Influence of different oxidants on the band alignment of HfO_2 films deposited by atomic layer deposition*

Fan Ji-Bin(樊继斌)†, Liu Hong-Xia(刘红侠), Gao Bo(高 博),
Ma Fei(马 飞), Zhuo Qing-Qing(卓青青), and Hao Yue(郝 跃)

School of Microelectronics, Key Laboratory of Wide Band-Gap Semiconductor Materials and Devices, Xidian University, Xi'an 710071, China

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Based on X-ray photoelectron spectroscopy (XPS), influences of different oxidants on band alignment of HfO_2 films deposited by atomic layer deposition (ALD) are investigated in this paper. The measured valence band offset (VBO) value for H_2O-based HfO_2 increases from 3.17 eV to 3.32 eV after annealing, whereas the VBO value for O_3-based HfO_2 decreases from 3.57 eV to 3.46 eV. The research results indicate that the silicate layer changes in different ways for H_2O-based and O_3-based HfO_2 films after the annealing process, which plays a key role in generating the internal electric field formed by the dipoles. The variations of the dipoles at the interface between the HfO_2 and SiO_2 after annealing may lead the VBO values of H_2O-based and O_3-based HfO_2 to vary in different ways, which fits with the variation of flat band (V_{FB}) voltage.

Keywords: HfO_2, band alignment, annealing, X-ray photoelectron spectroscopy, dipoles

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1. Introduction

HfO_2 film has been widely investigated as one of the most popular materials for nanoelectronic applications, and industries are converging to the integration of the HfO_2 based high-κ in a gate-last manner for the sub-30 nm Si complementary metal–oxide semiconductor (CMOS) process.[1,2] The valence and conduction band offsets of the materials are required to be greater than 1 eV.[3,4] However, the band alignment is always unintentionally changed after thermal annealing due to the formation of hafnium silicate between HfO_2 and SiO_2. The internal electric field built by the dipoles at the high-κ/interfacial layer is believed to influence the changes of band bending and the value of band offsets.[5] Variations of the band offsets have adverse effects on the effective V_{FB}, which subsequently changes the V_{TH} of the transistor and affects the device operation.[6] In order to clarify the issue of band discontinuity formation, a lot of theoretical and experimental research has been performed. For the HfO_2 dielectric deposited by ALD, H_2O or O_3 is used as an oxygen source, and tetrakis (ethylmethylamino) hafnium (TEMAH) is used as a hafnium precursor. Due to the fact that their reaction mechanisms are different, O_3-based HfO_2 and H_2O-based HfO_2 show some different physical properties such as impurities and defects, which affects the film characteristics after annealing. Therefore, we need to investigate the origin of the changes for a better understanding of influence of different processes on the band offset.

In order to investigate the influences of different oxidants on the band alignment of HfO_2 films, the O_3-based HfO_2 and H_2O-based HfO_2 films are deposited at 300 °C by ALD and then annealed in the nitrogen at 600 °C, which is compatible with a gate-last process in the fabrication of CMOS. XPS is used to investigate the band offsets between HfO_2 and Si.

2. Experiment

Before the deposition, the P-type (8 Ω·cm–12 Ω·cm) B-doped Si (100) wafers are obtained after RCA cleaning and a 30-s dip in diluted HF solution to remove the native oxide, which is followed by a 60 s rinse in deionized water. Then H_2O and O_3 are used as different oxygen sources and TEMAH is used as the hafnium precursor, and 5-nm and 10-nm HfO_2 films

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†Corresponding author. E-mail: jbfan@mail.xidian.edu.cn

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are deposited by ALD.

In this work, the valence band offset value ΔE_v is determined using the photoelectron-based method as[7]

$$\Delta E_v = (E_{\rm CL}^{\rm Si_{2p}} - E_v^{\rm Si})_{\rm bulk} - (E_{\rm CL}^{\rm Hf_{4f}} - E_v^{\rm HfO_2})_{\rm bulk} + (E_{\rm CL}^{\rm Si_{2p}} - E_{\rm CL}^{\rm Hf_{4f}})_{\rm HfO_2/Si}, \quad (1)$$

where $E_{\rm CL}^{\rm Si_{2p}}$ and $E_{\rm CL}^{\rm Hf_{4f}}$ are the binding energies of the Si_{2p} and Hf_{4f} shallow core levels respectively, $E_v^{\rm Si}$ and $E_v^{\rm HfO_2}$ are determined in bulk Si and thick HfO_2 films, which are the binding energy values corresponding to the valence band maximum (VBM) values in Si and HfO_2 respectively. The position of the VBM is determined using the linear method. In order to compensate for charging effects, the spectrum for the 5-nm HfO_2 film is referenced to the Si_{2p} peak from the clean Si at 99.0 eV. For a thick film (10 nm), the spectrum is calibrated against the adventitious C_{1s} peak at 285.0 eV to correct the differential charging.

