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ScienceDirect
Applied Surface Science 253 (2007) 3508–3511
applied surface science
www.elsevier.com/locate/apsusc

Band bending and band alignment at $HfO_2/HfSi_xO_y/Si$ interfaces

Weijie Song [a,*], Michiko Yoshitake [a], Ruiqin Tan [b], Isao Kojima [b]

[a] Nanomaterials Laboratory, National Institute for Materials Science, 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan
[b] Materials Characterization Division, National Metrology Institute of Japan, AIST Tsukuba Central 5, Higashi 1-1, Tsukuba, Ibaraki 305-8565, Japan

Received 13 February 2006; received in revised form 14 July 2006; accepted 18 July 2006
Available online 24 August 2006

Abstract

Band bending and band alignment at $HfO_2/SiO_2/Si$ and $HfO_2/Hf/SiO_2/Si$ interfaces were investigated using X-ray photoelectron spectroscopy. After Hf–metal pre-deposition, a 0.55 eV band bending in Si and a 1.80 eV binding energy decrease for Hf 4f and O 1s of HfO_2 were observed. This was attributed to the introduction of negative space charges at interface by Hf pre-deposition. Band bending decrease and synchronous binding energy increases of O 1s and Hf 4f for HfO_2 were observed during initial Ar^+ sputtering of the Hf pre-deposited sample. This was interpreted through the neutralization of negative space charges by sputtering-induced oxygen vacancies.
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PACS: 73.20.At; 77.55.+f; 77.22.Jp

Keywords: Band bending; HfO_2; Space charge

Photoelectron spectroscopic methods are widely adopted not only for chemical analysis, but also for band alignment and band bending at heterojunction interfaces. Chemical states at high-κ metal oxide/Si interface have been extensively studied using photoelectron spectroscopic methods with much attention focused on HfO_2/Si [1–7] because of their technological importance in ultra large-scale integration. In these studies, the measured binding energies (BEs) for HfO_2 and the interfacial layer differed from each other, which indicated that it was suspectable to identify the chemical states of the constituent materials only by the measured BEs. In fact, the measured BEs have direct correlations with space charge and band bending in the heterojunction structure [6]. Furthermore, from a practical viewpoint, the electronic structure at the oxide/Si interface is more significative to device-maker than chemical information. There have been both theoretical [8–10] and experimental studies [11–13] on the band structure of high-κ metal oxides and the band alignments at high-κ metal oxides/Si interfaces. Photoemission and inverse photoemission methods have been employed to determine the band structure of the high-κ metal oxide [2,11,12]. Recently, Lim et al. introduced femtosecond pump-probe photoelectron spectroscopy for measuring the band bending of Si in complex metal oxide–semiconductor systems [13]. It is clear that defects in the MOS structure play an important role in the band alignments. It is important to consider the effect of defects on photoelectron spectra [11]. However, this effect was not clearly resolved in most photoelectron spectroscopic studies.

We are interested in sputtering deposited HfO_2 on Si. Yamamoto et al. reported a Hf–metal pre-deposition method which reduced the interfacial layer thickness and the equivalent oxide thickness [1,14]. Recently, we studied the interfacial chemistry of the $HfO_2/Hf/SiO_2/Si$ system and optimized the Hf–metal layer thickness [15–18]. The interfacial layer between HfO_2 and Si was revealed to be Hf silicates ($HfSi_xO_y$), either Si-rich ($HfO_2/SiO_2/Si$) or Hf-rich (Hf pre-deposition) [1,17]. In this paper, we report high-resolution X-ray photoelectron spectroscopic studies on band bending and band alignment at $HfO_2/HfSi_xO_y/Si$ interfaces with specific focus on the contribution of defects to XPS BE shifts.

N-type Si(1 0 0) wafers (R = 1–10 Ω cm) with native SiO_2 (0.4 nm) over-layers were used as substrates. Hf and HfO_2 films were deposited using magnetron sputtering in an ultrahigh vacuum system. Details of substrate cleaning and deposition condition were given elsewhere [10]. Two sample structures: (a) HfO_2 (2 nm)/SiO_2/Si and (b) HfO_2 (2 nm)/Hf (1 nm)/SiO_2/

* Corresponding author.
E-mail address: song.weijie@nims.go.jp (W. Song).

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doi:10.1016/j.apsusc.2006.07.054

Si, were investigated here. XPS spectra were recorded using a VG ESCALAB 220i-XL system. The energy scale of the system was calibrated according to international standard ISO 15472 [19]. All spectra were collected using a monochromatic Al Kα (1486.6 eV) X-ray source operated at 150 W, and at a pass energy of 10 eV. Ar^+ (1 kV) sputtering was used for depth profile analysis.

