Determination of Energy Band Alignment in Ultrathin Hf-based Oxide/Pt System

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Abstract. Effect of incorporating a third element into HfO2 on the electronic structures has been studied by high resolution x-ray photoelectron spectroscopy (XPS). Hf-IIIa (La, Y, Gd, and Dy) oxide and Hf-Ti oxide films were deposited on a Pt layer by metal organic chemical vapor deposition (MOCVD) and co-sputtering and followed by post-deposition annealing in O2 ambience at 500ºC. The energy bandgap (Eg) of these Hf-based oxide films was determined by analyzing the energy loss spectra of O 1s photoelectrons in consideration of the overlap with Hf 4s core-line signals. From analyses of the valence band signals and the cut-off energy for photoelectrons, the valence band offset between the Hf based-oxide, and the Pt electrode and the work function value of the Pt layer were evaluated. By combining the oxide bandgap values, the valence band line-ups, and the Pt work function value, the energy band profile of the Hf-based oxide/Pt has been determined.

1. Introduction
The further scaling in metal-oxide-semiconductor field effect transistors (MOSFETs) and dynamic random access memory (DRAM) capacitors requires reducing the equivalent oxide thickness (EOT) with an implementation of dielectrics with higher k values [1]. Hafnium-based oxides have been intensively studied as alternative dielectrics because of their favorable barrier height and relatively good thermal stability [2, 3]. We reported an increase in the energy bandgap (Eg) with Al and Si incorporation into HfO2 (e.g., Hf-Al oxide (Al/(Hf+Al) = 30%) : Eg = 6.30 eV [4] and Hf-Si oxide (Hf/(Hf+Si) = 43%) : Eg = 6.40 eV [5]). Incorporating a more polar element into the oxide network and a structural phase transformation by doping another element are considered as an effective approach to increasing the k value more [6-9]. However, there are some drawbacks such as bandgap shrinkage and reduction of barrier height reflecting the energy bandgap of incorporated material [10]. The impact of incorporating a third element of the HfO2 network on the energy band profile has yet to be studied in detail.

In this work, we have studied the effect of incorporating a third element (La, Y, Gd, Dy, and Ti) into HfO2 on the electron barrier height at the Hf-based oxide/Pt interface using high resolution x-ray photoelectron spectroscopy (XPS).
2. Experimental Procedures

After the formation of a Pt layer on thermally-grown SiO$_2$/Si by direct-current (DC) sputtering, 3-5 nm-thick HfO$_2$ and Hf-IIa oxides (Y, La, Gd, and Dy) were deposited by metal-organic chemical vapor deposition (MOCVD) at 450°C in O$_2$ ambience at 10 Pa using di-pivaloy-methanato (DPM) precursors. And, ~5 nm-thick Hf-Ti oxide films with different Ti content were deposited by a co-sputtering method. Subsequently, post-deposition annealing was performed at 500°C in dry-O$_2$ ambience under atmospheric pressure to densify the films so prepared. From XPS core-line analyses, the cation content of the IIa element in the films after annealing was evaluated to be La/(Hf+La) = ~54 %, Y/(Hf+Y) = ~62 %, Gd/(Hf+Gd) = ~54 %, and Dy/(Hf+Dy) = ~60 %. And, in each Hf-based oxide film, a fairly good compositional uniformity was confirmed from the photoelectron take-off angle dependence of core-line signals.

To evaluate the energy band structure of the samples, O1s energy loss signals, valence band spectra, and the cut-off energy for photoelectrons were measured by utilizing monochromatized Al K$_\alpha$ radiation ($h\nu = 1486.6$ eV: S-XPS). To accurately determine the energy bandgaps of the films, energy loss spectra of O1s photoelectrons were measured by hard x-ray photoelectron spectroscopy (H-XPS) using excited synchrotron radiation ($h\nu = 7939$ eV) in SPring-8 as well as by S-XPS.

3. Results and Discussion

The $E_g$ values for the thin oxide films can be determined from the threshold energy of the energy loss signals of O 1s photoelectrons [4, 5, 11, 12]. In the case of Hf-based oxides, the superimposing of Hf 4s core-line signals on the energy loss signals of primary O 1s core-line signals makes it difficult to determine the onset of the energy loss signals. To overcome this difficulty, the binding energy position and spectral shape of Hf 4s signals were determined by x-ray excitation energy at about 7939 eV (Synchrotron: SPring-8) and 1486.6 eV (Al K$_\alpha$) as shown in figure 1. Because the ratio of the photo-ionized cross section of the Hf 4s core line to that of the Hf 4f core line increases significantly with increasing excitation energy [13], the Hf 4s signals excited by the synchrotron radiation with a binding energy of around 538 eV are clearly distinguished in comparison to the case excited by Al K$_\alpha$ radiation. As indicated in figure 1, one can determine that the energy separation between Hf 4s and Hf 4f core lines is about 519.65 eV. By subtracting the Hf 4s component from the measured O 1s photoelectron energy-loss spectrum, the energy separation between Hf 4s and Hf 4f signals was taken into account and the intensity was normalized by Hf 4f signal intensity (figure 2(a)). By applying the same procedure to the measured spectra, the inherent O 1s energy loss spectra were obtained as seen in figures 2(b) and 2(c), and then in each spectrum, the onset of the energy loss spectrum was defined by linearly extrapolating the segment of maximum negative slope to the background level. As a result,

![Figure 1. O 1s, Hf 4s, and Hf 4f spectra for HfO$_2$ after O$_2$ annealing at 500°C using excited Al K$_\alpha$ (1486.6 eV) and hard X-ray (7939 eV) radiation.](image-url)
the Eg values of pure HfO$_2$ and Hf-Y oxide were determined to be 6.10 eV within an accuracy of 0.1 eV. The Eg value is slightly increased by the incorporation of lanthanoids such as La, Gd, and Dy. For Hf-Ti oxides shown in figure 2(c), by incorporating Ti atoms, the Eg value of Hf-Ti oxide was gradually decreased. As the Ti/(Hf+Ti) content increased up to ~74 %, the Eg value decreased by 2.0 eV from the value of pure HfO$_2$.