3. Results and discussion

Figure 1 shows the XPS core level spectrum of Si_{2p} for a clean bulk P-type (8 Ω·cm–12 Ω·cm) B-doped Si (100) substrate. The spectrum of Si_{2p} is calibrated against the adventitious C_{1s} peak at 285.0 eV to correct the differential charging. The VBM is 0.76 eV determined by the linear method. The binding energy (BE) of Si_{2p} for the clean bulk Si substrate is 99.66 eV. The energy difference between the Si_{2p} core level and the silicon VBM is 98.9 eV, which accords well with the value given in Ref. [8].

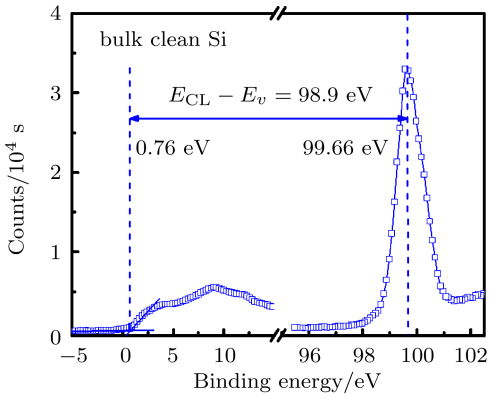


Fig. 1. (colour online) The XPS core-level spectrum of Si_{2p} for clean Si substrate.

Figure 2 shows the XPS core level spectra of Si_{2p} and Hf_{4f} for H_2O-based HfO_2 and O_3-based HfO_2 films deposited at 300 °C. The core level energies are obtained by fitting to ensure accurate BE. As shown in Fig. 2(a), the VBM values of as-deposited and annealed H_2O-based HfO_2 films are 3.32 eV and 3.07 eV, respectively. Therefore, the differences in Hf_{4f} level energy and VBM value between 10-nm as-deposited and annealed H_2O-based HfO_2 films are 14.16 eV and 14.03 eV respectively, which fits well with the values given in Refs. [5], [9], and [10]. Figure 2(b) shows that the energy differences between the Hf_{4f} and the Si_{2p} signals are 81.57 eV and 81.55 eV for 5-nm as-deposited and annealed thin H_2O-based HfO_2 films. Inserting these values into Eq. (1), one can obtain the VBO values for the as-deposited and annealed H_2O-based HfO_2 films, which are 3.17 eV and 3.32 eV respectively. The results indicate that the VBO value for H_2O-based HfO_2 increases to 0.15 eV after annealing, which is in good agreement with the reported values.[5,9]

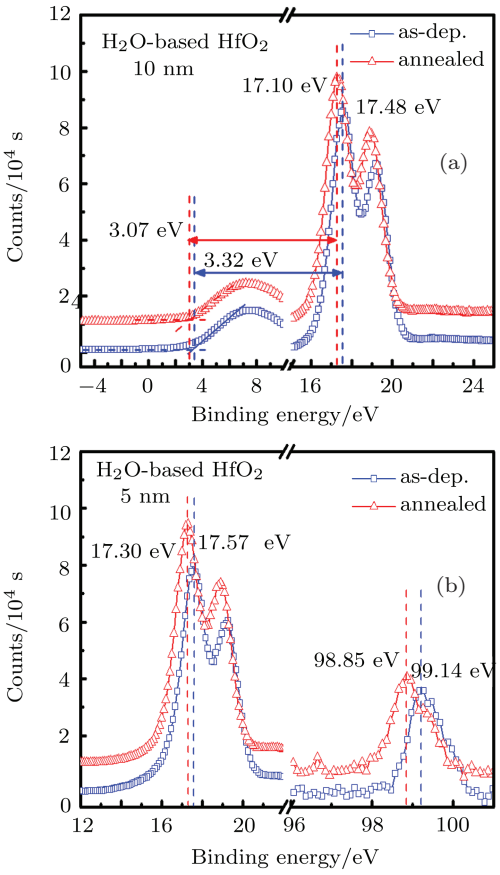


Fig. 2. (colour online) XPS core-level spectra of Si_{2p}, and Hf_{4f} for H_2O-based (a) bulk HfO_2 and (b) thin HfO_2.

