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Photoemission Study of Chemical Bonding Features and Electronic States of Ultrathin HfTiₓOᵧ/Pt System

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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 TiO₂ 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 TiO₂ as small as ~3.1eV [4].

In this work, to get an insight on such tradeoff between barrier height and dielectric constant, the electronic states in HfTiₓOᵧ 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

~5nm-thick HfTiₓOᵧ with a compositional ratio, Ti/(Hf+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°C films have been studied systematically as a function of chemical composition by x-ray photoelectron Spectroscopy (XPS) and total photoelectron yield spectroscopy (PYS).

3. Results and Discussion

Pt4f, Hf4f and Ti2p spectra for 700°C annealed samples with different Ti/(Hf+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 Ti/(Hf+Ti) content range over ~17%, chemically-shifted Pt4f signals due to the Pt-O bonding units around 74eV 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 O2 anneal even at 700°C. In the case of pure HfO₂, 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 HfO₂ 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 HfTiₓOᵧ and Pt, the depth profiling with XPS measurements was carried out at each oxide thickness step. Figure 2 shows a typical compositional profile which was obtained for the sample with a Ti/(Hf+Ti) content of ~39%. A formation of a PtOₓ layer as thin as ~1nm was confirmed at the interface between HfTiₓOᵧ and Pt. Also, a fairly uniform compositional profile was observed in the oxide except near the interface and the top oxide surface within 0.5nm.

The energy bandgap (Eg) of the HfTiₓOᵧ 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 8keV and 1486.6eV. 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 Eg value of pure HfO₂ was determined to be 6.10eV within an accuracy of 0.1eV. By the incorporation of Ti atoms, the Eg value of HfTiₓOᵧ is gradually decreased. As the Ti/(Hf+Ti) content is increased up to ~74%, the Eg value is decreased by 2.0eV from the value of pure HfO₂.

To evaluate the valence band (VB) offset, the VB spectra for sample are measured and deconvoluted into mainly three components originated from HfTiₓOᵧ, PtOₓ and Pt. From the energy separation of the tops of the deconvoluted VB spectra, the VB offset between HfO₂ and Pt is determined to be 2.90eV (Fig.

![Fig. 1](image-url)
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4(a)). In the case of HfTi xOy/PtOx/Pt structure, the VB offset is slightly decreased with Ti content, (Fig. 4(b)). After removing HfTi xOy layer, the VB offset between interfacial PtOx and Pt was determined to 0.60eV.

Based on the results of Figs. 3 and 4, the conduction band (CB) offsets between HfTi xOy 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., 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 HfTi xOy/PtOx 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.

In summary, the determination of energy band alignments for HfTi xOy/PtOx/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.

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References