Figure 2. O 1s energy loss spectrum measured for HfO$_2$ thin films and a demonstration of subtracting Hf 4s signals from the measured spectrum (a) and O1s energy loss spectra deconvoluted for Hf-IIIA (La, Y, Gd, and Dy) oxide films (b) and for Hf-Ti oxide films (c). For the spectra of (b) and (c), Hf 4s signals were subtracted completely from the measured spectra as demonstrated in (a). The onset of the energy loss signals for each sample was determined with an accuracy of ±0.05 eV.

Figure 3. Valence band spectra of HfO$_2$/Pt structure before and after spectral deconvolution (a) and deconvoluted valence band spectra of Hf-IIIA (La, Y, Gd, and Dy) oxide films (b) and of Hf-Ti oxide films (c) as shown in figure 2.
To evaluate the valence band offset, the valence band spectra for the samples were measured and deconvoluted into mainly two components originated from the Hf based oxide and Pt (figure 3(a)). A reference valence band spectrum of the Pt layer was used in the spectral deconvolution, which was separately measured for the sample before Hf-based oxide deposition. And, in each deconvoluted Hf based oxide signal, taking into account the potential drop in the dielectric layer, the binding energy was normalized by surface C-H bonding units in C 1s spectra. From the energy separation of the tops of the deconvoluted valence band spectra, the valence band offset between Pt and each of the Hf-based oxides was evaluated as shown in figures 3(b) and 3(c). The valence band offset with respect to the Fermi Level of Pt gradually decreases from 2.80 eV for Pure HfO$_2$ incorporating a rare-earth oxide such as Y, Gd, La, and Dy. In addition, the valence band offset between Hf-Ti oxide and Pt is slightly decreased from 2.80 to 2.60 eV with Ti content.

The work function (WF) of the Pt surface was evaluated from the cut-off energy for photoelectrons (figure 4). Photo-excited electrons passing though materials can suffer inelastic scatterings and lose their energy with some electronic excitations. If the kinetic energy of excited electrons becomes or is below the WF of a metallic material of interest, such low energy electrons can no longer emit to the outside. Thus, the WF value can be determined from the threshold energy for electrons near the lower limit in the kinetic energy scale. To determine precisely the WF value considering the thermal broadening in the metal Fermi surface, curve fitting to the photoelectron yield spectra near the lower limit in the kinetic energy scale was conducted by using a Fowler function [14] given by

$$\varphi(x) = \frac{x^2}{2} + \frac{x^3}{3} - \frac{e^{x^2}}{2} - \frac{e^{3x}}{3} + \cdots \quad (x \geq 0), \quad E_F = kT \cdot x$$  \hspace{1cm} (1)

The validity of this method was confirmed from the WF determination of pure metals such as Au and Ag. From a best fit result, the WF value for Pt was determined to be 5.55 eV.

Based on the results of figures 2, 3, and 4, the conduction band (CB) offsets between Pt and each Hf-based oxide, namely the barrier heights for electrons, were estimated and summarized as shown in figures 5, 6, and 7. The conduction band and valence band offset for the HfO$_2$/Pt interface were obtained to be 3.30 and 2.80 eV, respectively (figure 5). And, electron barrier heights over 3.3 eV

![Figure 4](image-url)  
Figure 4. The photoelectron yield spectra from Pt surface near the cut-off in the kinetic energy scale. Curve fitting with a Fowler function was also demonstrated.

![Figure 5](image-url)  
Figure 5. Energy band profile of HfO$_2$/Pt structure.
were obtained at the Pt/Hf-IIIa (Y, La, Gd, and Dy) oxide interfaces (figure 6). Obviously, the electron barrier height decreases with increasing Ti content up to 39 % and then saturates at ~1.5 eV with further increase in the Ti content (figure 7). While the valence band offset slightly decreases with Ti content, significant changes in the conduction band offset by third element addition can be interpreted in terms of the bottom of the oxide conduction band edge changing from unoccupied Hf 5d state to Y 4d, La 5d, Gd 5d, Dy 5p, and Ti 4d states. And, slight changes of valence band offset can be explained by the top of the oxide valence band being derived from non-bonding O 2p states irrespective of the third element addition.

4. Conclusion  
The energy band profile of Hf-based oxide/Pt has been determined by combining the oxide bandgap values and the valence band line-ups. The conduction band and valence band offset for HfO2/Pt interface were obtained to be 3.30 and 2.80 eV, respectively. Hf-IIIa (Y, La, Gd, and Dy) ternary oxides show an electron barrier of 3.4 eV and higher. With an increase in Ti content up to 39%, the conduction band offset is significantly decreased from 3.20 to 1.50 eV. The valence band offset is slightly decreased by incorporating Ti.

5. Acknowledgements  
The synchrotron radiation experiments were performed at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI/SPring-8) as Nanotechnology Support Project of the Ministry of Education, Culture, Sports, Science and Technology (Proposal No. 2007A0005, 2011A0026/BL-No.46XU). The authors would like to thank Prof. S. Zaima (Nagoya Univ.), Drs. J-Y. Son, M. Machida, H. Oji (JASRI), Drs. M. Tanioku, M. Horikawa, and A. Ogishima (Elpida.) for their fruitful discussions and assistance with the experiments. A part of this work was supported by the Research Institute for Nano-device and Bio Systems (RNBS), Hiroshima University, Japan.
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