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## Photoemission Study of Chemical Bonding Features and Electronic States of Ultrathin $\text{HfTi}_x\text{O}_y/\text{Pt}$ System

<sup>1</sup>Akio Ohta, <sup>1</sup>Hideki Murakami, <sup>1</sup>Seiichiro Higashi, <sup>1</sup>Seiichi Miyazaki

<sup>2</sup>Masami Tanioku, <sup>2</sup>Mitsuhiro Horikawa, and <sup>2</sup>Atsushi Ogishima

<sup>1</sup> Graduate School of AdSM, Hiroshima University 1-3-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8530

Phone: +81-82-424-7648, FAX: +81-82-424-7648, E-mail: semicon@hiroshima-u.ac.jp

<sup>2</sup>T&D Office, APD Gr., Elpida Memory Inc. 7-10, Yoshikawa Kogyo Danchi, Higashi-Hiroshima, Hiroshima 739-0153

### 1. Introduction

The further scaling in MOS FETs and DRAM capacitors requires reducing equivalent oxide thickness (EOT) with an implementation of dielectrics with higher  $k$  values [1]. Hafnium-based oxides have been intensively studied as most promising alternative dielectrics because of their moderate dielectric constants, favorable barrier height and relatively good thermal stability [2, 3]. An incorporation of more polar element into oxide network is one of effective approach to increasing  $k$  value. Considering fairly large  $k$  value in  $\text{TiO}_2$  among other binary oxides, the impact of Ti incorporation into Hf-oxide network on electrical properties is still a matter of research although there is a drawback of bandgap shrinkage reflecting the energy bandgap of  $\text{TiO}_2$  as small as  $\sim 3.1\text{eV}$  [4].

In this work, to get an insight on such tradeoff between barrier height and dielectric constant, the electronic states in  $\text{HfTi}_x\text{O}_y$  deposited on Pt films have been studied systematically as a function of chemical composition by x-ray photoelectron Spectroscopy (XPS) and total photoelectron yield spectroscopy (PYS).

### 2. Experimental

$\sim 5\text{nm}$ -thick  $\text{HfTi}_x\text{O}_y$  with a compositional ratio,  $\text{Ti}/(\text{Hf}+\text{Ti})$ , ranging from 0 to 83% films were deposited on Pt/Si(100) by a co-sputtering method. Post deposition anneal was performed at  $700^\circ\text{C}$  in  $\text{O}_2$  ambience. For the depth profiling with x-ray photoemission measurements using monochromatized Al  $K\alpha$  radiation, the oxide thinning was carried out repeatedly in a dilute HF solution at room temperature.

### 3. Results and Discussion

Pt4f, Hf4f and Ti2p spectra for  $700^\circ\text{C}$  annealed samples with different  $\text{Ti}/(\text{Hf}+\text{Ti})$  contents are shown in Fig. 1. Pt4f and Hf4f spectra are deconvoluted into 2 components in consideration of spin-orbit splitting of each core-line. For the samples with  $\text{Ti}/(\text{Hf}+\text{Ti})$  content range over  $\sim 17\%$ , chemically-shifted Pt4f signals due to the Pt-O bonding units around  $74\text{eV}$  were clearly observed, which indicates enhanced oxidation of Pt surface with incorporation of Ti ions. In fact, no oxidation is observable on the bare Pt surface after  $\text{O}_2$  anneal even at  $700^\circ\text{C}$ . In the case of pure  $\text{HfO}_2$ , relatively sharp Hf4f spectrum was observed, being associated with the crystallization. In addition, Hf4f and Ti2p signals are slightly shifted toward higher binding energy side with increasing Ti content. It is

likely that the incorporation of more electronegative Ti atoms into the  $\text{HfO}_2$  network is responsible for such observed energy shifts in Hf and Ti core lines.

To gain an understanding on the chemical bonding features near the interface between  $\text{HfTi}_x\text{O}_y$  and Pt, the depth profiling with XPS measurements was carried out at each oxide thinning step. Figure 2 shows a typical compositional profile which was obtained for the sample with a  $\text{Ti}/(\text{Hf}+\text{Ti})$  content of  $\sim 39\%$ . A formation of a  $\text{PtO}_x$  layer as thin as  $\sim 1\text{nm}$  was confirmed at the interface between  $\text{HfTi}_x\text{O}_y$  and Pt. Also, a fairly uniform compositional profile was observed in the oxide except near the interface and the top oxide surface within  $0.5\text{nm}$ .

The energy bandgap ( $E_g$ ) of the  $\text{HfTi}_x\text{O}_y$  films were determined by analyzing the energy loss spectra of O1s photoelectrons in consideration of the overlapping with Hf4s core line signals as shown in Fig. 3. The binding energy position and spectral shape of Hf4s signal were determined by x-ray excitation energy at about  $8\text{keV}$  and  $1486.6\text{eV}$ . After subtraction of Hf4s components from measured spectra (Fig. 3(b)), the onset of the energy-loss signal was defined by linearly extrapolating the segment of maximum negative slope to the background level. Thus, the  $E_g$  value of pure  $\text{HfO}_2$  was determined to be  $6.10\text{eV}$  within an accuracy of  $0.1\text{eV}$ . By the incorporation of Ti atoms, the  $E_g$  value of  $\text{HfTi}_x\text{O}_y$  is gradually decreased. As the  $\text{Ti}/(\text{Hf}+\text{Ti})$  content is increased up to  $\sim 74\%$ , the  $E_g$  value is decreased by  $2.0\text{eV}$  from the value of pure  $\text{HfO}_2$ .

To evaluate the valence band (VB) offset, the VB spectra for sample are measured and deconvoluted into mainly three components originated from  $\text{HfTi}_x\text{O}_y$ ,  $\text{PtO}_x$  and Pt. From the energy separation of the tops of the deconvoluted VB spectra, the VB offset between  $\text{HfO}_2$  and Pt is determined to be  $2.90\text{eV}$  (Fig.

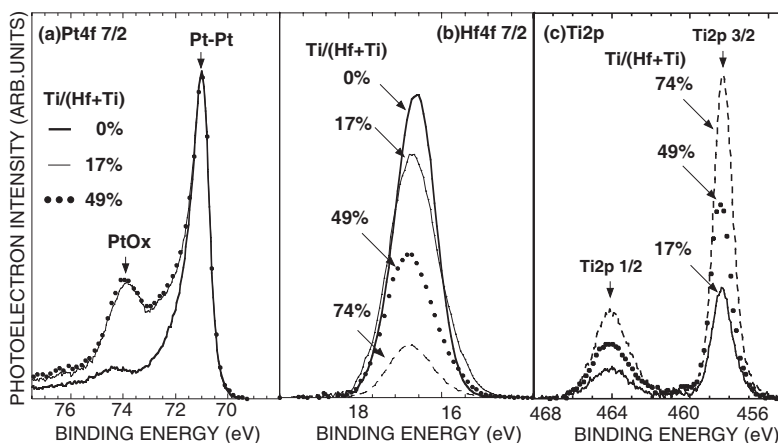


Fig. 1 (a)Pt4f 7/2, (b)Hf4f 7/2 and (c)Ti2p spectra for  $\sim 5\text{nm}$ -thick  $\text{HfTi}_x\text{O}_y/\text{Pt}$  system after  $700^\circ\text{C}$   $\text{O}_2$  anneal. The photoelectron take-off angle was set at  $90^\circ$ .

4(a)). In the case of  $\text{HfTi}_x\text{O}_y/\text{PtO}_x/\text{Pt}$  structure, the VB offset is slightly decreased with Ti content, (Fig. 4(b)). After removing  $\text{HfTi}_x\text{O}_y$  layer, the VB offset between interfacial  $\text{PtO}_x$  and Pt was determined to 0.60eV.

Based on the results of Figs. 3 and 4, the conduction band (CB) offsets between  $\text{HfTi}_x\text{O}_y$  and Pt, namely the barrier heights for electrons were estimated and summarized as shown in Fig. 5. Obviously, the electron barrier height decreases with increasing Ti content up to 38% and then saturated at  $\sim 1.5\text{eV}$  for further increase in the Ti content., which can be interpreted in terms that unoccupied Ti4d states determine the bottom of the oxide conduction band and non-bonding O2p states determine the top of the oxide valence band irrespective of the Ti content.

The energy distribution of electronic defect states in ultrathin dielectrics and at dielectric/Pt interfaces can be evaluated without gate fabrication by PYS [5]. Because valence electrons of the  $\text{HfTi}_x\text{O}_y/\text{PtO}_x$  layers can not be emitted by irradiation of photons with energies lower than 5.0eV, the photoelectron yield in the energy range from 4.0 to 4.8eV reflects filled defect states distributed in oxide layers and at the interfaces (Fig. 6). The yield intensities due to the defect states were markedly increased by Ti incorporation.

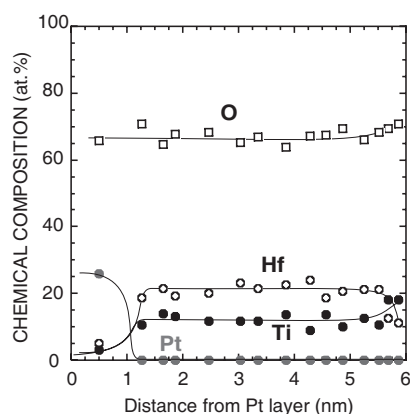


Fig. 2 Depth profile of chemical compositions for the 700°C annealed sample with a Ti/(Hf+Ti) content of  $\sim 39\%$ , which were determined from the change in the core-line signals at each step of  $\text{HfTi}_x\text{O}_y/\text{PtO}_x$  thinning.

