Micron 41 (2010) 15–19

Contents lists available at ScienceDirect

Micron

journal homepage: www.elsevier.com/locate/micron

Characterization of the interface between the Hf-based high-*k* thin film and the Si using spatially resolved electron energy-loss spectroscopy

X.F. Wang [a], Quan Li [a,*], P.F. Lee [b], J.Y. Dai [b], X.G. Gong [c]

[a] Department of Physics, The Chinese University of Hong Kong, Shatin, New Territory, Hong Kong
[b] Department of Applied Physic and Materials Research Center, The Hong Kong Polytechnic University, HongHom, Kowloon, Hong Kong
[c] Department of Physics, Fudan University, ShangHai, China

ARTICLE INFO

Article history:
Received 6 March 2009
Accepted 15 July 2009

Keywords:
High-*k* dielectric
Interface
Electron energy-loss spectroscopy
HfO_2
HfAlO

ABSTRACT

The interfacial structures of HfO_2 and HfAlO thin films on Si have been investigated using spatially resolved electron energy-loss spectroscopy. We have found that interfaces are not atomically sharp, and variation in the symmetry of the local atomic coordination lasts for a couple of monolayers for both the as-deposited HfO_2 and the HfAlO samples. Annealing of the HfO_2 film in the oxygen environment leads to the formation of a thick SiO_2/SiO_x stack layer in-between the original HfO_2 and the Si substrate. As a comparison, the interfacial stability is significantly improved by Al incorporation into the HfO_2 film (forming HfAlO), which effectively reduced/eliminated the interfacial silicon oxide formation during the oxygen annealing process. The mechanism of the high-*k* film/substrate stabilization by Al incorporation is discussed based on the experimental results.

1. Introduction

High-*k* materials have been widely studied as the gate dielectric to replace SiO_2 in the future complementary metal-oxide-semiconductor (CMOS) integrated circuit technology (Wilk et al., 2001; Wallace and Wilk, 2003). Among various candidates, HfO_2-based materials are considered to be the most promising ones due to their large dielectric constants, which ensure the improved device electrical performance at larger dielectric thickness compared to that of SiO_2. In 2007, using an undisclosed thick hafnium-based material as the gate dielectric, Intel released a 45 nm high-*k* silicon technology, in which reduced transistor leakage by more than 10 times over the current silicon dioxide technology was claimed, making the future of this family of materials more promising.

The major concern of using HfO_2 as the gate dielectric layer is its interfacial quality with the Si substrate, which determines the ultimate performance of the device (Robertson, 2004). Chemical reactions occurring at the film/substrate interface during the film growth and/or post-deposition treatment have been discussed in the literatures, in which two possible interfacial configurations have been suggested. Cho et al. (2002) have reported an interfacial layer of hafnium silicate was grown at an initial growth stage and changed into silicide layer when annealed at 700 °C under ultrahigh vacuum condition. Such a metallic silicide layer is highly undesirable as it would result in a large channel leakage between the source and drain. On the other hand, SiO_2 formation in-between the HfO_2 and the Si has also been observed both during deposition with high O partial pressure and after the post-deposition oxygen annealing process (Lu et al., 2006; Ferrari and Scarel, 2004). Although the oxidation mechanisms are still debated, the formed low-*k* SiO_2 layer will increase the overall equivalent oxide thickness (EOT) and degrade the device performance. Several strategies have been proposed to improve the interfacial stability of the high-*k* hafnium-based films on Si. For example, better stability against annealing at 1000 °C has been observed for HfO_2/SiO_xN_y film stack on Si (Bastos et al., 2002), in which direct incorporation of a third element (such Al, Si or N) in HfO_2 has also been attempted for this purpose (Visokay et al., 2002; Bae et al., 2003). Nevertheless, a detailed understanding on the interfacial structure of the HfO_2/Si, and the effect of a third element addition on the interfacial structure before and after the oxygen annealing remain unclear.

In this paper, we have carried out a systematic investigation on the interface between the HfO_2 film and the Si substrate before and after oxygen annealing. The effect of Al incorporation on the film/substrate interface has also been evaluated. In particular, we have employed electron energy-loss spectroscopy performed in a scanning transmission electron microscope (STEM) to acquire information on their local structure across the film/substrate interface. The subtle differences of the interfacial profiles obtained from these samples provide abundant information on their interface structural quality.

