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Band-offset Determination at Ge/GeO_2 Interface by Internal Photoemission and Charge-corrected X-ray Photo-electron Spectroscopies

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1. Introduction

GeO_2 attracts continuous research interests as the passivation layer owing to excellent GeO_2/Ge interface with low D_{it} [1]. The band line-up determination in GeO_2/Ge is essential for modeling the transport properties, while both valence and conduction band offset (VBO and CBO, respectively) reported by different groups ranges ~1eV [2-4]. X-ray photoelectron spectroscopy (XPS) is commonly used to determine VBO of the GeO_2/Ge stack, while artifact induced by the oxide charging is inevitable, which has been already pointed out on SiO_2/Si and HfO_2/Si stacks [5,6]. Meanwhile, the internal photoemission spectroscopy (IPE) offers a straightforward way to characterize CBO by measuring the electrons surmounting the barrier height at GeO_2/Ge interface.

In this work, we systematically determined the band offsets for GeO_2/Ge stack by using IPE and charge-corrected XPS measurements.

2. Experimental

For IPE investigation, 25nm thick GeO_2 was thermally-grown on HF-last p-type and n-type Ge (100) wafers at 530°C for 60min. The low temperature O_2 annealing (LOA) was then performed at 380 °C for 60min in O_2 to further repair GeO_2/Ge interface [7]. Semitransparent 15nm-thick metal gate electrodes (Au or Al) were evaporated onto GeO_2 to form MOS capacitors for the IPE measurement, which was performed in the photon energy ranging from 1.3 eV to 5 eV with the quantum yield (Y) defined as the photocurrent normalized by the incident photon flux. For XPS measurement, thin GeO_2/Ge stack was prepared with the same procedure as that for IPE samples except very short oxidation time (15 second). The XPS measurements were performed at the photo electron take-off angle of 80° by using a monochromic Al kα x-ray source (1486.7 eV).

3. Conduction band offset determination by IPE

Figure 1 (left) shows a series of $Y^{1/3}$-hν plots measured in n-(100)Ge/GeO_2(25nm)/Au(10-15nm) structure under various gate voltages (V_g>0 means the electron injection from Ge valence band (VB)). The spectral thresholds were experimentally determined and then linearly extrapolated to E=0 in the Schottky plot as shown in Figure 1 (right). Figure 1 (right) display series of Schottky plots for all the four samples. The resulting Φ(Ge-VB/GeO_2), which is 2.30± 0.1eV and corresponds to the CB offset (ΔEc) of 1.65 ± 0.1eV at GeO_2/Ge interface, is consistent within 0.1 eV accuracy regardless of Au or Al gate electrode both for p- and n-Ge substrates. This value agrees well with previous IPE results measured on the ultra-thin GeO_2/High-k oxide stacks [2] and with the theoretical calculation "without the valence alternation pair [8]".

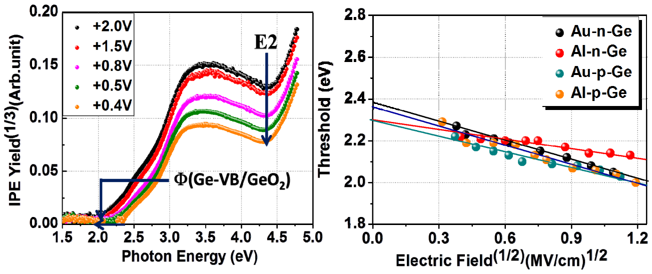

Figure 1 The cube root of IPE quantum yield as a function of photon energy for the n-type (100)Ge/GeO_2(25nm)/Au(10-15nm) structure under different strength of electric field in the oxide (left); and Schottky plots for oxide field dependence of the barrier heights at the GeO_2/Ge interface for all the samples (right). Note that E2 singularity in the spectra (hν=4.32eV) associated with direct optical excitation within the Ge crystal indicates Ge photo-electron injection.

4. Valence band offset determination by XPS

Kraut method [9], which assumes that the energy difference between the VB edge and the core-level peak of the substrate keeps constant with/without the over layer, is used to determine VBO for our Ge/GeO_2 stack as expressed by equation (1):

$$VBO= VBM^{GeO2}-[\, Ge3d^{stack}-\Delta(Ge3d^{Ge\_Sub}-VBM^{Ge\_Sub})] \quad (1)$$

and Figure 2(left) shows the relevant band diagram. Figure 2 (right) shows the Ge*3d* spectra of our Ge/GeO_2 stack, indicating a 29.55 eV $Ge3d^{stack}$ value.

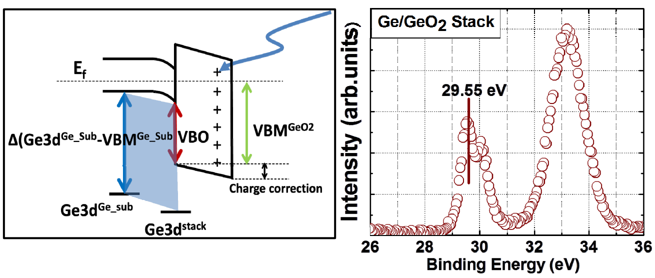

Figure 2 Band diagram representing the Ge/GeO_2 stack which illustrates the method to determine VBO value (left); and typical Ge*3d* spectra of our Ge/GeO_2 stack in XPS (right).