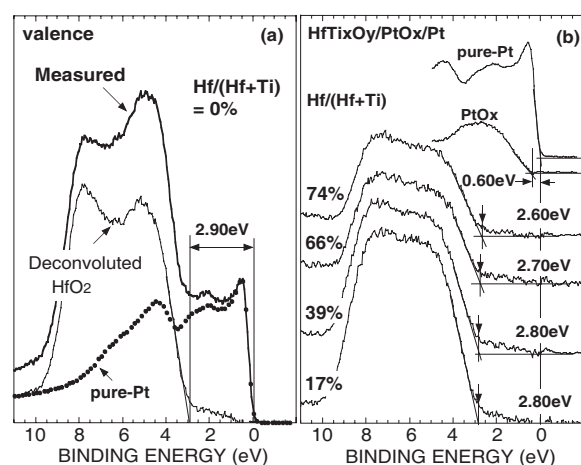


Fig. 4 Deconvoluted valence band spectra for (a)  $\text{HfO}_2/\text{Pt}$  and (b)  $\text{HfTi}_x\text{O}_y/\text{PtO}_x/\text{Pt}$  structure. For the spectral deconvolution, the valence band spectrum separately measured for Pt layer was used.

In summary, the determination of energy band alignments for  $\text{HfTi}_x\text{O}_y/\text{PtO}_x/\text{Pt}$  system has been demonstrated by combination of the oxide bandgap values determined from O1s energy loss spectra and the band offsets obtained from valence band spectra. With Ti content increased up to 40%, the CB offset is significantly decreased from 3.1 to 1.5eV. From the PYS analyses, the generation of defect states with Ti content was observed.

## Acknowledgements

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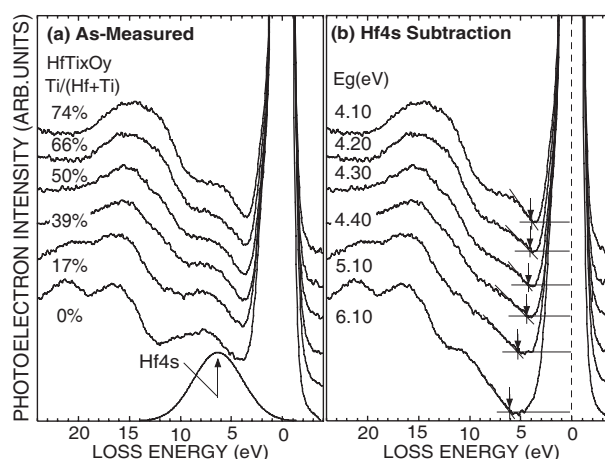


Fig. 3 Measured O1s energy loss spectra for  $\sim 5\text{nm}$ -thick  $\text{HfTi}_x\text{O}_y$  after 700°C  $\text{O}_2$  anneal (a) before and (b) after subtraction of Hf4s contribution from measured spectra.

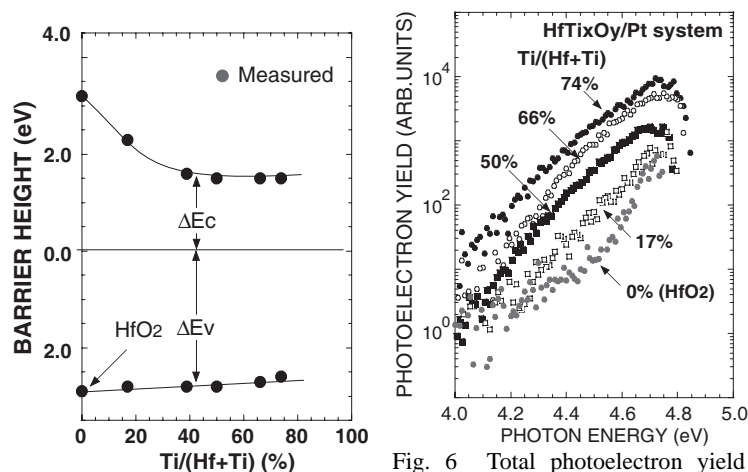


Fig. 5 Changes in the conduction band and valence band offsets between  $\text{HfTi}_x\text{O}_y$  and Pt as a function of the Ti/(Hf+Ti) content.

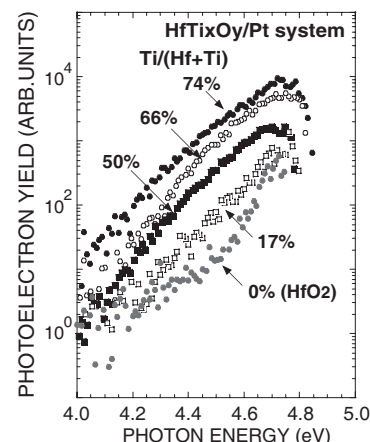


Fig. 6 Total photoelectron yield spectra for  $\text{HfTi}_x\text{O}_y/\text{Pt}$  system after  $\text{O}_2$  anneal at 700°C. The contribution of photoemission from the Pt layer to the yield was subtracted.