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Evaluation of Potential Change and Electrical Dipole in $HfO_2/SiO_2/Si$ Structure

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Abstract

Inner potential change and electrical dipole in the gate stack structure have been evaluated from the cut-off energy for secondary photoelectron measured by using XPS. By applying this measurement technique, abrupt potential change of 0.4eV was observed in the region near the HfO_2/SiO_2 interface.

1. Introduction

A clear insight into the inner potential changes in the MOS structure, such as the electrical dipole caused by metallic bonding states at the metal gate/high-k dielectric interface [1], the areal density difference of oxygen atoms at the high-k dielectric/SiO_2 interface [2], and oxygen vacancies in the dielectric [3], is strongly required to control the threshold voltages of advanced MOS transistors. We have so far studied such potential changes in TiN/HfSiON and Ru/HfSiON gate stacks from the back-side XPS measurements, and we confirm the work function change due to the dipole formation near the metal/high-k interface and the relief from the fermi level pinning phenomena by oxygen incorporation into HfSiON [4]. Photoemission measurements such as XPS is one of the powerful tool to evaluate the electrical dipole in the gate stack, because it enable us to know the energy level difference between the vacuum level (VL) and the valence band (VB) top for the interest materials from the combination of onset of the VB signals with the cut-off energy for the secondary photoelectrons in consideration of X-ray excitation energy [5]. It is interesting to note that the energy difference of VL between the different materials indicates the potential change including the electrical dipole formation.

In this work, from the VL difference measured by high resolution XPS under monochromatized Al Kα X-ray radiation ($h\nu$ = 1486.6 eV), the inner potential change and electrical dipole formation in the region near the SiO_2/Si and HfO_2/SiO_2 interface have been investigated precisely.

2. Experimental Procedure

A Si(100) substrate was wet-chemically cleaned with $NH_4OH : H_2O_2 : H_2O$ = 0.15 : 3 : 7 solution at 80 ºC for 10 min. Subsequently, the Si surface was terminated with hydrogen in 4.5% HF solution. For the growth of a SiO_2 layer, the dry oxidation at 850 ºC in pure O_2 was conducted. Subsequently, an HfO_2 layer in the thickness of 0.8 nm and 1.6 nm was deposited at 280 ºC by an atomic-layer controlled chemical vapour deposition (CVD) method using TEMA-Hf and O_3. Then, post deposition anneal (PDA) was performed at 850 °C to densify the dielectric layers.

3. Results and Discussion

Figure 1 shows the schematic view of photoemission of secondary photoelectron from the samples. When there exists a dipole layer at the interface between dielectric and semiconductor, resultant abrupt potential change causes the change in the measured cut-off energy for secondary photoelectrons, if the detected energy of photoelectron by analyzer was calibrated by the energy of core-line signals from the semiconductor (Si). This technique has an advantage to evaluate the electrical dipole without a consideration of change in the chemical bonding feature near the interface as compared to the discussion of dipole formation from the energy shift of core-line signals. In addition, electrical dipole at dielectric/dielectric interface such as HfO_2/SiO_2, can be evaluated by the same method as shown in Fig. 1.

Figure 2 shows the cut-off spectra for the secondary photoelectron taken for the thermally grown SiO_2/Si structure. For the depth analysis, thinning of SiO_2 layer with an initial thickness of 3.7 nm was performed by dipping into a dilute HF solution. With the thinning of the SiO_2 layer, cut-off energy for secondary photoelectron was slightly shifted toward the lower kinetic energy side due to the band bending of SiO_2 caused by the negative charge. After the removal of the SiO_2 layer, the cut-off energy was decreased by 0.15 ± 0.05 eV, which indicates the abrupt change in the electrical potential in the region near the SiO_2/Si interface as discussed in Fig. 1. Energy band diagram of SiO_2/Si structure was shown in Fig. 3, where reported values of electron affinity (χ), energy bandgap (Eg), conduction band offset (ΔE_C) and VB offset (ΔE_V) at SiO_2/Si interface were used [5, 6]. Obtained result of electrical dipole at SiO_2/Si interface is acceptable with taking into account of the measurement error of each value.

Then, potential change in the HfO_2/SiO_2 dielectrics was evaluated as shown in Figs. 4 and 5. From Si $2p_{3/2}$ spectra for the sample with different HfO_2 thicknesses, signals originating from Hf-O-Si bonds located at the HfO_2/SiO_2 interface were observed at the lower binding energy side from SiO_2. The energy position of Hf 4f signals from HfO_2 layer kept constant when the HfO_2 thickness was increased from 0.8 to 1.6 nm, which indicate band bending of HfO_2 layer was negligible small. Note that cut-off energy for the sample with HfO_2 was shifted by 0.4 eV toward lower energy side as compared to the reference spectrum of thermally grown SiO_2. Observed energy shift indicates the abrupt potential drop of HfO_2 in the region near the HfO_2/SiO_2 interface. From C-V analysis of Al gate MOS capacitor with 0.8nm-thick HfO_2

layer, we also confirmed the negative flat band voltage shift by ~0.4 V, which was consistent of the XPS results.

In summary, evaluation of interfacial electrical dipole by using XPS has been demonstrated, and energy band diagram of $HfO_2/SiO_2/Si$ system has been evaluated.

Acknowledgement

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References

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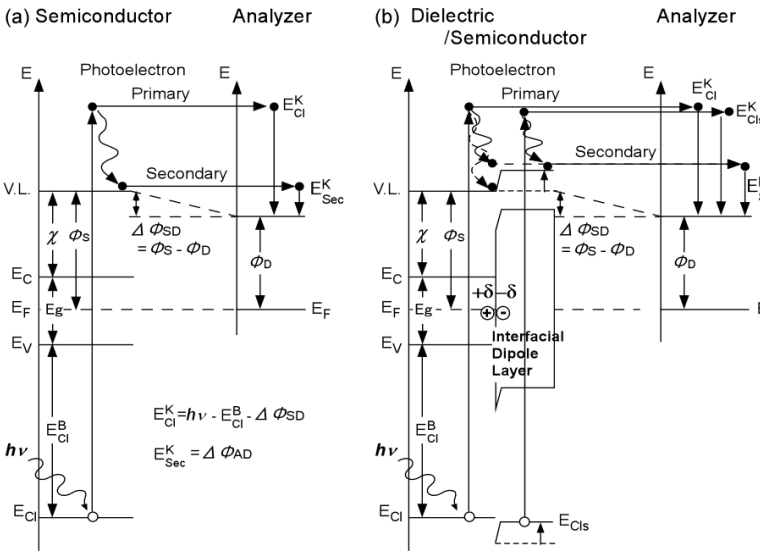

Fig. 1 Schematic view of photoemission from (a) semiconductor and (b) dielectric/semiconductor structure.

