

Formation of Pr oxide films by atomic layer deposition using $\text{Pr}(\text{EtCp})_3$ precursor

Hiroki Kondo, Hirotaka Matsui, Kazuya Furuta,
Mitsuo Sakashita, and Shigeaki Zaima

¹Nagoya University, Dept. of Crystalline Materials Science, Graduate School of Eng.
Furo-cho, Chikusa-ku, Nagoya, 464-8603 Japan
Phone: +81-52-789-3817, E-mail: hkondo@alice.xtal.nagoya-u.ac.jp

1. Introduction

For further scaling of equivalent oxide thickness (EOT) of a gate dielectric film in a metal-oxide-semiconductor field-effect-transistor (MOSFET) less than 1 nm, a new oxide material having a higher dielectric constant more than Hf-oxides are required. Rare-earth metal oxides, such as Pr-oxide and La-oxide are promising because of their dielectric constant more than 30 [1]. However, atomic layer deposition (ALD) techniques for rare-earth metal oxides, which are essential to practical application of them, have not been established yet. In this study, we investigated formation technique of Pr oxide by ALD using tris[ethyl-cyclopentadienyl]Pr ($\text{Pr}(\text{EtCp})_3$) precursor. Since the melting point of $\text{Pr}(\text{EtCp})_3$ is 72°C and its vapor pressure is 23.5 mTorr at a temperature of 130°C, this precursor can be stably delivered by conventional pulsing or bubbling techniques. Pr oxide films were formed on Si(100) and Si(111) substrates by ALD using $\text{Pr}(\text{EtCp})_3$ and H_2O in this study, and evaluated their crystalline structures and electrical properties.

2. Experimental

N-type Si(100) and Si(111) wafers were used as substrates. Firstly, they were subjected with conventional chemical cleaning using RCA solutions. After dilute HF treatments, Pr oxide films were formed by ALD using SUNALETM R-150B (Picosun). $\text{Pr}(\text{EtCp})_3$ precursor was set to 130°C and, $\text{Pr}(\text{EtCp})_3$ and H_2O vapors were introduced to the deposition chamber using N_2 as a carrier gas. The standard condition of the ALD process is as follows; 1.0 and 0.1 s of pulsing times of $\text{Pr}(\text{EtCp})_3$ and H_2O , respectively, and 15 s of purge times of them. The ALD process was performed at 130°C, and some samples were subjected to a post-deposition-annealing at 400°C for 15 s.

3. Results and discussions

Figure 1 shows thicknesses of Pr oxides formed on Si(100) as functions of pulsing and purge times of $\text{Pr}(\text{EtCp})_3$ and H_2O , respectively. Numbers of supplying cycles of $\text{Pr}(\text{EtCp})_3$ and H_2O , hereinafter called ALD cycle, are 200 times. Film thicknesses were measured by ellipsometry. