# Optimization of fabrication conditions of HfO<sub>2</sub>/SiO<sub>2</sub>/Si(100) and Y<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si(100) structures

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Abstract

HfO<sub>2</sub>/SiO<sub>2</sub>/Si(100) We prepared and  $Y_2O_3/SiO_2/Si(100)$ structures annealing of by HfO<sub>2</sub>/Si(100) and Y<sub>2</sub>O<sub>3</sub>/Si(100) precursors which were fabricated by PLD. From the structure analysis by XPS, we defined the optimal annealing condition which SiO<sub>2</sub> layer was grown at the HfO<sub>2</sub>/Si and Y<sub>2</sub>O<sub>3</sub>/Si interfaces. The C-V curves of the samples annealed with the optimal condition (700°C, 1 hour) showed a flat band voltage shift in opposite directions. We consider that the shifts are due to dipoles with two different polarities formed by the difference of areal density of oxygen atoms at the HfO<sub>2</sub>/SiO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>/Si interfaces.

# 1. Introduction

Heterointerface of two different materials exhibits unique properties different from each material in bulk state. Recently, Kita et al have reported that the heterointerface between high-k metal oxides (ionic bonding materials) and silicon oxide (a covalent bonding material) induces dipoles due to the displacement of oxygen ions. [1] The displacement is driven by the difference of areal density of oxygen atoms ( $\sigma$ ) for the each substance. Oxygen movement occurs from smaller- $\sigma$  ( $\sigma_s$ ) surface to larger- $\sigma$  ( $\sigma_l$ ) surface and the displaced oxygen ion with minus charges and the arising vacancy with plus charges form a countercharge polarization at the interface. The movement is terminated within nanometer scale at achieving equilibrium of the diffusion force with the Coulomb attraction. From the viewpoint of interface engineering, this phenomenon is quite interesting because the electric field arising from the dipoles is usable to modulate interface properties in heterojunctions without any external field. Hence we have attached importance to controlling the dipole properties by designing the stacking structure of high-k/SiO<sub>2</sub>.

Previously, the high- $k/SiO_2/Si$  stacks have been fabricated by which the high-k layers are deposited on preformed SiO<sub>2</sub>/Si stacks which are prepared by high-temperature oxidation of the Si substrate or deposition of SiO<sub>2</sub> layer. In order to omit the preforming process, we have tried the way to use precursor of high-k/Si. We expected to form the high- $k/SiO_2/Si$  structure by post-annealing treatment of the high-k/Si precursor.



Fig. 1 Schematic illustrates of the sample structures in each step of the fabrication process. (a) and (b) precursive structures of  $HfO_2/Si(100)$  and  $Y_2O_3/Si(100)$ . (c) and (d) Annealed samples of (a) and (b) and inducible dipole directions at the interfaces.

In this study, we demonstrated the formation of  $HfO_2/SiO_2/Si$  and  $Y_2O_3/SiO_2/Si$  stacks by using the  $HfO_2/Si$  and  $Y_2O_3/Si$  precursors. Furthermore we optimized the annealing condition by X-ray photoemission spectroscopy (XPS) and capacitance - voltage (C-V) measurements. We here describe the reason why  $HfO_2$  and  $Y_2O_3$  were chosen for the target materials. The reason consists in a difference of  $\sigma$  against the  $\sigma$  of SiO<sub>2</sub>. According to Kita's report, it is expected that  $HfO_2$  and  $Y_2O_3$  form two different type of interfaces with SiO<sub>2</sub>, that is,  $HfO_2(\sigma_i)/SiO_2(\sigma_s)$  and  $Y_2O_3(\sigma_s)/SiO_2(\sigma_i)$  interfaces are formed with dipoles in opposite directions.

# 2. Experimental

HfO<sub>2</sub>/SiO<sub>2</sub>/Si(100) and Y<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si(100) structures were fabricated by the following process. Figure 1 shows schematic illustrates of sample structures to be used to facilitate understanding of the sample fabrication process. Si(100) substrates were cleaned by a conventional RCA method and immersed in HF solution (10%) to remove native oxide layer at the substrate surface. HfO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> layers were directly deposited on the H-terminated Si(100) substrates by pulsed laser deposition (PLD) at room temperature (RT). The HfO<sub>2</sub>/Si(100) and Y<sub>2</sub>O<sub>3</sub>/Si(100) precursors were then annealed at various temperature from 500~ 800°C in oxygen flow of 1 atm by a quartz tube furnace. XPS measurements were carried out in order to characterize the sample structure and to optimize annealing conditions for growing the interfacial SiO<sub>2</sub>. C-V measurements were done for Au/HfO<sub>2</sub>/SiO<sub>2</sub>/Si(100)/Au and Au/Y<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si(100)/Au samples. The Au electrodes were fabricated by using a thermal evaporation technique.

