

## Chemical States and Electronic Structure of a $\text{HfO}_2 / \text{Ge}$ (001) Interface

Kang-ill Seo <sup>a)</sup>, and Paul C. McIntyre

*Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305*

Shiyu Sun, Dong-Ick Lee, and Piero Pianetta

*Stanford Synchrotron Radiation Laboratory, Stanford, CA 94305*

Krishna C. Saraswat

*Department of Electrical Engineering, Stanford University, Stanford, CA 94305*

We report the chemical bonding structure and valence band alignment at the  $\text{HfO}_2/\text{Ge}$  (001) interface by systematically probing various core level spectra as well as valence band spectra using soft x-rays at the Stanford Synchrotron Radiation Laboratory. We investigated the chemical bonding changes as a function of depth through the dielectric stack by taking a series of synchrotron photoemission spectra as we etched through the  $\text{HfO}_2$  film using a dilute HF-solution. We found that a very non-stoichiometric  $\text{GeO}_x$  layer exists at the  $\text{HfO}_2/\text{Ge}$  interface. The valence band spectra near the Fermi level in each different film structure were carefully analyzed, and as a result, the valence band offset between Ge and  $\text{GeO}_x$  was determined to be  $\Delta E_v (\text{Ge-GeO}_x) = 2.2 \pm 0.15$  eV, and that between Ge and  $\text{HfO}_2$ ,  $\Delta E_v (\text{Ge-HfO}_2) = 2.7 \pm 0.15$  eV.

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<sup>a)</sup> [kiseo@stanford.edu](mailto:kiseo@stanford.edu) ; corresponding author

Recently, high- $k$  dielectrics deposited on Ge substrates have been studied widely for MOSFET applications to take advantage of the high intrinsic electron mobility ( $2\times$ ) and hole mobility ( $4\times$ ) of Ge, compared to those of Si. It is also hoped that deposited high permittivity dielectrics developed for Si CMOS technology may exhibit better electrical characteristics than poor quality germanium oxide gate dielectric layer [1-6]. The high- $k$  gate insulators  $ZrO_2$  [1],  $HfO_2$  [2-4] and  $Al_2O_3$  [4, 5] as well as germanium oxy-nitride [6] have recently been studied for Ge MOS devices. Although many promising results have previously been reported, such as low gate leakage current density [2-6] and enhanced hole mobility [5,6], little attention has focused on the chemical nature of the interfacial layer between high- $k$  metal oxides and Ge substrate, and the associated energy band alignment at the interface.

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In this work, we study the chemical bonding structure and valence band alignment at the  $HfO_2/Ge$  (001) interface by systematically probing various core level spectra and valence band spectra using synchrotron soft x-ray radiation with high intensity and energy resolution. We investigated chemical bonding changes as a function of depth through the dielectric stack by taking a series of synchrotron radiation photoemission spectroscopy (SR-PES) spectra as we etched through the  $HfO_2$  film using a dilute HF-solution. The photon energy was tuned to achieve high surface sensitivity. As a result, we found that very thin non-stoichiometric  $GeO_x$  layer forms at the  $HfO_2$  and Ge interface. The valence band offsets between Ge and  $GeO_x$  and between Ge and  $HfO_2$  were determined by analyzing the valence band spectra.

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In sample fabrication, n-type  $\langle 100 \rangle$  Ge substrates with 10-15 ( $\Omega\text{-cm}$ ) resistivity were cleaned with dilute HF solution (DI:HF=50:1) to remove native  $GeO_x$ , and were immediately transferred to a deposition chamber. Ultrathin Hf metal films in the range of 2 nm thickness were deposited using e-beam evaporation without any intentional heating. The typical deposition rate was  $\sim 0.3 \text{ \AA}/\text{sec}$  and deposition pressure was  $\sim 2 \times 10^{-6}$  Torr. After Hf metal

deposition, the samples were transferred to an attached oxidation chamber without breaking vacuum, and ultra violet (UV) ozone oxidation of the metal precursor films was performed to fully oxidize Hf metal at 200°C for 1 hr under 1 atm oxygen pressure.

