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Direct Observation of Electrical Dipole and Atomic Density at High-k Dielectrics/SiO_2 Interface

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Abstract

Electrical dipole moment at the ultrathin high-k (HfO_2, Al_2O_3, and Y_2O_3)/SiO_2 interface and its correlation with the atomic density difference at the interface have been directly evaluated from the XPS analysis. We have experimentally clarified that the measured electrical dipole shows a linear relationship with the oxygen areal density ratio at the high-k/SiO_2 interface.

1. Introduction

In metal/high-k dielectric gate-stack technology, a clear understanding of inner potential changes at heterointerfaces is one of crucial issues from a viewpoint of precise tuning of threshold voltage for advanced MIS FETs. So far, it has been reported that metallic bonding states [1], oxygen density difference [2], electronegativity [3], dielectric contact induced gap states [4], and oxygen vacancies [5] are discussed as the possible cause of inner potential change by electrical dipole. To get an insight of electrical dipole formation, characterization of chemical structure and bonding features is indispensable. Formation of electrical dipole has been often discussed from flat band voltage shift of capacitance-voltage (C-V) characteristics [6]. However, if there exists some electrical dipoles in the gate stack, it is not so easy to distinguish the amount of each electrical dipole from C-V analysis. To overcome this difficulty, we focused on evaluation of electrical dipole using the photoemission measurements.

In this work, the dipole and oxygen density formed at the high-k/SiO_2 interface has been measured directly by XPS. Furthermore, we experimentally clarified the relationship between dipole moment and oxygen density.

2. Experimental Procedure

After a wet chemical cleaning of p-type Si(100) substrate with NH_4OH : H_2O_2 : H_2O = 0.15 : 3 : 7 solution at 80 ºC for 10 min, the Si surface was terminated with hydrogen in 4.5% HF solution. Then, the dry oxidation in pure O_2 was conducted for the growth of a ~200 nm-thick SiO_2 layer. In some samples, high-k dielectrics such as HfO_2, Al_2O_3, and Y_2O_3 thin film with a thickness of 0.4 ~ 1.3 nm were deposited on thermally-grown SiO_2/Si by the magnetron sputtering, in which the Ar/O_2 gas flow ratio and the power density kept constant at unity and 1.52 W/cm^2, respectively. Then, post deposition anneal (PDA) was performed at 600 °C in dry-N_2 for 5 min to densify the dielectric layers. Uniform coverage with ultrathin high-k dielectrics was also confirmed by AFM measurements. Electrical dipole at high-k/dielectric interface was evaluated from the cut-off energy of secondary photoelectrons (SEs) [7], which corresponds to the vacuum level difference caused by the abrupt potential change as shown in Fig. 1.

3. Results and Discussion

Figure 2 shows Si $2p_{3/2}$ spectra and cut-off energy of SEs measured before and after the formation of ultrathin high-k layers on thermally grown SiO_2/Si structure. In each spectrum, the binding energy was calibrated by Si $2p_{3/2}$ signals originated from the thermally-grown SiO_2 to eliminate the energy shift due to the charge up effect during measurements. After the formation of high-k layer on SiO_2, the Si $2p_{3/2}$ signals from Si-O-M (M=Hf, Al, Y) bonding units were slightly increased. From the Si $2p_{3/2}$ intensity ratio of Si-O-M to SiO_2 signals, thickness of Si-O-M layer was estimated to be 0.3~0.6 nm, indicating that an abrupt high-k/SiO_2 interface was formed, in other words, compositional mixing between high-k and SiO_2 was quite small. The cut-off energy of SEs taken for the sample after the formation of Al_2O_3 and HfO_2 on SiO_2 was shifted by around ~0.40 and ~0.10 eV toward the lower kinetic energy side, respectively (Fig. 2(b)). On the other hand, for the sample after Y_2O_3 formation, an opposite energy shift of ~0.05 eV was detected. In Fig. 3, high-k thickness dependence of cut-off energy of SEs was hardly detected in the thickness range from 0.4 to 1.3 nm. From these results, the observed energy shift in each high-k dielectric/SiO_2 stack is attributable to the abrupt potential change due to the presence of interface dipoles.

To get a better understanding the observed electrical dipole formation, atomic density (n_{top}) of high-k layer on SiO_2 was estimated from the analysis of O 1s signals using Eq. (1) [8],

$$n_{top} = \frac{\sigma_{top} \cdot \lambda_{top} \cdot I_{bottom} \cdot n_{bottom}}{\sigma_{bottom} \cdot \lambda_{bottom} \cdot I_{top}} \times \frac{1}{exp\left(\frac{d_{top}}{\lambda_{top} \sin\theta}\right) - 1} \quad (1)$$

where n, σ, λ, and d is the atomic density, photo-ionized cross section, photoelectron escape depth for O 1s [9], and thickness of high-k layer, respectively. I_{top} and I_{bottom} is the O 1s intensity originating from the high-k and SiO_2, respectively, which is obtained by the spectrum deconvolution of O 1s spectrum as seen in the Fig. 4. After that, the oxygen areal density (ρ) was calculated with taking into account of the dimension and chemical composition of high-k layer. Measured electrical dipole at each high-k/SiO_2 interface was summarized as a function of the calculated oxygen areal density ratio of high-k dielectric to SiO_2 as shown in Fig. 5. It was found that the liner relationship between the electrical dipole and oxygen areal density at the interface.

