Photoemission Study of Ultrathin GeO₂/Ge Heterostructures Formed by UV-O₃ Oxidation*

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The chemical bonding features and electronic states of ultrathin Ge oxide layers prepared on Ge(100) by UV-O₃ oxidation at room temperature or thermal oxidation at 550°C and 600°C were characterized by x-ray photoelectron spectroscopy (XPS) and total photoelectron yield spectroscopy (PYS), in comparison with those of ultrathin SiO₂/Si(100) cases. We have found that the oxidation of Ge(100) by UV-O₃ at room temperature proceeds in a layer by layer manner as well as the oxidation of Si(100) and that UV-O₃ oxidation rates of Ge(100) and Si(100) are almost the same at room temperature in the oxide thickness region below 1 nm. From the analysis of the onset of energy loss spectra of O1s and Ge2p_{3/2} photoelectrons, the energy bandgap of the GeO₂ films was measured to 5.70±0.05 eV in the thickness range from 0.9~1.9 nm, and the valence band offset at the interfaces between GeO₂ and Ge(100) was determined to be 4.00±0.05 eV. It is also confirmed from PYS measurements that ultrathin GeO₂/Ge(100) prepared by UV-O₃ oxidation contains defect states being about one order of magnitude larger than ultrathin SiO₂/Si(100) systems. [DOI: 10.1380/ejsnt.2006.174]

Keywords: germanium; x-ray photoelectron spectroscopy; total photoelectron yield spectroscopy; energy band diagram; electronic defect states

I. INTRODUCTION

In the aggressive scaling of metal-oxide-semiconductor field-effect-transistors (MOSFETs), improving device performance has required not only an increase in capacitive coupling between the gate and the channel within an allowable level in gate leakage current but also an enhancement of the channel mobility. Because of its potential advantage in the drivability over Si MIS FETs [1], the combination of high-*k* gate dielectric and Ge channel is attracting much attention. Considering that the interfacial oxidation and intermixing often occur during post deposition anneal (PDA) in a similar fashion as reported in many high-*k*/Si(100) systems [2], the chemical nature of the oxide/Ge heterostructures has yet to be studied in detail. Also, the energy band alignment of ultrathin GeO₂ to Ge substrate is still a matter of research.

In this work, we have studied surface oxidation of Ge(100) by UV-O₃ at room temperature and by thermal oxidation in dry O₂ ambience and compared with the results obtained for SiO₂/Si(100) prepared under the same conditions. We have also evaluated the energy bandgap of ultrathin GeO₂ layers from the analysis of energy loss spectra of O1s and Ge2p_{3/2} photoelectrons and determined the energy band alignment between GeO₂ and Ge(100) in combination with the result from the analysis of valence band spectra of GeO₂/Ge(100). In addition, the change in the energy distributions of electronic defect states in the oxides and at the interface with UV-O₂ oxidation time has been measured by total photoelectron yield spectroscopy.

II. EXPERIMENTAL

The substrates we used in this work were *p*-type Ge(100) with a resistivity of 0.9~13.5 Ωcm, *p*-type Si(100) with a resistivity of 0.01~0.02 Ωcm and *n*-type Si(100) with a resistivity of 0.08~0.12 Ωcm. After wet-chemically cleaning steps of Ge(100) and Si(100), HF-last surfaces were oxidized in the oxide thickness below 2 nm by an UV-O₃ treatment at room temperature, where 172 nm light from an excimer lamp was irradiated under an O₂ pressure of ~9.0 Torr. For the growth of thicker oxide layers, dry-O₂ oxidation was also performed at 550°C and 600°C under atmosphere pressure.

To characterize chemical bonding features in the oxides so prepared, high-resolution x-ray photoelectron spectroscopy (XPS) measurements were performed at a photoelectron take-off angle of 90° and 15° using a monochromatized AlK_α (1486.71 eV) radiation. The bandgap energy and valence band offsets were examined from O1s and Ge2p_{3/2} loss spectra and valence band spectra. The energy band profiles have been determined in combination of the oxide bandgap value and the valence band line-ups. The electronic defect states in GeO₂/Ge(100) and SiO₂/Si(100) prepared by UV-O₃ oxidation were measured by total photoelectron yield spectroscopy (PYS) [3].