After the sample fabrication, the sample was taken to beam line 8-1 at the Stanford Synchrotron Radiation Laboratory (SSRL) to perform photoemission experiments. The photoemission spectra were recorded by a PHI spherical energy analyzer in an ultrahigh vacuum chamber with base pressure below  $1 \times 10^{-10}$  Torr. A photon energy of 80 eV was selected to achieve good surface sensitivity. Both the Ge *3d* and Hf *4f* core levels, as well as valence band spectra, were monitored during the experiments. To probe chemical bonding information with film depth, we etched the HfO<sub>2</sub> film step by step using a dilute HF solution (DI:HF = 50:1) and took a photoemission spectrum after each etching step. The etching rate of HfO<sub>2</sub> in this solution was determined to be approximately 2 Å/sec. The HF etching was done inside a glove bag, which was filled with research grade Ar, and directly connected to the load lock of the photoemission chamber. After each time the sample was dipped into HF, it was blown dry by Ar, and immediately put into the load lock pre-filled with dry N<sub>2</sub>. Then, the load lock was pumped down by a turbo pump and the sample was transferred into the photoemission chamber. By taking these steps, we could minimize surface contamination after each etching process.

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In order to verify whether 2% HF-solution etching alters the structure of the HfO<sub>2</sub> film (for example, by increasing surface roughness or by pin-hole generation) which might affect interpretation of our spectra, AFM (atomic force microscopy) was used to analyze the sample surface. Figure 1 shows the surface morphology and roughness change of a HfO<sub>2</sub>/interface layer/Ge(001) sample as a function of HF-etching time. The AFM analysis used a scan area of  $1 \mu\text{m}^2$ . As the HF-etch time increased, the RMS (Root Mean Square) value rose slightly from 0.26nm for the as deposited sample to 0.28nm for 10sec etching, suggesting 2% HF-etching

doesn't significantly alter the surface roughness of the HfO<sub>2</sub> film. Also no pinholes were detected in the areas tested. Interestingly, the root mean square surface roughness was reduced to 0.20nm after 15 seconds of etching in HF. This amount of etching corresponds to removal of the entire HfO<sub>2</sub> overlayer, thus exposing the GeO<sub>x</sub>/Ge under-layer. This interpretation was confirmed by the following SR-PES results.

Figure 2 shows photoemission spectra taken at a photon energy of 80eV for increasing HF-etching times with the relative intensities normalized by the incident beam intensity ( $I_0$ ). From the figure, we can see in the as-deposited sample the Hf *4f* core level peak associated with fully-oxidized HfO<sub>2</sub> showing the expected spin-orbital splitting of 1.7eV. The Hf *4f* intensity rose after HF-etching for 8 seconds, due to the removal of surface contaminants such as adventitious carbon presumably formed when the sample was transferred from deposition chamber to SSRL, and then **decreases** with further HF-etching (13 s total) because of thinning of the HfO<sub>2</sub> layer. Finally, the Hf *4f* peak disappeared after 15 s of etching. This result is consistent with the AFM results in Fig. 1, which showed that the RMS value **decreases** when all HfO<sub>2</sub> layer was etched out after 15sec etching.

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The Ge *3d* features **consists** of photoelectron peaks from both the Ge substrate (kinetic energy = ~ 45.4eV) and an interfacial GeO<sub>x</sub> layer (42 ~ 44 eV). As the upper HfO<sub>2</sub> layer was etched by the HF-solution, the Ge *3d* (Ge substrate) feature increased in intensity once it appeared clearly after 13 s etching, while the Ge *3d* (GeO<sub>x</sub>) feature intensity reached a maximum after ~ 13 s, and diminished thereafter, almost disappearing after 17 s. It should be noted that the GeO<sub>x</sub> signal was observed while no HfO<sub>2</sub> signal was detected in the 15 s etching sample, which suggests that a continuous pure GeO<sub>x</sub> interfacial layer **exists** between HfO<sub>2</sub> gate dielectric and Ge substrate surface. Since we confirmed there was negligible germanium oxide on the initial HF-cleaned Ge substrate before HfO<sub>2</sub> deposition, it seems safe to conclude that the interfacial GeO<sub>x</sub>

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layer resulted from re-oxidation of the Ge surface when we oxidized the Hf metal film to form HfO<sub>2</sub>.