In summary, abrupt potential drop of Al_2O_3 and HfO_2 due to the electrical dipole at high-k/SiO_2 interface was evaluated to be ~0.40 and ~0.10 eV. Y_2O_3/SiO_2 stacked sample shows the opposite electrical dipole moment at the interface as much as ~0.05 eV. The magnitude of these electrical dipole was found to be a liner relationship to the measured oxygen areal density ratio of high-k to SiO_2.

Acknowledgement

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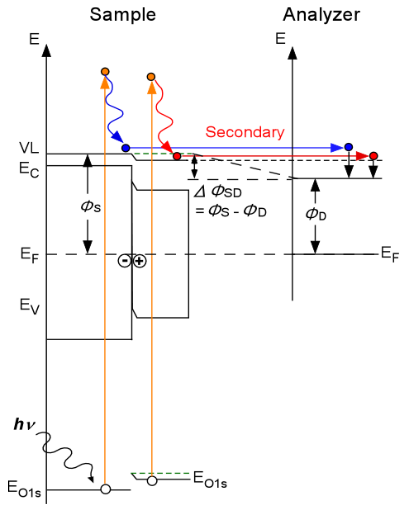

Fig. 1 Schematic illustration of photoemission from stacked dielectrics and influence of an abrupt potential change caused by electrical dipole at the dielectric interface on the cut-off energy for secondary photoelectrons from the underling dielectrics.

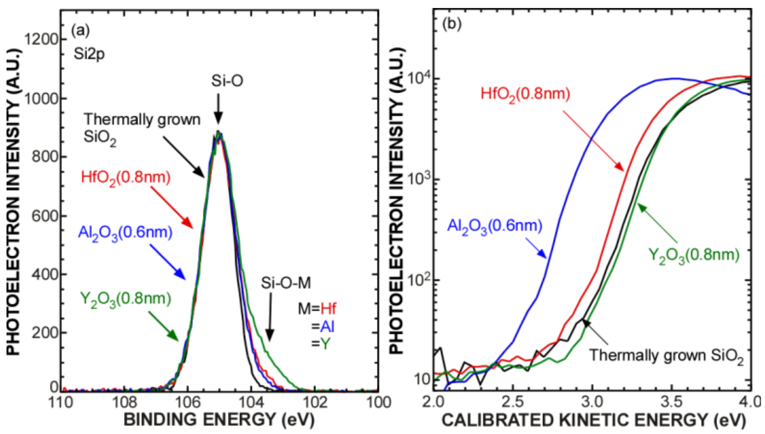

Fig. 2 (a) Si $2p_{3/2}$ signals and (b) cut-off energy of SEs taken for as-grown SiO_2 and high-k/SiO_2 stacks. In each spectrum, photoelectron take-off angle was set at 90º.

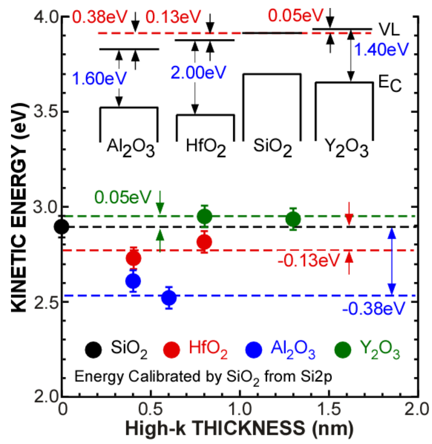

Fig. 3 Cut-off energy of SEs taken for high-k dielectric/SiO_2 structure with different high-k thicknesses.

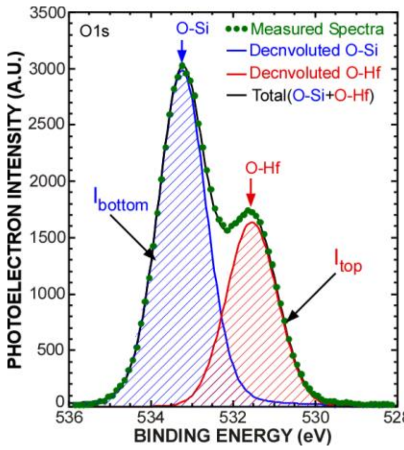

Fig. 4 Measured and deconvoluted O 1s signals taken for ~0.8 nm-thick HfO_2/ ~200 nm-thick SiO_2.

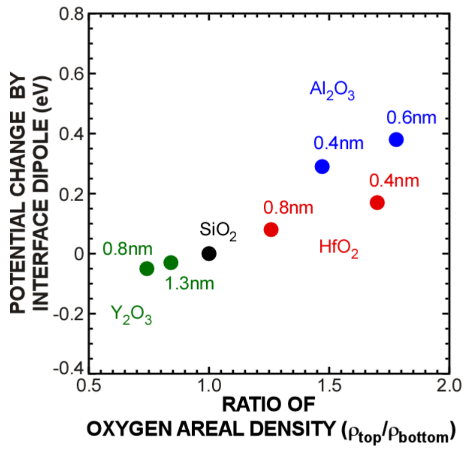

Fig. 5 Measured electrical dipole at high-k/SiO_2 interface as function of oxygen areal density ratio of high-k dielectric to SiO_2.