* Corresponding author.
E-mail address: liquan@phy.cuhk.edu.hk (Q. Li).

0968-4328/$ – see front matter. Crown Copyright © 2009 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.micron.2009.07.009

2. Experimental

HfO_2-based thin films with thickness of about 20 nm were deposited by pulsed laser deposition (PLD) on p-type (1 0 0) Si substrates, using high-purity targets of HfO_2 and hafnium aluminate (Hf/Al ratio 1:1). The silicon substrate were treated by an HF etch before the thin film deposition, to leave the silicon surface terminated by hydrogen. The substrate temperature was maintained at 550 °C during the deposition, and the post-deposition annealing was performed in O_2 at 750 °C for 45 min.

The high resolution STEM images were taken using a high angle annular dark field (HAADF) detector in a STEM (Tecnai G2, FEG). The electron energy-loss spectroscopy (EELS) was performed in the STEM line scan mode, using a Gatan imaging filtering (GIF) system attached to the same microscope. The electron probe size was maintained at 0.3 nm during the line scan. After subtraction of the background with a power-law method, the energy-loss spectra were fitted using Gaussian multi-peak fitting.

3. Results and discussion

HAADF image taken at the as-deposited HfO_2 dielectric and the Si substrate shows a sharp interface—the Si crystalline fringes extends to the boundary of the bright/dark contrast (Fig. 1(a)). After oxygen annealing, an amorphous interfacial layer of ~3 nm thickness is found to develop in-between the bright contrast (corresponding to the high-*k* film) and the crystalline fringes of Si (Fig. 1(b)). Similar to the interface between the as-deposited pure HfO_2 and Si, the one between the as-deposited HfAlO and the substrate appears to be sharp (Fig. 1(c)) as well. Although an amorphous interfacial layer also appears after the O_2 annealing of HfAlO (Fig. 1(d)), the thickness of such a layer has been reduced to ≤1 nm, being much smaller than that of the annealed HfO_2 on Si.

More detailed information on the interfacial structures of these samples are obtained from the O K-edge energy-loss spectra taken in the STEM line scan mode across the interface between the high-*k* films and the Si substrate. Fig. 2 shows such spectra recorded from the as-deposited HfO_2. The open circle markers on the HAADF image illustrate the positions of the electron probes, and consequently from which location each spectrum was taken. Away from the HfO_2/Si interface, the oxygen K-edge gives a double-peak feature (line 1), which is slowly broadened as the electron probe approaches the interface (lines 2 and 3). A single broad peak is observed for the oxygen K-edge (line 4), which intensity rapidly falls off as the electron probe moves into the Si (line 5).

A significantly different interfacial profile (Fig. 3) has been observed for the oxygen K-edge recorded across the interface of the annealed HfO_2 thin film and the Si. The double-peak feature (lines 1 and 2) is still observed at regions away from the interface when bright contrast is observed in the corresponding HAADF image, although the relative intensity of the two peaks has changed

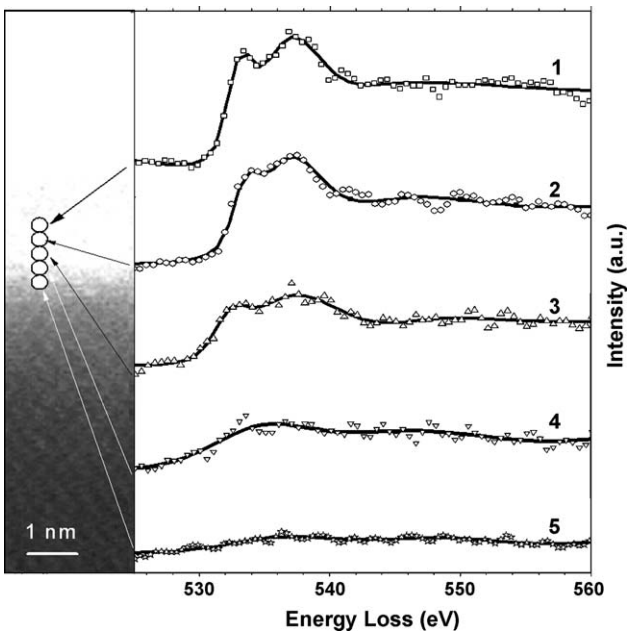

Fig. 2. O K-edge energy-loss spectra recorded across the as-deposited HfO_2/Si interface.