We fitted the Ge 3*d* core level spectra to determine the chemical bonding structure of the interfacial GeO<sub>x</sub> layer as a function of HF-etching time as shown in Fig. 3. As the upper layer of HfO<sub>2</sub> was etched away, we observed increasing intensity of the Ge substrate feature after 15 seconds of etching. We decomposed the chemically shifted peaks of GeO<sub>x</sub> using three sub-oxide peaks (Ge<sup>1+</sup>, Ge<sup>2+</sup>, Ge<sup>3+</sup>) with relative chemical shifts from the bulk Ge peak of 1.1 eV, 1.8 eV and 2.6 eV, respectively [8]. It is interesting, however, that our analysis did not resolve a Ge<sup>4+</sup> feature (+3.4eV shift from bulk Ge [8]) associated with stoichiometric GeO<sub>2</sub>. This suggests that the re-oxidation of the Ge substrate during Hf metal oxidation produces a non-stoichiometric GeO<sub>x</sub> interfacial layer between HfO<sub>2</sub> and Ge substrate. A similar result was reported in the ZrO<sub>2</sub> on Ge system by Chi et. al. [7].

The change of the area under each peak associated with a different germanium oxidation state can help understand where the different species are located in the dielectric layer. Before the interfacial GeO<sub>x</sub> was exposed to the HF-solution (etching time ≤ 13sec), all Ge<sup>0</sup>, Ge<sup>1+</sup>, Ge<sup>2+</sup> and Ge<sup>3+</sup> peak areas increased with HF-etching because there were more photoelectrons detected from the interfacial layer and Ge substrate as the upper HfO<sub>2</sub> layer became thinner. However, when the GeO<sub>x</sub> began to be etched (etching time ≥ 15sec), following its exposure to the HF-solution, the Ge<sup>2+</sup> and Ge<sup>3+</sup> peak areas decayed while those of Ge<sup>1+</sup> and Ge<sup>0</sup> kept increasing. This suggests that the Ge<sup>2+</sup> and Ge<sup>3+</sup> bonding states exist in the upper part of the interfacial layer while Ge<sup>1+</sup> bonding is more typical near the Ge substrate. Similar vertical variation of interface layer oxidation states has been reported previously for the HfO<sub>2</sub>/Si interface [16]. This sub-stoichiometric GeO<sub>x</sub> interfacial layer may be responsible for poor electrical properties such as high density of interface states in the ZrO<sub>2</sub>- and HfO<sub>2</sub>-on-Ge structures [3].

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Next, we determined valence band offsets for the  $\text{HfO}_2/\text{GeO}_x/\text{Ge}(001)$  stack from the valence band spectra. Figure 4 (a) shows a valence band spectrum from the 17 s HF-etched sample, which can be considered as HF-cleaned Ge with negligible surface oxide. The valence band maximum (VBM) is determined at the intersection point of the best straight line fit representing the decay in the photoemission intensity near the Fermi energy with the base line intensity [10]. We extracted a VBM for the Ge substrate of 74.8 eV. Figure 4 (b) indicates how we extracted the  $\text{GeO}_x$  valence band spectra from the valence band spectrum of a combined  $\text{GeO}_x/\text{Ge}$  film structure (15 s etching sample). Because the upper  $\text{GeO}_x$  layer was very thin, the measured spectrum contains valence band states from both the  $\text{GeO}_x$  layer and Ge substrate. Therefore, to obtain a “pure  $\text{GeO}_x$ ” valence band spectrum, we subtracted the Ge substrate contribution shown in the Fig. 4 (a) from the measured  $\text{GeO}_x/\text{Ge}$  spectrum in the same manner described in the Ref. 11. The valence band maximum fitting procedure indicated that the VBM of the  $\text{GeO}_x$  layer was 72.6 eV. Similarly, we obtained a “pure  $\text{HfO}_2$ ” valence band spectrum contribution (● in the Fig. 4 (c)) by subtracting the  $\text{GeO}_x/\text{Ge}$  spectrum (15 s HF-etching) from the  $\text{HfO}_2/\text{GeO}_x/\text{Ge}$  spectrum (8 s HF-etching). Using the same fitting method, we determined that the VBM of the  $\text{HfO}_2$  film was 72.1 eV.