III. RESULTS AND DISCUSSION

The evolution of oxide network in UV-O₃ oxidation of Ge(100) and Si(100) were evaluated by *in-situ* XPS measurements. Figure 1 shows Ge2p_{3/2} and Si2p spectra for HF last *p*-type Ge(100) and Si(100) before and after UV-O₃ oxidation at room temperature. And, each spectrum was normalized by Ge2p_{3/2}⁰⁺ and Si2p_{3/2}⁰⁺ peaks at 1218.0 eV and 99.3 eV. For the pre-cleaned Ge(100) substrate, weak signals in the higher binding energy side from metallic Ge2p_{3/2} indicate that about one monolayer thick na-

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FIG. 1: (a) Ge $2p_{3/2}$ and (b) Si $2p$ spectra measured after GeO $_2$ and SiO $_2$ formed by UV-O $_3$ oxidation on pre-cleaned Ge(100) and Si(100) at a photoelectron take-off angle of 15°. The binding energy was calibrated with the Ge $2p_{3/2}^{0+}$ peak from Ge(100) peaked at 1218.0 eV (a) or with the Si $2p_{3/2}^{0+}$ peak from Si(100) at 99.3 eV (b), and the intensity was normalized by the Ge $2p_{3/2}^{0+}$ peak intensity (a) or by the Si $2p_{3/2}^{0+}$ peak intensity (b).

FIG. 2: The thickness of oxides grown on Ge(100) and Si(100) by UV-O $_3$ oxidation at room temperature as a function of oxidation time, which was determined from the data of Fig. 1.

tive oxide was formed at Ge(100) surface by pure-water rinse. With increasing UV-O $_3$ oxidation time, chemically shifted Ge $2p_{3/2}$ spectra due to the oxidized state around 1220.5 eV in binding energy are increased. In the Si $2p$ spectra, the signals originated from Si-H bonding unit (~ 100 eV) were markedly decreased by UV-O $_3$ oxidation and the evolution of SiO $_2$ component (~ 103 eV) with progressive UV-O $_3$ was observed as in the case of Ge $2p_{3/2}$ spectra. Because of lower kinetic energy of Ge $2p$ photoelectrons than Si $2p$, Ge $2p$ signals are surface sensitive,

which reflects in the rapid evolution of Ge oxide component with respect to the substrate component in comparison with the Si(100) case. Considering the energy dependence of photoelectron escape depth, the escape depth for Ge $2p_{3/2}$ photoelectrons excited by AlK α radiation is approximately 45% of that for Si $2p$ photoelectrons. Assuming that the Ge $2p$ photoelectron escape depths in Ge and its oxide are 1.3 and 1.6 nm, respectively, the oxide thickness evaluated from the intensity ratio of the oxide component to the substrate component as shown in Fig. 2. In evaluating the SiO $_2$ thickness on Si(100), 2.7 and 3.4 nm were used for the Si $2p$ photoelectron escape depths in Si and SiO $_2$, respectively. Obviously, the oxidation of Ge(100) surface proceeds in a layer by layer manner using by UV-O $_3$ as in the case of Si(100). And no significant differences in the oxidation time and the amount of sub-oxides between Ge(100) and Si(100) are observable in the oxide thickness below ~ 1 nm.

