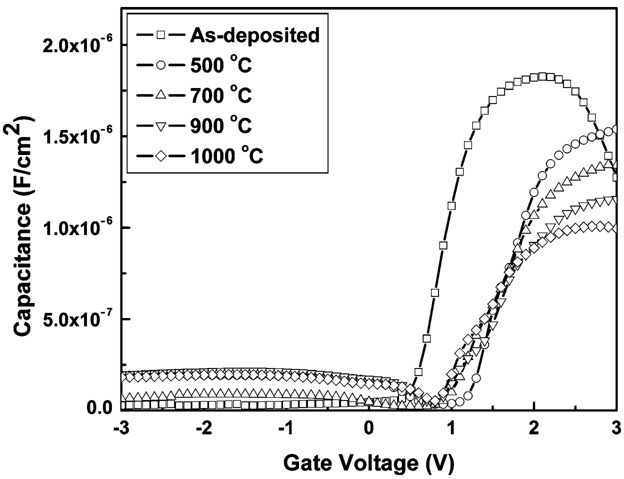

Fig. 4 Capacitance-voltage characteristics of as-deposited HfO_2 film (~4 nm) and films with rapid thermal annealing at different temperatures

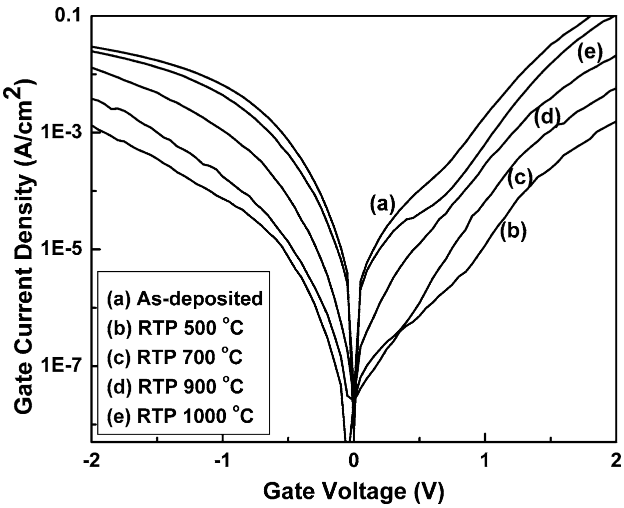

Fig. 5 Current density-voltage characteristics of as-deposited HfO_2 film (~4 nm) and films with rapid thermal annealing at different temperatures

HfO_2 film in the accumulation region was $2\times10^{-6}\mu F/cm^2$. As the annealing temperature increasing, the capacitance density decreased to $1\times10^{-6}\mu F/cm^2$. The decrement of capacitance may be caused by the decreasing of the series capacitance while the interfacial layer increasing. If we assumed that the dielectric constant of interface layer is close to the value of $SiO_2(k = 3.9)$, the dielectric constants of HfO_2 layers were determined to be in the range of 15–22 for the annealed samples [1]. It is worth noting that the effective dielectric constant of the annealed HfO_2 film at 500°C has the largest k value (~22). The dielectric constant of HfO_2 film annealed at 500°C is well agreement with the value (~21) reported by Callegari et al. [17]. The better performance for sample annealed at 500°C may be attributed to the greatly reduction of interface traps during the annealing process. In addition, it may account for the thinner interface layer and amorphous structure.

The flat band voltages shifted with respect to the ideal flat band condition were enhanced with the increasing of annealing temperature. The possible reason is that the annealing prior to Al deposition in our experiment introduced a large number of oxide charges by diffusion. It has been reported that the rapid thermal annealing will result in removal of interface traps and introduce oxide traps [18]. Thereafter, it is suggested that the trade-off between the interface charge density and oxide traps density should be considered to obtain the better electrical performance.

Typical leakage current characteristics (current density-voltage or I-V) of Al/HfO_2/Si capacitor were obtained in different annealing temperature compared with as-deposited film (shown in Fig. 5). The leakage current density of the as-deposited HfO_2 film is rather high (0.1 A/cm^2 bias at 1V), which may be due to the excess Hf metal component remaining inside the HfO_2 film. After 500°C RTA in N_2 for 10 s, the leakage current of HfO_2 film greatly decreased to 10^{-5}A/cm^2, which indicates that the film was fully oxidized and densified by RTA. In addition, the leakage current obtained was comparable to the results obtained by the thermal evaporation HfO_2 film [19]. However, the leakage current density was increased rapidly from 10^{-5} A/cm^2 to 10^{-3} A/cm^2 at 1 V after RTA higher than 700°C. Combined with results obtained from HRTEM images, the large leakage current may be caused by the crystallization of HfO_2 film when temperature higher than 700°C. It is worthwhile to point out that the thinnest interfacial layer and the lowest leakage current was obtained for the HfO_2 sample annealed at 500°C.

Conclusions

In summary, amorphous HfO_2 thin film was fabricated by plasma oxidation of pre-deposited metallic Hf film on Si substrate. The interfacial structure, film microstructure, and electrical properties of HfO_2 film were analyzed. It was found that pre-deposition of Hf metal can suppress the formation of interfacial layer. As a result of higher annealing temperature, effective dielectric constant and leakage current were significantly influenced by the formation of interface layer and the crystallization of HfO_2 films. It should be noted that the better electrical performance was obtained by the HfO_2 sample annealing at 500°C in N_2 for 10 s.

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