We are most interested in the difference between the VBM values rather than the precise energies of VBM edges. From the results in Fig. 4, we estimate that the valence band offset of Ge and  $\text{GeO}_x$ ,  $\Delta E_v(\text{Ge-GeO}_x)$  is  $\sim 2.2 \pm 0.15$  eV, and the valence band offset of Ge and  $\text{HfO}_2$ ,  $\Delta E_v(\text{Ge-HfO}_2)$  is  $\sim 2.7 \pm 0.15$  eV. The represented error range of  $\pm 0.15$  eV is greater than the x-ray spectrometer energy resolution of  $\sim 0.05$  eV, because of uncertainty in the fitting method used to obtain the VBM values [12]. These VB offsets are in good agreement with the results recently reported by V. V. Afanas'ev et. al. using the internal photoemission method [13]. Since we determined VB offsets precisely, we can estimate conduction band offsets if an accurate band

gap energy of  $\text{HfO}_2$  becomes available. In the literature, band gaps in the range of 5.2 - 6.0 eV have been reported for  $\text{HfO}_2$  depending on the film deposition technique, post deposition thermal treatment and measurement method [11,14,15]. With the well known Ge band gap of 0.66 eV, we have estimated conduction band offsets between Ge and  $\text{HfO}_2$  as 1.8~2.6 eV. In the case of  $\text{GeO}_x$ , we cannot determine the conduction band offset because we have no reliable energy gap data for this ultra-thin and non-stoichiometric material. The band alignment diagram for these multilayer gate stacks is summarized in Fig. 4 (d).

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## References

- <sup>1</sup> C. O. Chui, S. Ramanathan, B. B. Triplett, P. C. McIntyre and K. C. Saraswat, *IEEE Elect. Dev. Lett.* **23**, 473 (2002).
- <sup>2</sup> C. O. Chui, H. Kim, P. C. McIntyre and K. C. Saraswat, *IEEE Elect. Dev. Lett.* **25**, 274, (2004).
- <sup>3</sup> N. Wu, Q. Zhang, C. Zhu, C. C. Yeo, S. J. Whang, D. S. H. Chan, M. F. Li, B. J. Cho, A. Chin, D.-L. Kwong, A. Y. Du, C. H. Tung and N. Balasubramanian, *Appl. Phys. Lett.* **84**, 3741 (2004).
- <sup>4</sup> J. J. Chen, N. A. Bojarczuk, H. Shang, M. Copel, J. B. Hannon, J. Karasinski, E. Preisler, S. K. Banerjee and S. Guha, *IEEE Trans. Elec. Devices.* **51** ,1441 (2004)
- <sup>5</sup> C. H. Huang, M. Y. Yang, A. Chin, W. J. Chen, C. X. Zhu, B. J. Cho, M.-F. Li and D. L. Kwong, *VLSI Tech. Digest of Tech. Papers*, pp 119, (2003).
- <sup>6</sup> , H. Shang, H. Okorn-Schmidt, J. Ott, P. Kozlowski, E. C. Jones, H.-S. P. Wong, and W. Hanesch, *IEEE Trans. Elec. Devices*, ?
- <sup>7</sup> D. Chi, C. O. Chui, K. C. Saraswat, B. B. Triplett and P. C. McIntyre, *J. Appl. Phys.* **96**, 813 (2004)
- <sup>8</sup> D. Schmeisser, R. D. Schnell, A. Bogen, F. J. Himpsel and D. Rieger, *Surf. Sci.* **172**, 455 (1986)
- <sup>9</sup> X-ray Data Booklet, Lawrence Berkeley National Laboratory, p 3-10 (2002)
- <sup>10</sup> S. Miyazaki, *J. Vac. Sci. Technol. B* **19**, 2122 (2001)
- <sup>11</sup> M. Oshima, S. Toyoda, T. Okumura, J. Okabayashi, H. Kumigashira, K. Ono, M. Niwa, K. Usuda, and N. Hirashita, *Appl. Phys. Lett.* **83**, 2172 (2003)
- <sup>12</sup> S. Sayan, E. Garfunkel and S. Suzer, *Appl. Phys. Lett.* **80**, 2135 (2002)
- <sup>13</sup> V. V. Afannas'ev and A. Stesmans, *Appl. Phys. Lett.* **84**, 2319 (2004)
- <sup>14</sup> J. Robertson, *J. Vac. Sci. Tech. B*, **18**, 1785, (2000)



<sup>15</sup> V. V. Afannas'ev, A. Stesmans, F. Chen, X. Shi and S. A. Campbell, Appl. Phys. Lett. **81**, 1053 (2002)

<sup>16</sup> J.-C. Lee, S. -J. Oh, M. Cho, C. S. Hwang and R. Jung, Appl. Phys. Lett. **84**, 1305 (2004)

## Figure Captions

Figure 1. Surface roughness change of  $\text{HfO}_2/\text{I.L.}/\text{Ge}(001)$  as HF-etching time increases; AFM scan area of  $1 \mu\text{m}^2$ .