The Si 2p XPS spectra for the hydrofluoric acid-treated Si(1 0 0) and the SiO_2/Si substrates without HF treatments are shown in Fig. 1. The BE of Si^0 $2p_{3/2}$ for un-doped Si, which has been using as a BE calibration reference, was 99.30 eV [20,21]. The Fermi level of the *n*-Si(1 0 0) substrates (R = 1–10 Ω cm) was calculated to be 0.32 ± 0.03 eV higher than that of native Si at room temperature (as illustrated in the inset) [22]. The energy band of the HF-treated *n*-Si(1 0 0) was almost flat near the surface region [23–25]. The measured binding Si^0 2p energy for the HF-treated *n*-Si(1 0 0) was 99.58 eV. This indicated that the Fermi level of the *n*-Si(1 0 0) in this work was 0.28 eV higher than that of native wafer, which was in accord with calculated data [22]. The Si^0 2p BE of the SiO_2/*n*-Si(1 0 0) substrate was measured at 99.31 eV. This indicated that band bending occurred in Si near the SiO_2/Si interface. The relative shifts of the valance band maximum (VBM) and the conduction band minimum (CBM) near the SiO_2/Si interface were illustrated in the inset of Fig. 1. The Fermi level pinned near the position of native Si wafer. The thickness of the band bending region was estimated to be several hundred nanometers (200–600 nm) range, which was much larger than the XPS information depth (typically several nanometer). Thus the measured BE of Si^0 2p peak revealed the amount of band bending. The peaks of Si^{ox} 2p and O 1s for SiO_2 were centered at 103.19 and 532.72 eV, respectively, and the BE difference between O 1s and Si^{ox} 2p was 429.53 eV. This value was considered to be a good measure of chemical state independent of electric charge, and the measured data was consistent with previous reports [25,26].

The XPS spectra for samples: (a) HfO_2/SiO_2/Si and (b) HfO_2/Hf/SiO_2/Si are shown in Fig. 2. The BE of Si^0 $2p_{3/2}$ was 99.44 eV for sample (a). This indicated a weak band bending in Si near the interface as illustrated in the inset. The BE of Hf $4f_{7/2}$ and O 1s for HfO_2 were 18.00 and 531.20 eV, respectively. Sayan et al. reported that the BE difference between Hf $4f_{7/2}$ and VBM of HfO_2 was 14.50 eV [6]. Thus the VBM of HfO_2 was 3.50 eV below the Fermi level. This result was close to the HfO_2/SiO_2/*p*-Si(1 0 0) results [6]. The BE of Si^0 $2p_{3/2}$ was measured at 99.03 eV for sample (b). This indicated that a band bending of 0.55 eV occurred in Si near the interface as illustrated in the inset of Fig. 2. As no external bias was applied to the structure, the band bending was most probably induced by the negative space charge which was introduced to the interface during Hf predeposition. As a result of the negative space charge, the measured BEs of Hf 4f, O 1s and Si^{ox} 2p peaks for the HfO_2 and the interfacial layer should shift all to the lower BE side. This was confirmed by the Hf 4f, O 1s and Si^{ox} 2p peaks in Fig. 2. For both samples (a) and (b), their O 1s peaks were fitted into two peaks: lower BE peak for HfO_2 and higher BE peak for $HfSi_xO_y$. The BEs of Hf $4f_{7/2}$ and O 1s for HfO_2 of sample (b) were 16.20 and 529.40 eV, respectively, which were both 1.80 eV lower than that of sample (a). The BE difference between Hf $4f_{7/2}$ and O 1s for HfO_2 of sample (b) was the same as that of sample (a), indicating the same chemical nature of the HfO_2 over-layers.

We have reported the XPS depth profile results for sample (b) elsewhere [17]. The original BE shifts at the initial sputtering stage are shown in Fig. 3 together with the energy level diagrams for the original structure and the sample after 1600 s sputtering. The VBM and CBM values for HfO_2 were calculated from the Hf $4f_{7/2}$ BE, the BE difference between Hf $4f_{7/2}$ and VBM (14.50 eV) and the band gap (E_g = 5.60 eV) [6]. The BE of Si^0 2p shifted ∼0.38 eV to higher BE side during sputtering, which indicated a decrease of band bending in Si near the interface. As the origin of the band bending, the

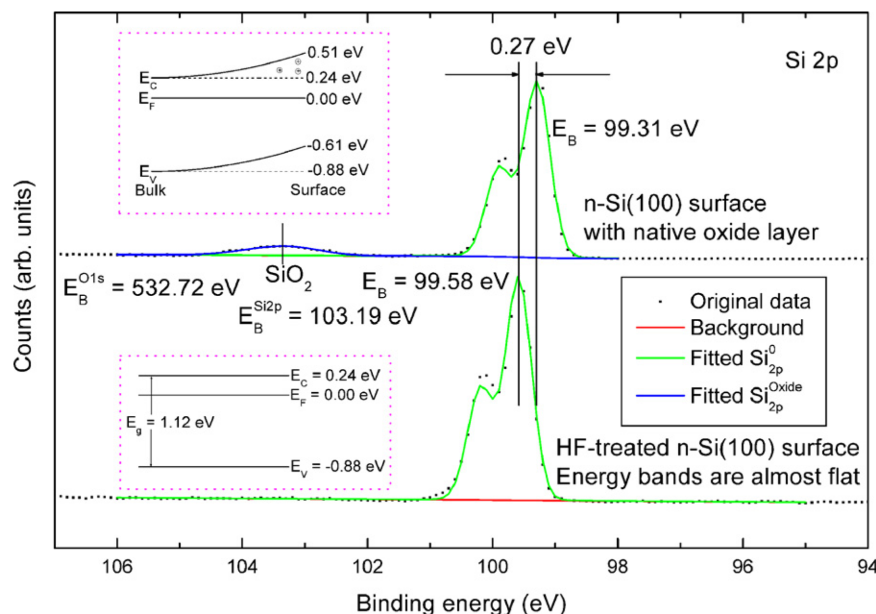

Fig. 1. Si 2p spectra for HF-cleaned Si and SiO_2/Si.

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