For O_3-based HfO_2 films, the differences in Hf_{4f} level energy and VBM value between the as-deposited and annealed O_3-based HfO_2 films are 13.88 eV and

14.23 eV respectively, as shown in Fig. 3(a). Furthermore, the energy differences between the Hf_{4f} and the Si_{2p} signals for 5-nm HfO_2 are 81.45 eV and 81.21 eV, respectively. The VBO values of O_3-based HfO_2 films are 3.57 eV and 3.46 eV for as-deposited and annealed O_3-based HfO_2 films respectively. VBO value reduces to 0.11 eV after annealing. The band gap of HfO_2 is 5.7 eV, and both the valence band offsets and conduction band offsets for H_2O-based and O_3-based HfO_2 films are larger than 1 eV before and after annealing.

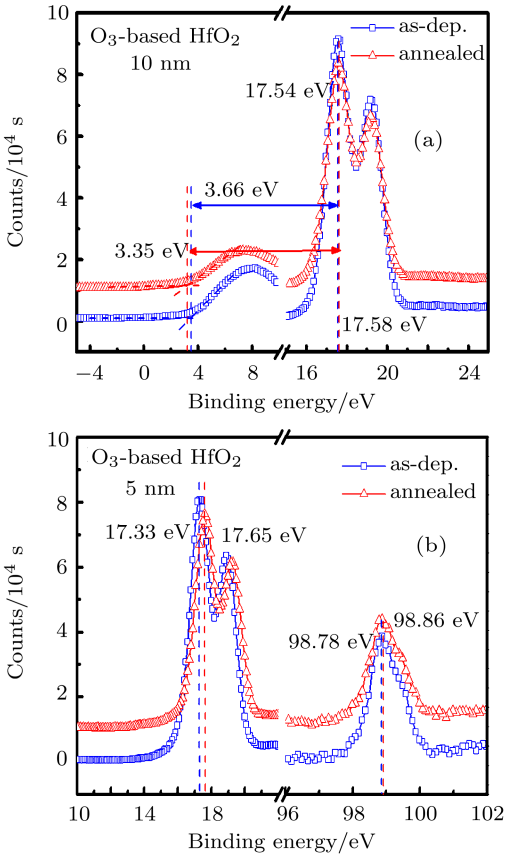


Fig. 3. (colour online) The XPS core-level spectra of Si_{2p} and Hf_{4f} for O_3-based (a) bulk HfO_2, (b) thin HfO_2.

Figure 4 shows the spectra of Si_{2p} for the H_2O-based HfO_2 and O_3-based HfO_2 films. As shown in Fig. 4(a), for as-deposited and annealed H_2O-based HfO_2, the binding energy peaks are located at the 102.53 eV and 102.87 eV respectively, which is attributed to the silicate.[11,12] Furthermore, the significant increase of the silicate peak intensity indicates that the growth of the silicate occurs after annealing due to the diffusion of the O atoms and Si atoms. On the other hand, the binding energy peaks located at 101.93 eV and 102.68 eV shows that the silicate exists for the O_3-based HfO_2 before and after annealing as shown in Fig. 4(b). Furthermore, a small increase of the silicate peak intensity is observed after annealing. The variation is supposed to be due to the interdiffusion of the N atoms after annealing which exists in the as-deposited O_3-based HfO_2.[13–15]

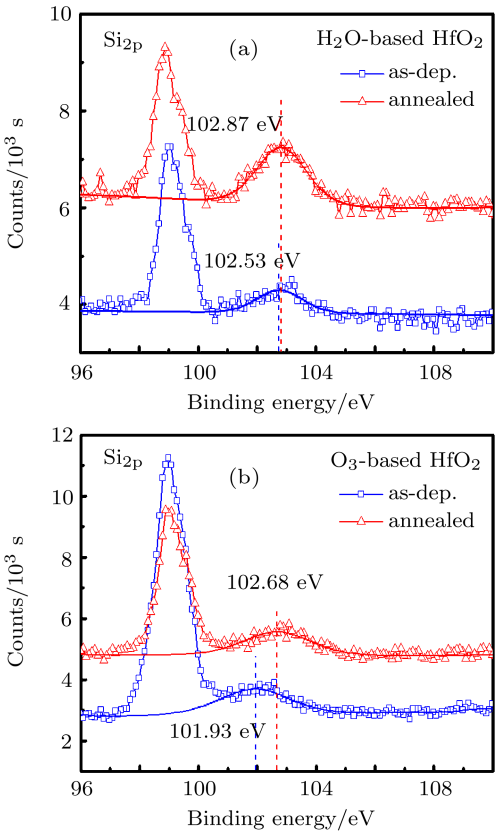


Fig. 4. (colour online) The XPS spectra of Si_{2p} for 5-nm H_2O-based (a) and O_3-based (b) HfO_2 films after annealing.