Figure 2. Photoemission spectra from  $\text{HfO}_2/\text{I.L.}/\text{Ge}(001)$  stack at the photon energy of 80eV vs. HF-etching time.

Figure 3. Results of Ge  $3d$  core level fitting after consecutive HF-etching times showing the chemical shift associated with each oxidation state

Figure 4. Valence band spectra associated with different film structures and determination of valence band offsets of (a) Ge-substrate, (b) interfacial  $\text{GeO}_x$ , and (c)  $\text{HfO}_2$  layer by the subtraction method, and (d) schematics of band alignment in the  $\text{HfO}_2/\text{GeO}_x/\text{Ge}(001)$  stack.

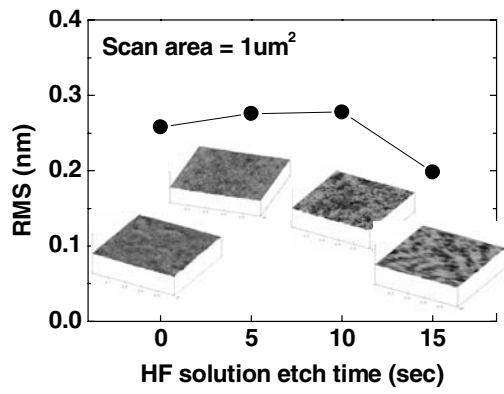


Fig. 1 Kang-ill Seo *et al.*

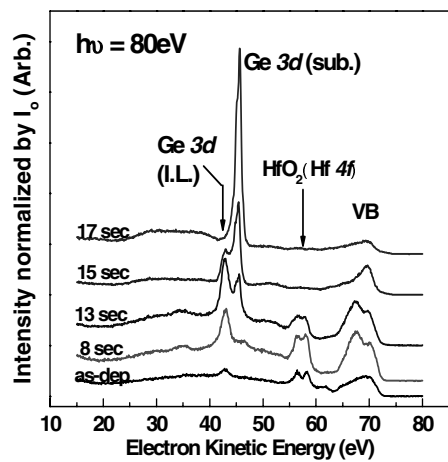


Fig. 2 Kang-ill Seo *et al.*

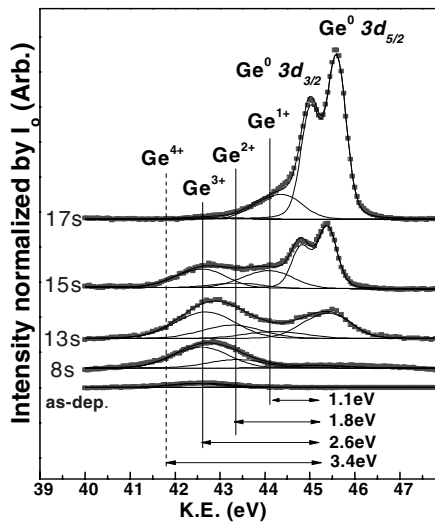


Fig. 3 Kang-ill Seo *et al.*

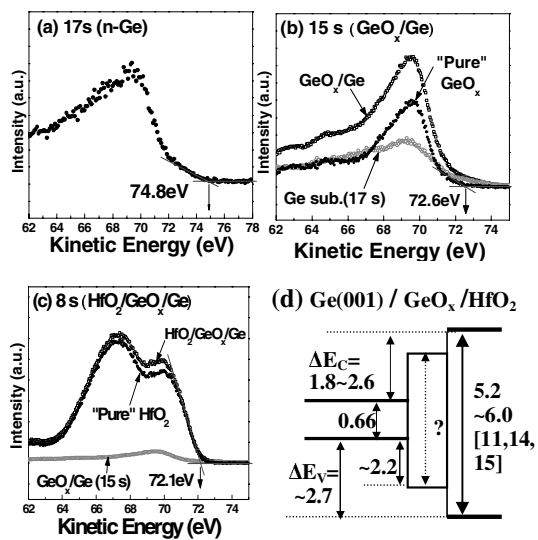


Fig. 4 (a), (b), (c), (d) Kang-ill Seo *et al.*