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# Pr-Oxide-Based Dielectric Films on Ge Substrates

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## 1. Introduction

Recently, Ge channel metal-oxide-semiconductor field-effect-transistors (MOSFETs) with high-k gate dielectrics attract much attention from a viewpoint of realizing high speed and low voltage operation devices. One of serious and essential issues to develop high-k film/Ge systems is to understand and control the reaction between high-k materials and Ge substrates. Pr oxide, which has a high dielectric constant and low current leakages, is one of promising candidates of high-k materials and has effectively been applied to high-k/Si systems[1][2]. In this work, we investigated structures and electrical properties of Pr oxide films formed on Ge substrates. We used pulsed laser deposition (PLD) to grow films under various growth conditions with different growth atmospheres, either Ar or vacuum. Effectiveness of substrate surface passivation on properties of Pr-oxide films was also examined using radical nitridation of Ge substrates.

## 2. Experiments

All films were prepared using PLD. Substrates used were n-type Ge(001). Before the process, Ge substrates were treated by chemical cleaning. For some samples, radical nitridation was also performed at a substrate temperature of 250°C using an inductively-coupled plasma (ICP) gun in an ultrahigh vacuum chamber at a $N_2$ partial pressure of 0.13 Pa. Pr oxide films were then deposited by ablating a sintered $Pr_6O_{11}$ target in ambient Ar (20 Pa) and vacuum ($0.5{\sim}1\times10^{-5}$ Pa), where the substrate temperature was 200°C. Cross-sectional film structures were observed by transmission electron microscopy (TEM). Angle resolved X-ray photoelectron spectroscopy (ARXPS) was measured by ESCAlab210 (VG Scienta) and, for samples with thicker high-k films, measured at BL47XU beam line in SPring-8. MOS capacitors with Pt top electrodes ($1.5\text{-}1.9\times10^{-4}$ $cm^2$) were fabricated to measure capacitance-voltage characteristics.

## 3. Results and Discussion

Figures 1(a) and (b) are cross-sectional TEM images of deposited films on Ge substrates in Ar and vacuum, respectively. It was found that Pr oxide films in both samples exhibit amorphous, forming a single layer structures. The corresponding Ge 3d core level spectra obtained by ESCAlab210 are respectively shown in Figs. 2(a) and 2(b), which are normalized by the peak intensity of Pr 3d. In the sample deposited in Ar, the peaks at a binding energy of 32 eV are attributed to $GeO_x$. The peak intensity increased with decreasing the take-off angle, because of $GeO_x$ distribution through the Pr oxide film reflecting Ge diffusion from the substrate. In the case of vacuum deposition, on the other hand, the peak attributed to $GeO_x$ is found to be shifted to 31.5 eV. The intensity is independent of take-off angle, indicating that $GeO_x$ is distributed uniformly through the Pr oxide film. The fact that the $GeO_x$ peak intensity is lower than that for the deposition in Ar means that $GeO_x$ diffusion was suppressed in the case of the vacuum deposition. Table I shows effective dielectric constant $\varepsilon_r$ of the films, obtained from the measured accumulation capacitance of MOS capacitors. As a result, higher $\varepsilon_r$ can be obtained by the vacuum deposition than the Ar deposition.

Figure 3 is a cross-sectional TEM image of the Pr oxide film formed on a surface-nitrided Ge substrate in vacuum. A germanium nitride (GeN) passivation layer (~2.5 nm in thickness) can be clearly observed between the deposited film and the Ge substrate. Ge 2p core level spectra measured at SPring-8, which is normalized by the peak intensity of Pr 3d, are shown in Fig. 4. It is observed that subpeaks are located at a binding energy between $GeO_2$ and $Ge_3N_4$, indicating the oxidation of GeN passivation layers in air when the sample was transferred to the deposition chamber after the nitridation, or in the chamber during PLD. The intensity ratio of Ge 2p at 1219.3 eV to N 1s (Ge/N), depending on the take-off angle, is shown in Fig. 5. In this figure, solid line is the calculated intensity ratio assuming GeON is only formed at the interface and Ge-O bonding is not included in $Pr_2O_3$. It should be noticed that the experimental results are corresponding to the calculation result well. This indicates that the observed subpeaks come from the oxidized GeN layer at the interface. Measured $\varepsilon_r$ of this film is also shown in Table I. The largest $\varepsilon_r$ can be obtained for Pr-oxide/GeN/Ge among the films prepared in this study, because the $GeO_x$ incorporation into the Pr oxide film is suppressed by the GeN passivation layer.

## 4. Conclusions

It is found that $GeO_x$ incorporation into the Pr oxide film is obvious by depositing in Ar, leading to reduction of dielectric constant, whereas it is suppressed in vacuum deposition. Surface nitridation of Ge substrates prior to Pr oxide deposition is very effective in suppressing $GeO_x$ incorporation, resulting in improved dielectric constants.