In characterizing chemical bonding features of thermally grown GeO $_2$ on Ge(100), Ge $3d$ spectra were measured taking into account the escape depth of Ge $3d$ photoelectron is larger by a factor of 2.3 that of Ge $2p$ photoelectrons and suitable for the analysis of the interface with thicker oxides. Figure 3(a) shows the evolution of oxide components in Ge $3d$ spectra for thermal oxidation of Ge(100) at 550°C and 600°C and the oxide thicknesses determined from the analysis of Ge $3d$ spectra were summarized in Fig. 3 (b) in comparison with the results obtained for p-Si(100). As for the average oxidation rate roughly estimated from the slopes of lines fitted to the data points shown in Fig. 3 (b), one can find that, in

FIG. 3: (a) Ge3d spectra measured for GeO₂ on p-Ge(100) grown at 550°C and 600°C at a photoelectron take-off angle of 90° and (b) the oxide thickness derived from (a). Each spectrum was normalized by the Ge3d_{5/2}⁰⁺ peak due to Ge(100) at 29.9 eV. The spectral intensity for the case at 600°C for 10 min was reduced by a factor 3. In (b), the oxide thicknesses obtained for thermal oxidation of p-Si(100) were also shown as references.

FIG. 4: (a) O1s energy loss spectra for thermally-grown GeO₂ films in the thickness range from 3.8 to 15.5 nm grown on Ge(100) and (b) wide-scan spectra around O1s core line for thinner GeO₂ on Ge(100). In (b), the spectrum for 15.5 nm-thick GeO₂ was also shown as a reference. The photoelectron take-off angle was 90°.

either oxidation at 550°C and 600°C, the oxidation rate of Ge(100) is about 5 times higher than that of Si(100).

Since photoexcited electrons can suffer energy losses

due to electronic excitations such as plasmons and band-to-band transitions during passing through materials, the energy loss spectra of core lines can be used to evaluate

FIG. 5: $\text{Ge}2p_{3/2}$ energy loss spectra for 0.9~1.9 nm-thick $\text{GeO}_2/\text{Ge}(100)$ formed by UV- O_3 oxidation. The photoelectron take-off angle was 15° .

FIG. 6: (a) Measured valence band spectra for 1.0~1.9 nm-thick $\text{GeO}_2/\text{Ge}(100)$ formed by UV- O_3 oxidation, where the photoelectron take-off angle was set at 90° , (b) deconvoluted spectra for the samples shown in (a), and (c) deconvoluted spectra for the samples with 3.8~10.0 nm-thick thermally-grown GeO_2 . In the spectral deconvolution, the valence band spectrum separately measured for wet-chemically prepared H-terminated $\text{Ge}(100)$ was used.

electronic excitations in the materials. For many various insulators such as SiO_2 , Si_3N_4 and high- k dielectrics, the energy bandgap value was determined from the onset of energy loss spectrum of $\text{O}1s$ photoelectrons for oxides or $\text{N}1s$ photoelectrons for nitrides [4–6]. As shown

in Fig. 4(a), from the onset of the energy loss spectrum of $\text{O}1s$ photoelectrons, which was defined by linearly extrapolating the segment of maximum negative slope to the background level, the energy band gap of thermally-grown GeO_2 was determined to be 5.70 eV within an ac-

FIG. 7: Total photoelectron yield spectra for the samples before and after UV- O_3 oxidation of (a) $\text{p-Ge}(100)$ and (b) $\text{p-Si}(100)$. The gray region corresponds to the yield of Si valence electrons. The E_V denotes the valence band top measured from the vacuum level.

FIG. 8: Energy distributions of filled state densities derived from the yield spectra for (a) $\text{GeO}_2/\text{Ge}(100)$ and (b) $\text{SiO}_2/\text{Si}(100)$ system formed by UV- O_3 oxidation shown in Fig. 7.

curacy of 0.1 eV in the thickness range from 3.8 to 15.5 nm. However, in the cases with GeO_2 thicknesses below ~ 3 nm, since metallic Ge $\text{L}_{3\text{M}_{23}\text{M}_{23}}$ Auger signals overlap with the energy loss spectrum of the primary O1s core line signals (Fig. 4(b)), it becomes very difficult to determine the onset, namely the energy bandgap. Thus, we carefully measured energy loss signals of $\text{Ge}2p_{3/2}$ photoelectrons from GeO_2 and determined the onset from the Ge^{4+} peak to determine the energy bandgap. We confirmed that, for GeO_2 with thicknesses of 3.8–15.5 nm, no significant difference in the energy bandgap values be-

tween the value obtained from O1s and $\text{Ge}2p_{3/2}$ energy loss spectrum is observable. Also, as shown in Fig. 5, the same value (5.70 eV) within an accuracy of 0.1 eV is also evaluated in the thickness range from 0.9–1.9 nm for GeO_2 grown by UV- O_3 oxidation. This energy bandgap value is almost the same as the value of glassy GeO_2 measured by optical reflectance (5.63 eV) [7].

