Evaluation of Potential Change and Electrical Dipole in HfO₂/SiO₂/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 0.4 eV was observed in the region near the HfO₂/SiO₂ 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/SiO₂ 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 enables us to know the energy level difference between the vacuum level (VL) and the valence band (VB) bias 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 (hv = 1486.6 eV), the inner potential change and electrical dipole formation in the region near the SiO₂/Si and HfO₂/SiO₂ interface have been investigated precisely.

2. Experimental Procedure

A Si(100) substrate was wet-chemically cleaned with NH₄OH : H₂O₂ : H₂O = 0.15 : 3 : 7 solution at 80 °C for 10 min. Subsequently, the Si surface was terminated with hydrogen in 4.5% HF solution. For the growth of a SiO₂ layer, the dry oxidation at 850 °C in pure O₂ was conducted. Subsequently, an HfO₂ layer in the thickness of 0.8 nm and 1.6 nm was deposited at 280 °C by an atomic-layer controlled chemical vapour deposition (CVD) method using TEMA-Hf and O₃. 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 HfO₂/SiO₂, 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 SiO₂/Si structure. For the depth analysis, thinning of SiO₂ layer with an initial thickness of 3.7 nm was performed by dipping into a dilute HF solution. With the thinning of the SiO₂ layer, cut-off energy for secondary photoelectron was slightly shifted toward the lower kinetic energy side due to the band bending of SiO₂ caused by the negative charge. After the removal of the SiO₂ 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 SiO₂/Si interface as discussed in Fig. 1. Energy band diagram of SiO₂/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 SiO₂/Si interface were used [5, 6]. Obtained result of electrical dipole at SiO₂/Si interface is acceptable with taking into account of the measurement error of each value.

Then, potential change in the HfO₂/SiO₂ dielectrics was evaluated as shown in Figs. 4 and 5. From Si 2p₃/₂ spectra for the sample with different HfO₂ thicknesses, signals originating from Hf-O-Si bonds located at the HfO₂/SiO₂ interface were observed at the lower binding energy side from SiO₂. The energy position of Hf 4f signals from HfO₂ layer kept constant when the HfO₂ thickness was increased from 0.8 to 1.6 nm, which indicate band bending of HfO₂ layer was negligible small. Note that cut-off energy for the sample with HfO₂ was shifted by 0.4 eV toward lower energy side as compared to the reference spectrum of thermally grown SiO₂. Observed energy shift indicates the abrupt potential drop of HfO₂ in the region near the HfO₂/SiO₂ interface. From C-V analysis of Al gate MOS capacitor with 0.8nm-thick HfO₂.
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 HfO₂/SiO₂/Si system has been evaluated.

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**References**