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# Preparation and Characterization of High-k Lanthanoid Oxide Thin Films Deposited by Pulsed Laser Deposition

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## 1. Introduction

In recent yeas, high-k oxide film has gathered much attention as $SiO_2$-equivalent thickness (EOT) in the gate insulator should be reduced very much for the next-generation ULSI fabrication. Although $Ta_2O_5$ and $ZrO_2$ films have been suggested as a candidate, lanthanoid oxides such as $PrO_x$ and $La_2O_3$, attract attention recently, because very thin film of EOT 1-2 nm has been obtained [1-3]. In this paper, we have prepared $PrO_x$ and other lanthanoid oxides thin films by PLD (Pulsed Laser Deposition) method and characterize these electrical properties and its interfacial layer with Si.

## 2. Experimental

P-type Si (100) wafer was cleaned by RCA method, treated by dilute HF, and set in PLD chamber. ArF excimer laser beam (wavelength 193 nm) was applied to $Pr_6O_{11}$ ceramic target and ablated particles are deposited on a Si substrate. The detail of PLD condition is shown in Table I. Some of the film have been irradiated by oxygen radical. These films were characterized by XRD and XPS. MIS (Au/$PrO_x$/p-Si/Al) structure with active area $5.0 \times 10^{-4}$ $cm^2$ was fabricated for electrical characterization.

## 3. Results and Discussion

Surface of $PrO_x$ thin films were observed by AFM and average roughness (Ra) was calculated. Temperature dependence of roughness was shown in Fig. 1. Roughness increased at more than 500°C. Critical angles measured by GIXR (Grazing Incidence X-ray Reflectometry) were correlated to average electron density. This increases until 400°C and so the oxide thickness increases. XRD measurement was done for the thin films deposited at various temperatures (Fig. 2). It seems that the $PrO_x$ thin films were crystallized above 400°C. Crystalline orientation changes at 300-400°C from (100) to (111). The surface roughness is small in amorphous phase, and increases in crystal phase.

Figure 3 shows cross-sectional TEM picture of $PrO_x$ thin film on Si(100) substrate with physical thickness of 5.5 nm $PrO_x$ and 2.5 nm amorphous interfacial layer. This $PrO_x$ thin film was deposited at 400°C in $O_2$ gas of 0.2 Torr. C-V characteristics of MIS capacitor are shown in Fig. 4. EOT of as-deposited thin film is about 4.0 nm estimated from the accumulation capacitance. These thin films were annealed in $O_2$ ambient for 30 minutes. Annealing temperature is 400°C and 600°C. Figure 5 shows J-V characteristics as a parameter of anneal temperature. It shows that leakage current decreases as anneal temperature goes up, but EOT of these films also

Table I Deposition condition of $PrO_x$ thin films by pulsed laser deposition.

| | |
|---|---|
| Substrate temperature | RT-600°C |
| Gas | $O_2$, $N_2$ |
| Gas pressure | 0.2 Torr |
| Laser | ArF excimer laser |
| Repetition frequency | 1 Hz |
| Beam size | 0.03 $cm^2$ |
| Strength | 2-5 $J/cm^2$ |
| Target-substrate distance | 40 mm |

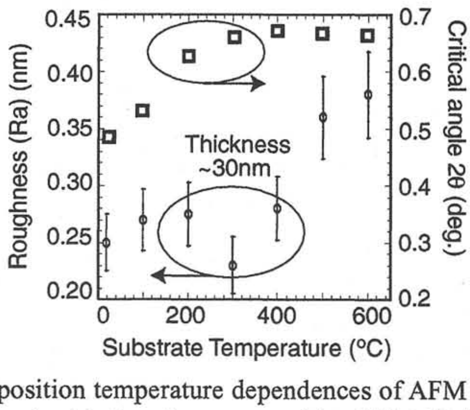


Fig. 1. Deposition temperature dependences of AFM roughness (left) and critical angles measured by GIXR (right).

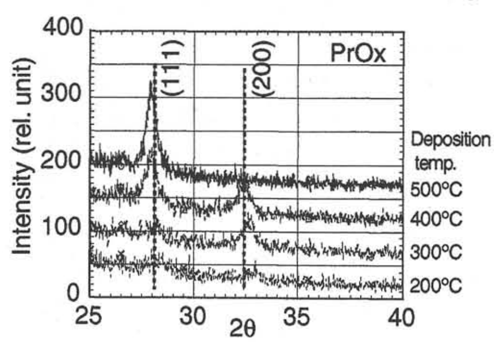


Fig. 2. Deposition temperature dependence of XRD patterns of $PrO_x$ thin film.