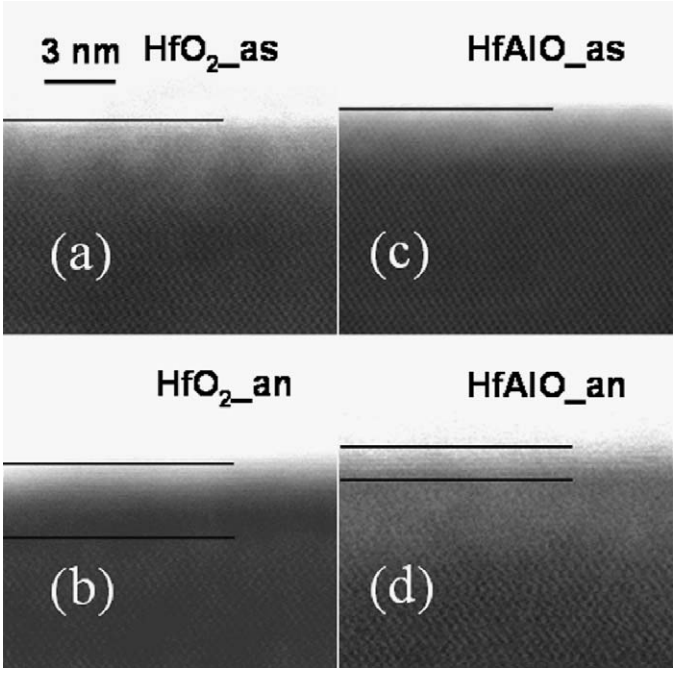

Fig. 1. HAADF image of the HfO_2 (HfAlO)/Si interface before and after annealing.

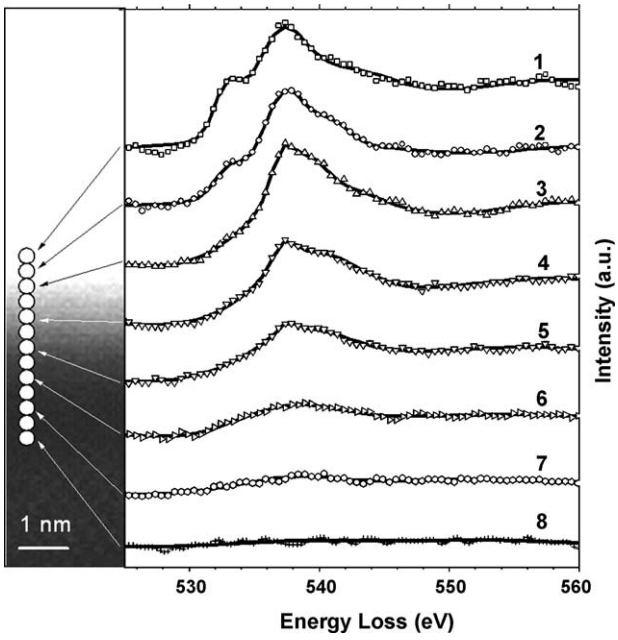

Fig. 3. O K-edge energy-loss spectra recorded across the HfO_2/Si interface after oxygen annealing.