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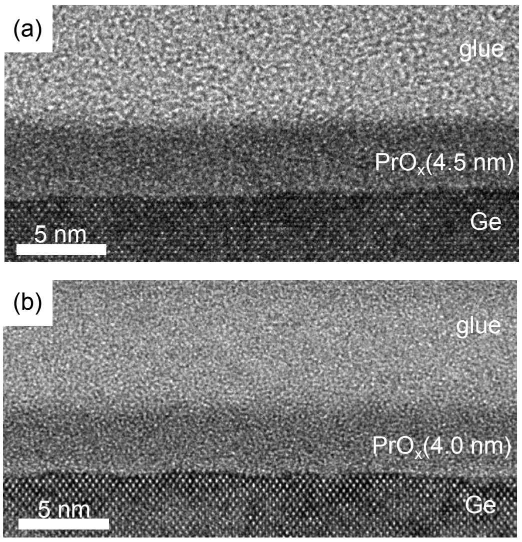


Fig. 1. Cross-sectional TEM images of Pr oxide films deposited on Ge(001) in (a) Ar and (b) vacuum.

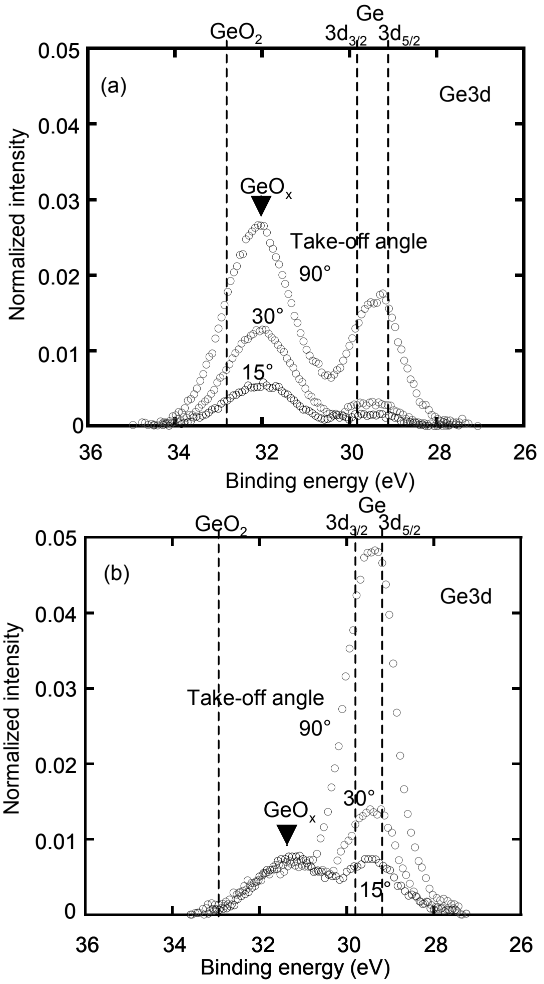


Fig. 2. Ge3d ARXPS spectra of of Pr oxide films deposited in (a) Ar and (b) vacuum. Intensity is normalized by Pr3d intensity.

## References

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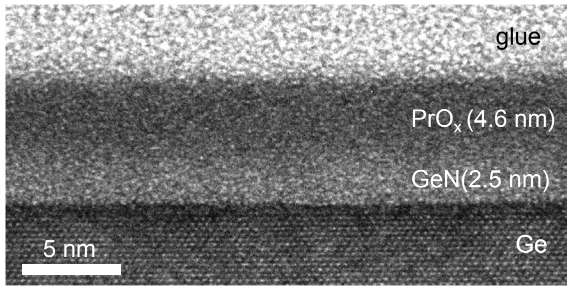


Fig. 3. Cross-sectional TEM image of Pr oxide film formed on a nitrided Ge substrate in vacuum.

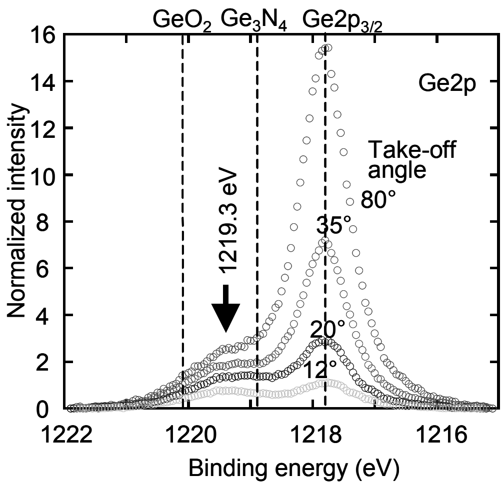


Fig. 4. Ge2p ARXPS spectra of of Pr oxide films deposited in vacuum. Intensity is normalized by Pr3d intensity.

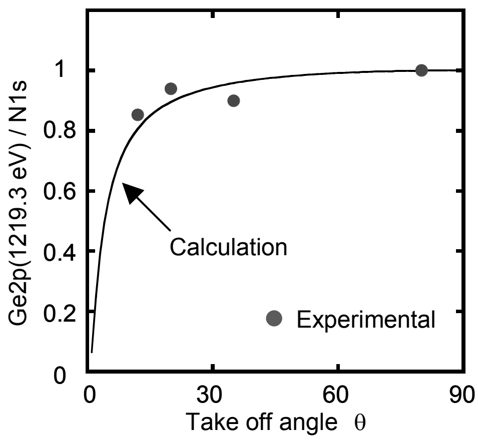


Fig. 5. Area intensity ration of Ge2p(1219.3 eV) to N1s.

Table. I. Effective dielectric constants.

| on Ge | | |
|---|---|---|
| in Ar | in vacuum | on GeON/Ge in vacuum |
| 6.1 | 8.2～13.6 | 15.4 |