

Effect of Valence State of Pr on Interfacial Structure and Electrical Properties of Pr-oxide/PrON/Ge Gate Stack Structure

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1. Introduction

Control of interfacial properties of high-k/Ge gate stack structures are absolutely important to realize high-speed and low power consumption germanium (Ge) channel metal oxide semiconductor field effect transistors (MOSFETs). We have focused on praseodymium (Pr) oxide as a high-k material, which has very large dielectric constant ($\epsilon_r \sim 31$) and low leakage current density [1-3]. Pr-oxide has several crystalline structures such as cubic (cub-) PrO_2 , cub- Pr_2O_3 , and hexagonal (hex-) Pr_2O_3 according to valence states [4-6]. However, the relationship between the interfacial structure or electrical properties and the valence state of Pr-oxide has not been clarified yet. On the other hand, it is reported that an oxynitride interlayer are promising materials to control electrical properties of high-k/Ge suppressing of Ge diffusion into high-k films [7-9].

In this study, we evaluated the depth profile of the valence state of Pr-oxide, the interfacial structure and electrical properties of various Pr-oxide/Pr-oxynitride (PrON)/Ge gate stack structures.

2. Experimental

After chemical cleaning of Ge(001) substrate, a 1 nm-thick Ge-nitride layer was formed at 300°C using radical nitridation technique in an ultra-high vacuum chamber. Then, Pr-oxide layers were deposited at 300°C by atomic layer deposition (ALD) method using $\text{Pr}(\text{EtCp})_3$ and isopropyl alcohol (IPA). The thickness of Pr-oxide layers were ranging from 12 to 17 nm. Rapid thermal oxidation (RTO) was carried out for some samples. To fabricate MOS capacitors, Al gate electrodes were deposited using vacuum evaporation with a metal mask. Some samples were additionally annealed at 300°C for 30 min in H_2 ambient (PMA).

Capacitance-voltage (C-V) and current-voltage (I-V) characteristics were measured. The interface state density was evaluated using conductance method. Crystalline structures were observed using transmission electron microscopy (TEM) and the chemical bonding states were measured using x-ray photoemission spectroscopy (XPS) with Ar ion sputtering.

3. Results and discussion

Figures 1(a)-1(c) show the C-V characteristics of MOS capacitors before and after PMA measured at 190 K; (a)

Al/Pr-oxide/Ge, (b) Al/Pr-oxide/PrON/Ge, and (c) Al/Pr-oxide/PrON/Ge with RTO. The accumulation capacitance of the Al/Pr-oxide/PrON/Ge sample with RTO decreases after PMA, though those of the other samples don't change after PMA. In addition, the TEM observation of this sample revealed an increase in a film thickness after PMA. These results indicate formation of a Ge-oxide interlayer and diffusion of Ge atoms into the Pr-oxide film due to interfacial reaction. On the other hand, the hysteresis width increases only in this sample after PMA. This result suggests that formation of defects in the Pr-oxide film and diffusion of Ge atoms are caused with PMA.

The interface state density of the sample with a nitride interlayer decreases after PMA. The minimum values of the interface state density of these samples are similar ones as low as $4 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$. On the other hand, that of the sample without a nitride interlayer slightly increases after PMA. These results mean that a nitrogen interlayer promises to suppress the degradation of electrical properties of high-k/Ge gate stacks.

Figure 2 shows the $\text{Pr}3d_{5/2}$ photoelectron core spectra of Pr-oxide/PrON/Ge sample with RTO after Ar ion sputtering for several times. This figure shows the binding energy of $\text{Pr}3d_{5/2}$ increases with sputtering time. The binding energy of $\text{Pr}3d_{5/2}$ depends on the valence state of Pr-oxide, and those of cub- $\text{PrO}_2(\text{Pr}^{4+})$, cub- $\text{Pr}_2\text{O}_3(\text{Pr}^{3+})$ and hex- $\text{Pr}_2\text{O}_3(\text{Pr}^{3+})$ are about 933.0, 933.5 and 933.8 eV, respectively [2,10]. This result indicates the crystalline structure of Pr-oxide changes with the depth. Here, the crystalline structure of cub- Pr_2O_3 is similar to cub- PrO_2 , but cub- Pr_2O_3 includes 25% oxygen vacancy compared to cub- PrO_2 . The oxygen component of cub- PrO_2 is larger than cub- and hex- Pr_2O_3 .