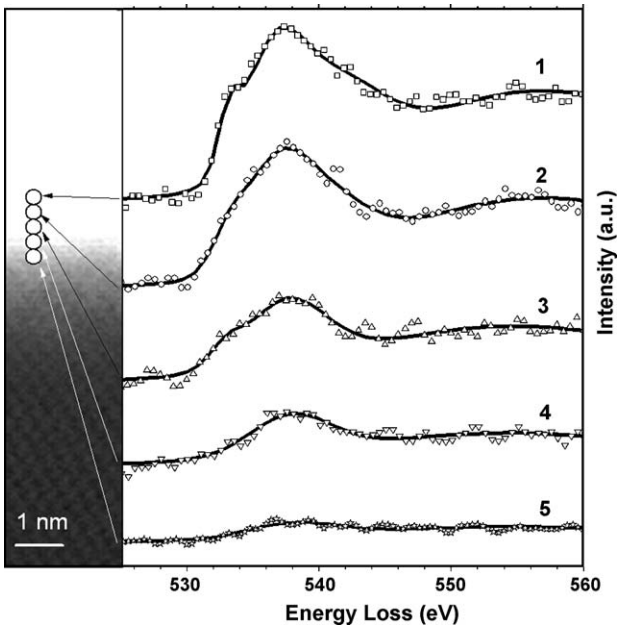

Fig. 4. O K-edge energy-loss spectra recorded across the as-deposited HfAlO/Si interface.

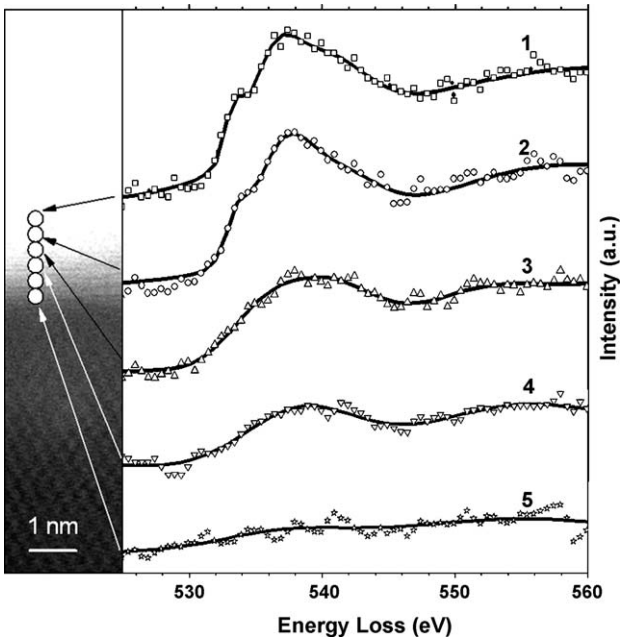

Fig. 5. O K-edge energy-loss spectra recorded across the HfAlO/Si interface after oxygen annealing.

compared to the as-deposited sample. The double-peak feature quickly evolves to single peak (lines 3–5), with line shape being characteristic of that of the oxygen in the SiO_2 (Wilk and Muller, 2003). Such a feature persists for a number of monolayers, before it slowly broadens together with an intensity decrease (line 6). The signal of the oxygen K-edge eventually falls off, when the crystalline fringes of Si start to show in the corresponding high resolution HAADF image.

Fig. 4 shows the oxygen K-edge EELS spectra recorded across the interface between the as-deposited HfAlO and the Si substrate. In the HfAlO film away form the interface, the oxygen K-edge presents a major peak with a shoulder occurring at low energy loss (line 1). The major peak broadens with a decrease in intensity as the electron probe approaches the interface (lines 2 and 3), making the shoulder peak less obvious. A single peak with low intensity is also observed for the oxygen K-edge (line 4) recorded at the interface, and its signal falls off as the electron probe move into the Si (line 5).

Being different than that of pure HfO_2, only a slightly different interfacial profile (Fig. 5) has been observed for the oxygen K-edge recorded across the interface after the oxygen annealing of the HfAlO film. Little change in the O K-edge energy-loss spectra is observed at regions away from the interface (lines 1 and 2). As the electron probe scans towards the interface, a broad single peak is observed, which feature lasts for a couple of monolayers with its intensity decreasing (lines 3 and 4) and eventually becomes non-detectable (line 5) when crystalline fringes of Si start to show in the corresponding HAADF image.

The seemingly sharp interfaces observed in both the as-deposited HfO_2 and HfAlO thin films on Si in the HAADF image not necessarily suggest a chemically/structurally sharp interface of the high-*k* film and the Si substrate. On the other hand, the interfacial amorphous layers observed in both films after oxygen annealing indeed indicate a change at the interface, likely being related to the annealing atmosphere–oxygen, although more evidence is needed to support such an argument (as discussed in later sections). More importantly, the different thickness of the observed interfacial layer suggests a different interfacial property of the HfO_2 and the HfAlO films after annealing.