#### 3. Result and discussion

Figures 2(a) and (b) show the XPS spectra of Si 2p core-level region for the HfO<sub>2</sub>(2.5nm)/Si and  $Y_2O_3(1.5nm)/Si$  samples, respectively. The horizontal axes are plotted as the relative binding energy to the energy position of Si<sup>0</sup> peak which comes from the silicon substrate. As seen by the  $Si^0$  peak in both the spectra, the HfO<sub>2</sub> and  $Y_2O_3$  thicknesses are thin enough to observe the interface structure by XPS. The broad peaks located at higher-binding-energy region of the Si<sup>0</sup> peaks are identified with overlayer Si atoms. The intensity ratio of overlayer peak and to Si<sup>0</sup> peak corresponds to thickness of overlayer. Overlayer thickness d is given by,

$$d = I_{OL} \ln \left( \frac{I_{OL}}{I_{Si}} \frac{I_0}{I_{\infty}} + 1 \right),$$

where  $I_{OL}$  and  $I_{Si}$  are the intensity of overlayer peak and  $Si^0$  peak, respectively.  $I_0/I_\infty$  is the experimental intensity ratio for a bear Si peak ( $I_0$ ) to an infinitely thick overlayer peak ( $I_\infty$ ). In Figs.2 (a) and (b), the  $I_{OL}/I_{Si}$  values for the HfO<sub>2</sub> and  $Y_2O_3$  layer dramatically increase above 700°C. Simultaneously, the overlayer peaks shift to higher binding energy position which can be attributed to the oxidization state of SiO<sub>2</sub>. From these things, we consider that SiO<sub>2</sub> layers were grown at the HfO<sub>2</sub>/Si and  $Y_2O_3/Si$  interfaces by the annealing.

Next, we measured the C-V characteristics of the Au/HfO<sub>2</sub>(25nm)/Si(100)/Au and Au/Y2O3(15nm)/Si(100)/Au structures. Figure 3 shows typical C-V curves for the samples annealed at 700°C for 1 hour. In each curve, a flat band voltage shift in opposite directions was observed. Additionally the samples annealed blow 600°C did not show such large  $V_{FB}$  shifts. Since the C-V curves show no hump feature and small clockwise hysteresis, we presume that the effects of interface states and mobile ions are low on the V<sub>FB</sub> shifts. Other possible origin of the V<sub>FB</sub> shifts are induction of fixed charges inside the layer or (and) the dipoles at the interfaces. If the fixed charge induction is dominant, the V<sub>FB</sub> shifts of HfO<sub>2</sub>/Si and Y<sub>2</sub>O<sub>3</sub>/Si should be the same direction, because the cause of the fixed charges is mainly oxygen vacancy which has positive charge, in oxide material. On the other hand, if the dipole induction is dominant, we can consistently explain the  $V_{FB}$  shifts in the C-V curves. The XPS result indicates annealing above 700 °C formed the HfO<sub>2</sub>/SiO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> interfaces in the samples. This temperature corresponds to generation temperature of the  $V_{FB}$  shift in the C-V curve. In addition, the dipole formations of "+/-" polarity at the HfO<sub>2</sub>/SiO<sub>2</sub> interface and "-/+" polarity at the  $Y_2O_3/SiO_2$  interface can explain the different directions of the  $V_{FB}$  shift in each samples. Hence, we conclude that the interface dipoles with the opposite polarity are generated at the interface.



Fig. 2 Si 2p core-level spectra for (a)  $HfO_2/Si(100)$  and (b)  $Y_2O_3/Si(100)$  samples annealed at several temperature.

## 4. Conclusions

In this study, we prepared HfO<sub>2</sub>/SiO<sub>2</sub>/Si(100) and Y<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si(100) structures from HfO<sub>2</sub>/Si(100) and  $Y_2O_3/Si(100)$  precursors by the annealing treatment and confirm the dipole formation at the HfO<sub>2</sub>/SiO<sub>2</sub> and  $Y_2O_3/SiO_2$  interfaces. The HfO<sub>2</sub>/Si(100) and  $Y_2O_3/Si(100)$ structures were fabricated by PLD. For annealing treatment above 700°C for 1 hour, considerable thickness of a SiO<sub>2</sub> layer was grown at the HfO<sub>2</sub>/Si(100) and Y<sub>2</sub>O<sub>3</sub>/Si(100) interfaces, and the V<sub>FB</sub> shifts caused by the dipole formation were observed in the samples. From the results, the optimal conditions for the annealing treatment was defined at 700°C for 1 hour. We conclude that high-k/SiO<sub>2</sub> structure with the interface dipoles can be achieved by the way to using precursive structures which we demonstrate in this study. We believe that this way offer a simple method to fabricate high-k/SiO<sub>2</sub> stacks. And the interface dipoles also offer new avenues to control internal electric field in heterojunction devices without external field.



Fig. 3 C-V curves of the HfO<sub>2</sub>/p-Si(100) and  $Y_2O_3/Si(100)$  samples annealed at 700°C for 1hour.

### References

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- [2] L. Q. Zhu et al. Jpn. J. Appl. Phys. 50 (2011) 031502