The band offset variations for H_2O-based and O_3-based HfO_2 after annealing are attributed to the changes of the dipoles at the Hf silicate interfacial layer. Figure 5 shows the schematics of the internal electric field effect on the band offset for HfO_2. As shown in Fig. 5(a), for 5-nm H_2O-based HfO_2 film, the oxygen ions can penetrate into the SiO_2 layer in the annealing process, and create oxygen vacancies in the silicate layer due to the oxygen areal density difference.[16] Because the oxygen vacancies are regarded as positive charges while oxygen ions are negative charges, an internal electric field is built between the oxygen vacancies and oxygen ions, which causes the band bending. After annealing, a high internal electronic field is built due to the growth of a Hf silicate, which makes the VBO increase. However, for

the 5-nm O_3-based HfO_2 film, a higher concentration of nitrogen impurity is observed by XPS analysis. In the annealing process, the N atoms diffuse into the Hf silicate layer and are substituted for the oxygen atoms in the silicate layer due to the same atom size.[14,17] Meanwhile, the oxygen ions are generated in the Hf silicate layer, and the N atoms are incorporated in the silicate. Compared with the scenario in the H_2O-based HfO_2, after annealing the opposite polarity electric field is formed, which causes the VBO to decrease.

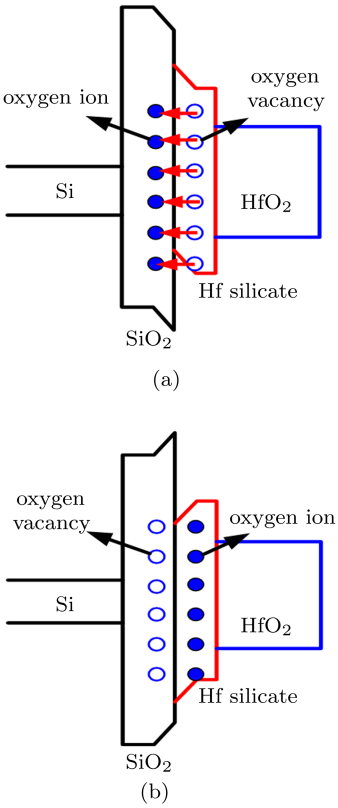


Fig. 5. (colour online) Schematic plot of internal electric field for H_2O-based (a) and O_3-based (b) HfO_2 films.

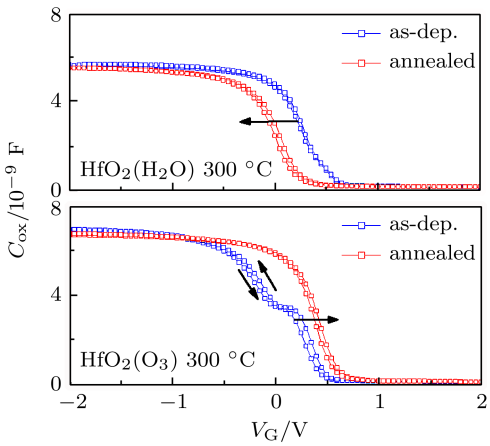


Fig. 6. (colour online) Influence of dipoles on the V_{FB} for the H_2O-based and O_3-based HfO_2 films.

Figure 6 shows the C–V curves for H_2O-based and O_3-based HfO_2 films before and after annealing. Because the internal electric field varies after annealing, the shifts of the V_{FB} are observed for H_2O-based and O_3-based HfO_2. For H_2O-based HfO_2 film, the V_{FB} shifts toward the negative direction after annealing, whereas the V_{FB} shifts toward the positive direction for O_3-based HfO_2. This result is consistent with the variation of the internal electric field and VBO.

4. Conclusions

In this paper, the different oxidants H_2O and O_3 and precursor TEMAH are used to deposit HfO_2 films by ALD and the films are annealed with a compatible gate-last process in the fabrication of complementary metal–oxide semiconductor. A significant growth of the silicate is observed for H_2O-based HfO_2 after annealing, whereas no obvious change is observed for O_3-based HfO_2 due to the incorporation of the nitrogen in the Hf silicate layer after annealing. Because different polarity internal electric fields are formed by the dipoles at the interface of the Hf silicate layer, the variations of VBO for H_2O-based and O_3-based HfO_2 films are different after annealing. The shifts of V_{FB} for H_2O-based and O_3-based HfO_2 films after annealing fit well with the variation of the VBO.

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