We now discuss the O K-edge EELS results taken from the four samples. The double-peak feature of the oxygen K-edge was commonly interpreted as resulting from the crystal-field splitting, which requires an eight-fold coordination of the Hf by the O atom in the cubic HfO_2 (McComb, 1996). In the monoclinic HfO_2 (such as in the present case), Hf coordination would be reduced to seven. Although the double-peak feature would remain, the lower symmetry (compared to that of cubic HfO_2) leads to slightly broadening of the peaks. In this sense, the less resolved double-peak features recorded near the HfO_2/Si interface suggest a further degradation on the local symmetry of the Hf atoms. On the other hand, the characteristic of the single broad peak recorded at the interface agrees with neither the O K-edge of HfO_2, nor that of silicon oxide. The low intensity of the peak and lack of information of the interfacial atomic structure make the exact identification of its origin difficult, but one may assign it to a monolayer of interfacial oxide of mixed nature (when Hf, Si and O co-exist). The rapid decrease in the peak intensity in the last curve (line 5 in Fig. 2) suggests a fast disappearance of the O signal, being consistent with the observation of Si lattice fringe from the corresponding location in the HAADF image.

The 750 °C annealing temperature is not expected to cause any phase change in the as-deposited HfO_2, when considering the high transition temperature from the monoclinic to tetragonal (1720 °C) and cubic (2600 °C) phase (Wang et al., 1992). Therefore, the slight modification in the line shape of the double-peak feature in the O K-edge profile of HfO_2 after annealing should not result from the change in its crystalline structure, but likely the change in the film defect structure. In fact, theoretical simulation has suggested that the O K-edge line shape is sensitive to the presence of various point defects, in particular, O related defects (Ostanin et al., 2000). The single peak feature and its line shape characteristic observed in the O K-edge EELS (from line 3 to 5 in Fig. 3) suggest the formation of SiO_2 layer directly underneath the HfO_2 film after annealing. In addition, no Hf signal is detected in such a region, excluding the possibility of hafnium silicide formation. Below the SiO_2 layer, not only the intensity of the O K-edge signal decreases, but also its line shape evolves to that characteristic of SiO_x (with $x < 2$) (Muller and Wilk, 2001).

The formation of SiO_2/SiO_x stack at the interface of the annealed HfO_2 and Si substrate suggest interfacial oxidation during the annealing process. Although an intuitive idea of the oxygen supply would be the annealing atmosphere—O_2 molecules could diffuse through the high-*k* thin film and reach the film/substrate interface, where chemical reaction occurs, the details of such diffusion deserves some elaboration. In fact, the diffusion mechanism of O_2 in HfO_2 has been discussed by Liu (2002), who have reported oxygen penetrating a 40 Å HfO_2 film via grain boundary diffusion. Theoretically, Foster et al. (2002) have calculated oxygen incorporation and diffusion in monoclinic HfO_2 for a range of oxygen species of both charged and neutral states, and suggested that the diffusion of singly charged oxygen interstitials serve as the most favorable route for the passage of oxygen in the HfO_2 (and to the interface). It has also been argued that the O in the HfO_2 has greater affinity to Si, and is likely to diffuse from the film interior to the interface to react with Si during the annealing process even in the absence of O_2 atmosphere (Hakala et al., 2006). When thicker SiO_2 layer is formed, further diffusion of O to the Si substrate becomes difficult, and that explain the formation of the non-stoichiometry silicon oxide (SiO_x) closer to the Si substrate.

Incorporation of Al to HfO_2 has been reported to increase its crystallization temperature to above 900 °C (Zhu et al., 2002). This is consistent with the observation that the as-deposited HfAlO film is amorphous (film deposition temperature 550 °C). In such a case, the specific line shape of the O K-edge as observed in line 1 of Fig. 4 should reflect the local symmetry of the Hf atom in the absence of long-range order. Comparing to the pure HfO_2, the added Al atoms and possible point defects induced by the Al incorporation would contribute to the degradation of the local symmetry of the Hf atoms, which explains the difference of the O K-edge line shape characteristics in the two films. Similar to the as-deposited HfO_2 film on Si, the broadening of the peaks when getting closer to the HfAlO/Si interface suggests that such local symmetry is further destroyed. At the interface, the single peak with a distinctly different line shape (as compared to that of HfAlO in the film interior) may result from the coexistence of Hf, Al, Si and O with monolayer thickness. The EELS results indicate that both the as-deposited HfO_2/Si and the HfAlO/Si interfaces are not atomically sharp, although the Si crystalline fringes extend to the boundary of the dark/light contrast in both HAADF images. A slow evolution in the local atomic symmetry (likely induced by the interfacial chemical composition change) with a couple of monolayer thickness exists in both samples.