The determination mainly involves four steps: (i). $\Delta(Ge3d^{Ge\_Sub}-VBM^{Ge\_Sub})$ determination (Fig. 3); (ii). VBM^{GeO2} deconvolution from the measured VB spectrum

[10] (Fig. 4); (iii). Charge correction (Fig. 5); and (iv). VBO and CBO analysis. Figure 3 shows the VB and Ge*3d* spectra of bare p-Ge (100) substrate, and the energy difference between the VB edge and the core level Ge$3d_{5/2}$ peak is determined to be 29.30±0.1 eV. Note that such value is consistent with previous report [3]. Figure 4 shows the measured VB spectra of Ge/GeO_2 stack, and the components originating from GeO_2 was further deconvoluted as 4.15 eV (the measured VB spectrum of HF-cleaned Ge substrate was used to separate contribution from Ge substrate).

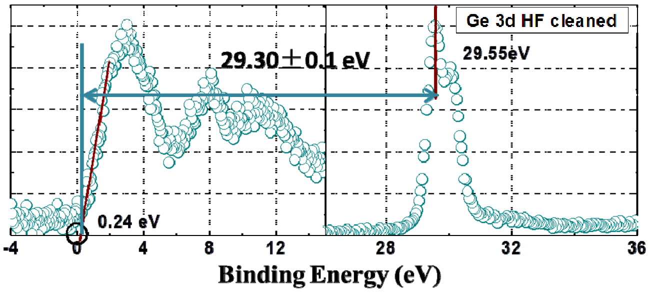

Figure 3 The VB and Ge*3d* spectra of bare Ge substrate. The energy difference between the VB edge and the core level $Ge_{3d5/2}$ peak is determined to be 29.30±0.1 eV.

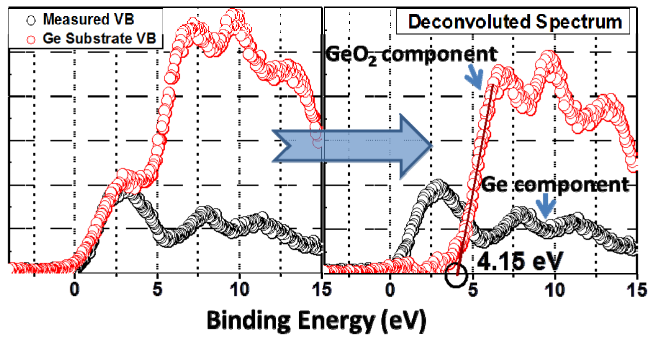

Figure 4 The valence-band Spectra of Ge/GeO_2 stack. (left) as measured VB spectra from Ge substrate and Ge/GeO_2 stack; (right) deconvoluted spectra for the GeO_2 component.

Next, the charge correction was carried out considering that positive charges might be built up during the x-ray irradiation. Figure 5 shows the x-ray irradiation time dependence of the Ge*3d* peak from Ge/GeO_2 (Fig. 5, left). Ge$3d^{stack}$ peak exhibits only negligible shifts with the irradiation time, whereas Ge$3d^{4+}$ shows a ~0.30 eV shift (long *vs* short scan), which due to electrical charging instead of chemical states changes because the O1s peak also shifts a ~0.30 eV in the same direction (Fig. 5 right). Positive charges created in the Ge bulk can be compensated by electrons supplied from sample holder, whereas those in GeO_2 layer may not completely be compensated only by tunneling electrons from the substrate, thus modifying the energy position of the oxide VB edge. Therefore, the VB edge energy (VBM^{GeO2}) should be corrected by 0.30 eV which is the difference between long time irradiation and the shortest irradiation (as the energy reference) to eliminate the oxide charging contribution.

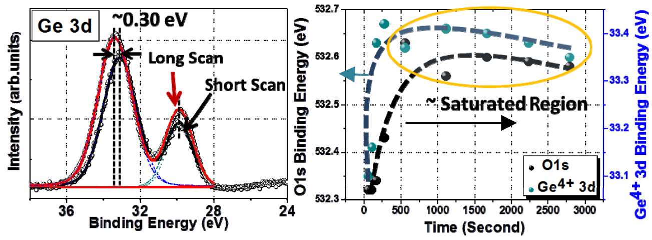

Figure 5 Peak shifts of Ge*3d* (including Ge^0 and Ge^{4+}) and O1S peaks for Ge/GeO_2 dependence with the x-ray irradiation time.

By substituting the values obtained above into equation 1, the VBO at Ge(001)/GeO_2 interface is calculated to be 3.70±0.2 eV. CBO can be determined using equation 2:

$$VBO+CBO=E_{g(GeO2)}-E_{g(Ge)}, \qquad (2)$$

where band gap of bulk GeO_2 (~6.0 eV) from our previous results by spectroscopic ellipsometry (SE) measurement and that of Ge substrate (0.67 eV) were used. Thus, CBO at Ge(100)/GeO_2 is calculated to be 1.60±0.2 eV, which is consistent with our IPE result.

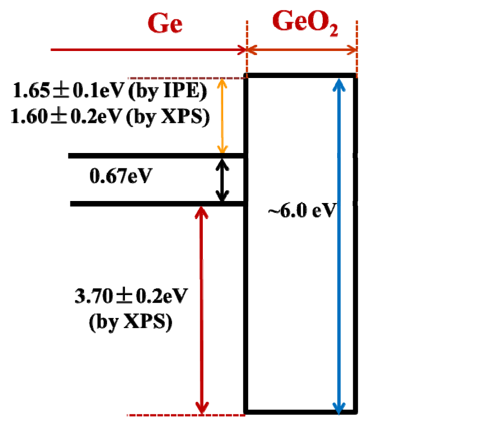

Figure 6 Band diagram reconstruction for Ge/GeO_2 by IPE and XPS.

5. Conclusion

We have systematically determined the band offsets for GeO_2/Ge stack by combined IPE and charge-corrected XPS measurements. The CBO larger than 1.5 eV is quite consistent between two different experiments and it is sufficient to minimize the leakage current and gives a strong support of GeO_2 as the potential passivation layer for future Ge-based CMOS devices.

Acknowledgements

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