To evaluate the valence band (VB) offset between GeO_2 and $\text{Ge}(100)$, the VB spectra for $\text{GeO}_2/\text{Ge}(100)$ were measured and deconvoluted into two components originated from GeO_2 and $\text{Ge}(100)$ as shown Fig. 6. In the

spectral deconvolution, the VB spectrum separately measured for wet-cleaned Ge(100) was used. From the energy separation of the tops of the deconvoluted VB spectra, the VB offset between GeO₂ and Ge(100) is determined to be 4.00 ± 0.05 eV in the GeO₂ thickness range from 1.0 to 10.0 nm. Considering the energy bandgap of crystal Ge (0.66 eV [8]) and these result, the conduction band offset between GeO₂ and Ge(100) is obtained to be 1.04 eV.

To get an insight into the quality of the interface between the oxide and Ge(100) or Si(100) formed UV-O₃ oxidation at room temperature, the energy distribution of electronic defect states for the samples before and after UV-O₃ oxidation were examined by total photoelectron yield measurements as shown in Fig. 7. Considering the fact that the photoemission of valence electrons becomes significant for incident photon energies higher than 4.66 eV for Ge and 5.15 eV for Si as shown in the grayed region of Fig. 7, observed high yields for lower incident photon energies indicate that there exist significant amount of defects located in the energy region from the valence band edge toward the conduction band. In either case on Ge(100) or Si(100), the photoelectron yield in the energy region corresponding to the bandgap of the substrate is markedly increased with progressive UV-O₃ oxidation until the oxide thickness reaches 0.51 nm on Ge(100) and 0.56 nm on Si(100), and then the yield is dramatically decreased with further progressive oxidation. A significant increase in the yield in the early stages of oxidation implies that hydrogen desorption from the HF-last surface promotes under UV-O₃ oxidation and results in the generation of Ge or Si dangling bonds. Less stability of Ge hydrides than Si hydrides might be responsible for more enhanced yield in the early stages of UV-O₃ oxidation of Ge(100) than Si(100). The dangling bonds so generated are likely to be eliminated by O incorporation bridging between neighboring dangling bonds with progressive UV-O₃ oxidation.

From the 1st derivative of the yield spectrum with re-

spect to energy, the energy distribution of the filled defect state density was crudely estimated in each case using the same manner described in Ref. [3]. As shown in Fig. 8 (a), in the UV-O₃ oxidation of Ge(100), the midgap state density increases up to its maximum as much as $\sim 2 \times 10^{13}$ cm⁻²/eV while the 0.51 nm-thick oxide layer is formed, and it decreases to 1×10^{12} cm⁻²/eV with an increase in the oxide thickness only by 0.09 nm. In contrast, in the UV-O₃ oxidation of Si(100), the maximum midgap state density is at most $\sim 1 \times 10^{11}$ cm⁻²/eV, in which 0.56 nm-thick oxide is formed, and it reduced to initial level with progressive oxidation as shown in Fig. 8 (b).

IV. CONCLUSIONS

We have confirmed that, for UV-O₃ oxidation, the oxidation of Ge(100) surface proceeds in layer by layer manner as in the case of Si(100) and there is no significant difference in the oxidation rate between Ge(100) and Si(100) in the oxide thickness region below ~ 1 nm. The energy band offsets between 1~15 nm-thick GeO₂ and Ge(100) are ~ 4.0 eV in the valence band edge and ~ 1.04 eV in the conduction band edge, respectively. From the total PYS measurements, it is found that filled defect states at the GeO₂/Ge(100) interface is about one order of magnitude larger than that at SiO₂/Si(100) interface.

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