No change in the crystallinity of HfAlO film is expected before and after annealing, as the 750 °C annealing temperature is not high enough for the crystallization of HfAlO. Consequently, the similar O K-edge energy-loss spectra taken in the interior of HfAlO before and after annealing (line 1 in Fig. 4 vs. 5) suggest little change in the local symmetry of the amorphous films. Compared to the as-deposited HfAlO sample, the single peak feature (lines 3 and 4 in Fig. 5) is very similar to that observed in line 4 of Fig. 4, but lasts to a larger thickness (~1 nm in the annealed vs. ~0.3 nm in as-deposited HfAlO). It is interesting to note the line shape of such a peak is consistent with that of neither SiO_2 (line 3 in Fig. 3) nor SiO_x (line 6 in Fig. 3), suggesting little SiO_2 (SiO_x) formation directly underneath the HfAlO after annealing, and the composition of such an interfacial layer could be similar to that of the as-deposited HfAlO, i.e., Hf, Al, Si and O.

The experimental results suggest that oxidation of Si at the high-*k* film/substrate interface is effectively suppressed when Al is incorporated into the HfO_2. Although it is intuitive to assume such a difference could be caused by the formation of Al_2O_3 in the HfO_2 (oxygen is difficult to diffuse through alumina), this assumption is lack of scientific evidence. As a matter of fact, our early study on the structure of amorphous HfAlO has shown that it is a single phase without any phase separation of HfO_2 and Al_2O_3 (Wang et al., 2007). On the other hand, Yu et al. (2002) have argued that the amorphous nature of HfAlO makes it impossible for O_2 diffusion through the grain boundaries, which are abundant in pure HfO_2. As suggested by Foster et al. (2002), singly charged oxygen interstitial serves as the most possible route for oxygen diffusion through the HfO_2 and eventually reaches the high-*k* film/Si interface. We have take a step forward to compare the activation barriers energy for different charged states of oxygen interstitial defects in HfO_2 with and without Al substitution, and found that the Al incorporation indeed resists the diffusion of neutral and singly charged oxygen interstitial defects in HfO_2 by increasing the corresponding barrier energies (Hou et al., 2008).

4. Conclusions

We have examined the interface between the HfO_2 film and the Si substrate before and after the oxygen annealing. Although the HAADF image seems to suggest a sharp interface between as-deposited HfO_2 film and the Si substrate, the oxygen K-edge energy-loss spectra discloses the evolution of the local atomic coordination in the vicinity of the film/substrate interface. Significantly different interfacial configuration is observed when such a film is annealed in the O_2—a SiO_2/SiO_x stack layer is observed to develop in-between the original HfO_2 and the Si. Although Al incorporation into the HfO_2 film does not improve the interfacial sharpness of the as-deposited sample, it effectively suppresses the oxygen diffusion to the interface during the annealing process, which contributes to the absence of the silicon oxide layer in-between the HfAlO film and the Si substrate.

Acknowledgement

This work is supported by a grant from the research grant council from HKSAR (project No. CUHK 402105).

References

Bae, S.H., Lee, C.H., Clark, R., Kwong, D.L., 2003. MOS characteristics of ultrathin CVD HfAlO gate dielectrics. IEEE Electron Device Lett. 24, 556–558.

Bastos, K.P., Morais, J., Miotti, L., Pezzi, R.P., Soares, G.V., Baumvol, I.J.R., Tseng, H.H., Hedge, R.I., Tobin, P.J., 2002. Oxygen reaction-diffusion in metal organic chemical vapor deposition HfO_2 films annealed in O_2. Appl. Phys. Lett. 81, 1669–1671.