Figure 3 shows the binding energy of the main peak in $\text{Pr}3d_{5/2}$ photoelectron core spectra of Pr-oxide/(PrON)/Ge samples before and after annealing as a function of the distance from the interface. Pr-oxide layers are mainly composed of cub- Pr_2O_3 and cub- PrO_2 in the Pr-oxide/PrON/Ge sample without RTO and the Pr-oxide/Ge sample. Furthermore, cub- Pr_2O_3 exists in the oxide layer and cub- PrO_2 exists at the interfacial region of these samples. On the other hand, cub- Pr_2O_3 exists near the interface and cub- PrO_2 exists in the layer region of the Pr-oxide/PrON/Ge sample with RTO. In addition, XPS result reveals an increase in the Ge component in the Pr-oxide layer of this sample with annealing. Here, we

deduce that there are two possible reasons of the Ge diffusion into Pr-oxide layer of this sample. The first one is the formation of cub-PrO₂ in the layer. As mentioned above, oxygen component of cub-PrO₂ is larger than the other structures. O atoms are probably provided from Pr-oxide film to Pr-oxide/Ge interface. The second one is the formation of cub-Pr₂O₃ at the interfacial region. Since cub-Pr₂O₃ has many oxygen vacancies in the crystalline structure, it is suggested that diffusion of Ge atoms from the substrate or diffusion of O atoms into the Pr-oxide/Ge interface easily occur. In addition, formation of a Ge-oxide interlayer and diffusion of Ge leads to the decrease in the accumulation capacitance and the increase in the hysteresis width with PMA of this sample.

4. Conclusions

We have investigated the electrical properties and chemical bonding states of Al/Pr-oxide/PrON/Ge gate stack structures. From the C-V characteristics, the interface state density of samples with a nitride interlayer decreases after PMA. On the other hand, the decrease in the accumulation capacitance and the increase in the hysteresis width are observed only in the Al/Pr-oxide/PrON/Ge sample with RTO. From the depth profile of the chemical bonding states, diffusion of Ge atoms into Pr-oxide layers occurs in this sample. In addition, we focused on the depth profiles of the

valence structures of Pr-oxide layers and clarified that cub-Pr₂O₃ exists at the interfacial region and cub-PrO₂ exists. These results indicate that control of the valence state of Pr both in the layer and interfacial is the key factor to suppress the interfacial reaction and the diffusion of Ge atoms into high-k layers. As a result, the degradation of electrical properties of Pr-oxide/Ge gate stack structures will be effectively suppressed.

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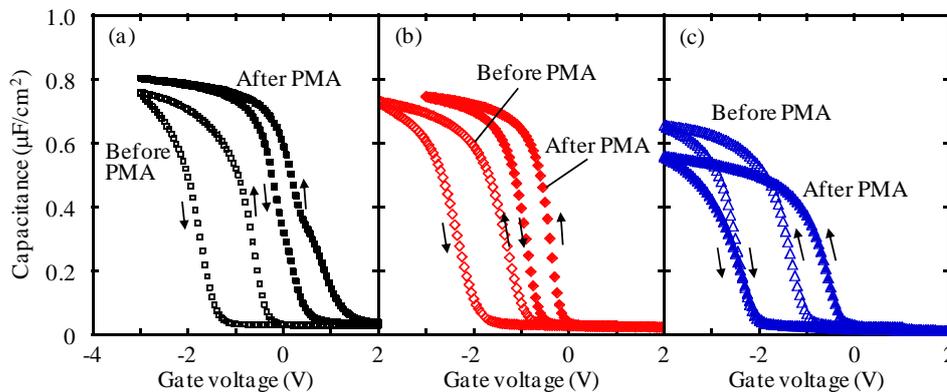


Fig. 1 C-V characteristics of (a)Al/Pr-oxide/Ge, (b)Al/Pr-oxide/PrON/Ge, and (c)Al/Pr-oxide/PrON/Ge with RTO MOS capacitors before and after PMA.

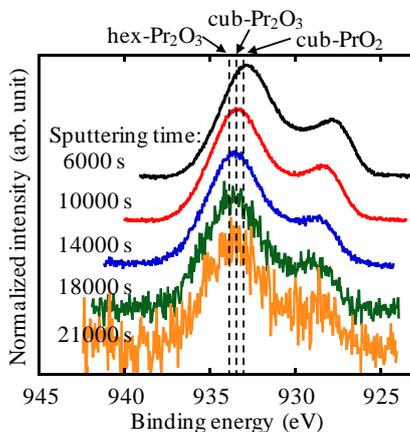


Fig. 2 Pr_{3d_{5/2}} photoelectron core spectra of Pr-oxide/PrON/Ge with RTO before annealing sample after Ar ion sputtering.

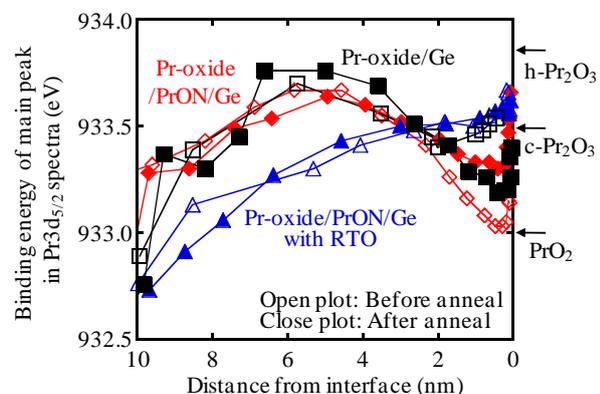


Fig. 3 Binding energy of the main peaks of Pr_{3d_{5/2}} spectra as a function of the distance from the insulator/Ge interface.