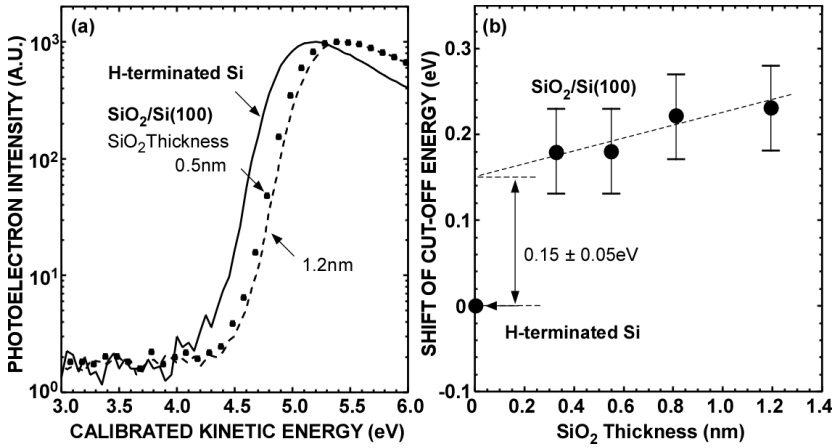

Fig. 2 (a) cut-off spectra for the secondary photoelectron taken for the thermally grown SiO_2/Si structure and (b) change in the cut-off energy with thinning of SiO_2 layer. In each spectrum, energy level was calibrated by Si-Si bonding units from Si substrate in Si $2p_{3/2}$ signals. The remaining SiO_2 thickness after the thinning was estimated from the intensity of Si $2p_{3/2}$ signals.

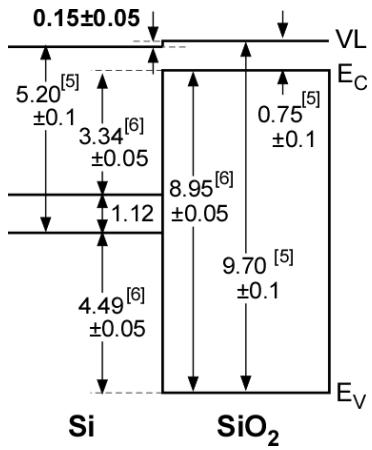

Fig. 3 Energy band diagram for thermally grown SiO_2/Si structure under flat band condition. Reported values of χ, Eg, ΔE_C, and ΔE_V were used [5, 6].

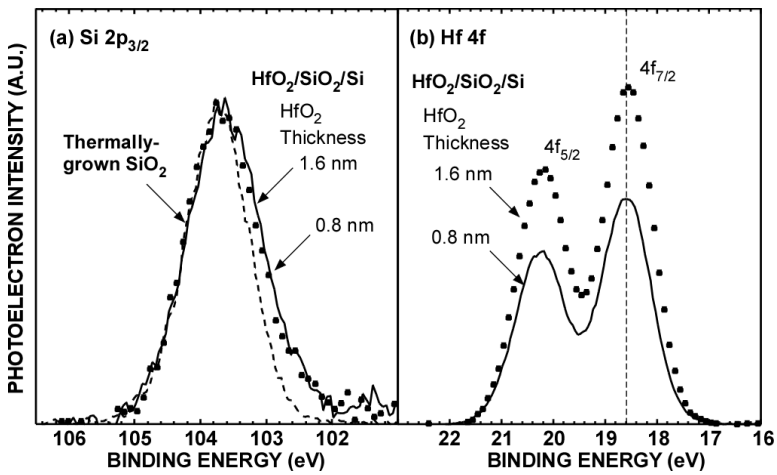

Fig. 4 (a) Si $2p_{3/2}$ and (b) Hf 4f spectra taken for the $HfO_2/SiO_2/Si$ structure with different HfO_2 thickness. In each spectrum, binding energy calibration and photoelectron intensity normalization were made by SiO_2 component in Si $2p_{3/2}$ signals. A spectrum of the thermally grown SiO_2 was also shown as a reference.

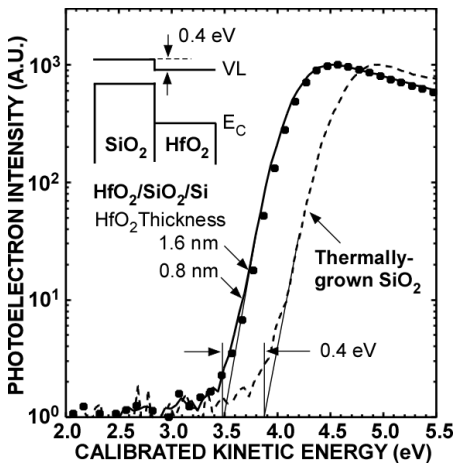

Fig. 5 Cut-off spectra for the secondary photoelectron taken for the samples shown in Fig. 5.