# Film structures and electrical properties of Pr silicate formed by pulsed laser deposition

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## 1. Introduction

Further scaling of metal-oxide-semiconductor field effect transistors (MOSFETs) requires introduction of high-k gate dielectrics. Rare earth metal oxides are now intensively studied to be applied to future semiconductor devices and  $Pr_2O_3$  is one of the potential candidates [1]. Some of the serious problems to be overcome to exploit the attractive properties from this material are formation of an interfacial layer with a low dielectric constant [2] and crystallization at relatively low temperatures [1]. Pr silicate can be a possible solution to these difficulties. We have reported that Pr silicate layers formed by post deposition annealing (PDA) at high temperatures have a single layer structure without an interfacial layer, a greater thermal stability and a larger bandgap than those of as-grown films [3]. However, the dependence of the film structures and electrical properties on film growth and annealing conditions has not been fully understood. In this study, the effects exerted by controlling ambient gases during deposition and by PDA are investigated in terms of structures and electrical properties of the Pr silicate films to examine the interaction occurring during the fabrication processes.

### 2. Experiments

Samples were prepared by pulsed laser deposition (PLD). The substrates used were n-type Si(100), which were treated with dilute HF to remove the native oxide. Pr oxide films were deposited by ablating a sintered  $Pr_6O_{11}$  target in ambient  $O_2$  or Ar at 20 Pa, where the substrate temperature was 300°C. PDA was carried out in N<sub>2</sub> atmosphere at 1000°C for 15 s. Cross-sectional film structures were observed by transmission electron microscopy (TEM). Angle resolved X-ray photoelectron spectroscopy (ARXPS) was used to analyze the chemical bonding and composition. Spectra were acquired at take-off angles ( $\theta$ ) of 90°, 60°, 45° and 35°. MOS capacitors with Pt top electrodes were fabricated to measure capacitance-voltage (C-V) and leakage current-voltage (J-V) characteristics.

#### 3. Results and Discussion

Figure 1(a) shows the cross-sectional TEM image of an as-grown Pr oxide film deposited in  $O_2$ . An interlayer of 1.3 nm in thickness was observed between the Si substrate and the upper amorphous layer, and the total film thickness was 4.0 nm. Figure 1(b) shows the TEM image of this film after PDA at 1000°C, where the interlayer disappeared and the film thickness was reduced to 2.7 nm. This result demonstrates that PDA induces intermixing of the interlayer and the upper layer, and densification of the film.

Figures 2(a) and 2(b) show O 1s spectra by ARXPS of the as-grown and PDA-treated films, respectively. Considering that O 1s peaks of SiO<sub>2</sub> and Pr<sub>2</sub>O<sub>3</sub> appear approximately at 533 eV and 530 eV [4], the peaks centered around 532.5 eV and 531 eV can be assigned to Si-O bonding and Pr silicate, respectively. In Fig. 2(a), larger shoulders indicating Si-O bonding are found in the spectra taken at larger take-off angles, revealing that the interlayer in the as-grown film observed by TEM consisted mainly of SiO<sub>x</sub>. On the other hand, Fig. 2(b) exhibits a smaller contribution of Si-O bonding to the spectra of  $\theta = 90^\circ$ ,  $60^\circ$  and  $45^\circ$ , which assures that PDA caused intermixing of the film to form Pr silicate. In addition, it can be found that the Si-O shoulder is larger in the spectra of the smaller take-off angles, representing a larger amount of SiO<sub>x</sub> in regions closer to the film surface.

Figures 3(a) and 3(b) show the cross-sectional TEM images of as-grown and PDA-treated films deposited in Ar, respectively. As shown in Fig. 3(a), a 1.3-nm-thick interlayer was observed and the total film thickness was 4.5 nm. Figure 3(b) indicates that PDA resulted in disappearance of the interlayer, similarly to the case of the film deposited in  $O_2$ . It should be noted that PDA caused the film to shrink from 4.5 to 4.3 nm in thickness. This behavior implies that the density of the as-grown film deposited in Ar was higher than that in O<sub>2</sub>, and as a result, PDA brought a minor effect of densification. It is also important to mention that the PDA-treated film was partially crystallized (see the arrow), which is possibly related to the density of the as-grown film. ARXPS spectra derived from these films had similar features to those from the films deposited in  $O_2$ : the interlayer in the as-grown film consisted primarily of SiO<sub>x</sub> and a larger amount of  $SiO_x$  appeared closer to the surface of the PDA-treated film. However, in the O 1s spectrum of this film shown in Fig. 2(c), the Pr silicate components were located at lower binding energies than those of the film deposited in O<sub>2</sub>, suggesting that the PDA-treated film deposited in Ar was richer in Pr-O bonding.

Electrical properties of these films are plotted in Fig. 4. The inset of Fig. 4 indicates the C-V characteristics of the as-grown and PDA-treated films deposited in  $O_2$ . The capacitance equivalent oxide thickness (CET) calculated from these C-V curves decreased from 1.9 to 1.1 nm through PDA, and their effective dielectric constants ( $\varepsilon_r$ ) increased from 8.0 to 9.6. At the same time, the leakage current density (J) at the flat-band voltage (V<sub>FB</sub>) +1V increased drastically from 5×10<sup>-6</sup> to 2×10<sup>-2</sup> A/cm<sup>2</sup>. It can be deduced that the changes of the CET and the leakage current density of this film were mainly attributed to thinning of the film. In the film deposited in Ar, by contrast, PDA led to a decrease in the CET from 2.2 to 1.4 nm, where  $\varepsilon_r$  increased from 8.0 to 12. The larger  $\varepsilon_r$  may have arisen from the richness of Pr-O bonding in the PDA-treated film. In this case, J at V<sub>FB</sub>







Fig. 2. O 1s ARXPS spectra of (a) as-grown, (b) PDA-treated films deposited in O<sub>2</sub> acquired at take-off angles ( $\theta$ ) of 90°, 60°, 45° and 35° and (c) PDA-treated film deposited in Ar taken at  $\theta = 90^{\circ}$ .

+1V increased only by one order from  $4 \times 10^{-7}$  to  $5 \times 10^{-6}$  A/cm<sup>2</sup>. Therefore, it can be concluded that deposition in ambient Ar is useful in suppressing the increase in the leakage current caused by PDA with the CET being decreased.

#### 4. Conclusions

The Pr silicate layers were fabricated by performing PDA on the PLD-grown films. Different ambient gases during deposition made substantial differences of the effects of PDA on film structures and electrical properties. On the films deposited both in  $O_2$  and Ar, PDA functioned to resolve the interlayer between the Si substrate and Pr oxide and to reduce the CET effectively. The considerable difference resulting from the ambient gases during deposition was the greater densification of the film deposited in  $O_2$ . Consequently, in the film deposited in Ar, the effective dielectric constant increased more significantly, and the increase of the leakage current density by PDA was less severe.

## References

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Fig. 3. Cross-sectional TEM images of the (a) as-grown and (b) PDA-treated films deposited in Ar.



Fig. 4. Electrical properties of the films deposited in  $O_2$  and Ar. The inset shows C-V characteristics of the as-grown and PDA-treated films deposited in  $O_2$ .