Cho, M.H., Roh, Y.S., Whang, C.N., Jeong, K., Nahm, S.W., Ko, D.H., Lee, J.H., Lee, N.I., Fujihara, K., 2002. Thermal stability and structural characteristics of HfO_2 films on Si (100) grown by atomic layer deposition. Appl. Phys. Lett. 81, 472–474.

Ferrari, S., Scarel, G., 2004. Oxygen diffusion in atomic layer deposited ZrO_2 and HfO_2 thin films on Si(100). J. Appl. Phys. 96, 144–149.

Foster, A.S., Shluger, A.L., Nieminen, R.M., 2002. Mechanism of interstitial oxygen diffusion in hafnia. Phys. Rev. Lett. 89, 225901.

Hou, Z.F., Gong, X.G., Quan, Li., 2008. Al-induced reduction of the oxygen diffusion in HfO_2: ab initio study. J. Phys.: Cond. Matter 20, 135206.

Hakala, M.H., Foster, A.S., Gavartin, J.L., Havu, P., Puska, M.J., Nieminen, R.M., 2006. Interfacial oxide growth at silicon/high-k oxide interfaces: first principles modeling of the Si-HfO_2 interface. J. Appl. Phys. 100, 043708.

Liu, C.L., 2002. Ab-initio modeling of boron and oxygen diffusion in polycrystalline HfO_2 films. Physica Status Solidi B 233, 18–23.

Lu, Y.K., Zhu, W., Chen, X.F., Gopalkrishnan, R., 2006. Interface control in the laser MBE growth of hafnium oxide. Thin Solid Films 504, 188–191.

McComb, D.W., 1996. Bonding and electronic structure in zirconia pseudopolymorphs investigated by electron energy-loss spectroscopy. Phys. Rev. B 54, 7094–7102.

Muller, D.A., Wilk, G.D., 2001. Atomic scale measurements of the interfacial electronic structure and chemistry of zirconium silicate gate dielectrics. Appl. Phys. Lett. 79, 4195–4197.

Ostanin, S., Craven, A.J., McComb, D.W., Vlachos, D., Alavi, A., Finnis, M.W., Paxton, A.T., 2000. Effect of relaxation on the oxygen K-edge electron energy-loss near-edge structure in yttria-stabilized zirconia. Phys. Rev. B 62, 14728–14735.

Robertson, J., 2004. High dielectric constant oxides. Eur. Phys. J. Appl. Phys. 28, 265–291.

Visokay, M.R., Chambers, J.J., Rotondaro, A.L.P., Shanware, A., Colombo, L., 2002. Application of HfSiON as a gate dielectric material. Appl. Phys. Lett. 80, 3183–3185.

Wilk, G.D., Muller, D.A., 2003. Correlation of annealing effects on local electronic structure and macroscopic electrical properties for HfO_2 deposited by atomic layer deposition. Appl. Phys. Lett. 83, 3984–3986.

Wilk, G.D., Wallace, R.M., Anthony, J.M., 2001. High-k gate dielectric: current status and materials properties considerations. J. Appl. Phys. 89, 5243–5275.

Wallace, R.M., Wilk, G.D., 2003. High-k dielectric materials for microelectronics. Crit. Rev. Solid State Mater. Sci. 28, 231–285.

Wang, J., Li, H.P., Stevens, R., 1992. Hafnia and Hafnia-toughened ceramics. J. Mater. Sci. 27, 5397–5430.

Wang, X.F., Quan Li, Egerton, R.F., Lee, P.F., Dai, J.Y., Hou, Z.F., Gong, X.G., 2007. Effect of Al addition on the microstructure and electronic structure of HfO_2 film. J. Appl. Phys. 101, 013514.

Yu, H.Y., Wu, N., Li, M.F., Zhu, C.X., Cho, B.J., 2002. Thermal stability of $(HfO_2)(x)(-Al_2O_3)(1-x)$ on Si. Appl. Phys. Lett. 81, 3618–3620.

Zhu, W.J., Tamagawa, T., Gibson, M., Furukawa, T., Ma, T.P., 2002. Effect of Al inclusion in HfO_2 on the physical and electrical properties of the dielectrics. IEEE Electron Device Lett. 23, 649–651.