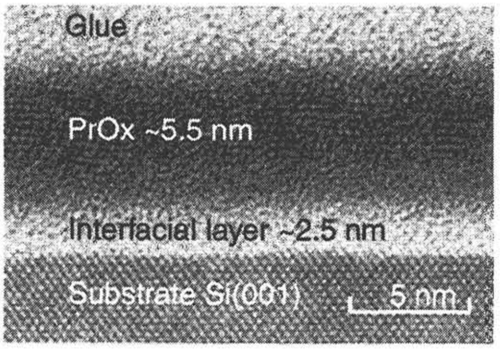


Fig. 3. Cross-sectional TEM picture of $PrO_x$ thin film on Si. The thin film was deposited at 400°C.

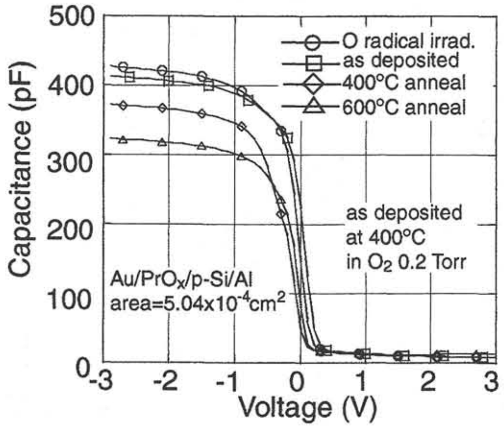


Fig. 4. C-V characteristics of $PrO_x$ thin film deposited at 400°C, and the treated films

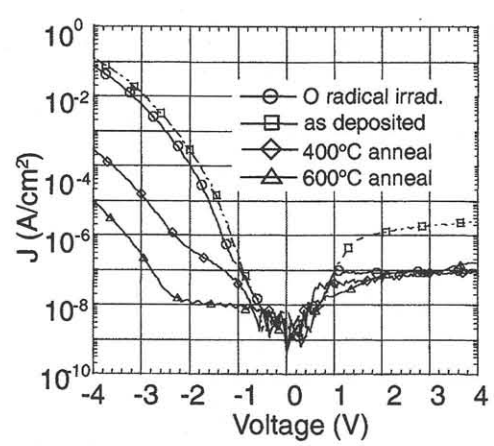


Fig. 5. J-V characteristics of $PrO_x$ thin films deposited at 400°C, and the treated film.

increases. From XPS Si 2p signal, it was found that Si-O bond peak in annealed thin film increases. These facts suggests growth of interfacial layer. The sample irradiated by the oxygen radical had little change in electrical property and XPS signal of Si 2p.

$PrO_x$ thin films were deposited at RT to prevent the growth of interfacial layer. Figure 6 shows C-V characteristics of MIS capacitor deposited in high vacuum ($1 \times 10^{-7}$ Torr). This EOT is almost equivalent to that deposited in $O_2$ ambient. However leakage current and hysteresis are larger. In the same figure,

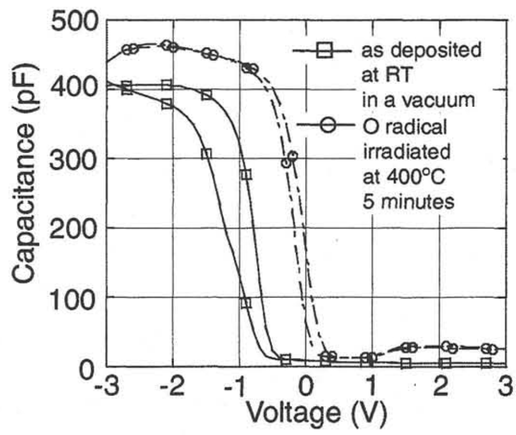


Fig. 6. C-V characteristics of $PrO_x$ thin films deposited at RT and the sample irradiated with oxygen radical.

that of oxygen-radical irradiated films (400°C, 5 minutes) are shown. This treatment was carried out using radical gun with RF discharge in $O_2$ low pressure ($2 \times 10^{-5}$ Torr) to prevent growth of interfacial layer. In comparison to as-deposited thin film, the irradiated one had thinner EOT and its hysteresis and leakage current decreased.

In addition, we have prepared and evaluated other lanthanoid oxides thin films ($Yb_2O_3$, $Er_2O_3$, $Tb_4O_7$ and $Sm_2O_3$) in the same way. These oxide thin films also begin to crystallize at 400°C, and has electrical properties roughly like $PrO_x$.

## 4. Conclusions

$PrO_x$ thin films have been prepared by pulsed laser deposition method on p-Si(100). Crystallization and roughness of increase above 400°C. From HRTEM observation of film deposited in $O_2$ ambient, it was shown that interfacial layer (2.5 nm) exists between $PrO_x$ and Si substrate. Leakage current decreases by annealing, but growth of interfacial layer was suggested by XPS signal. Thin films was prepared at RT in high vacuum, and treated with oxygen radical. After the annealing, leakage current and hysteresis are improved, and accumulation capacitance increases.

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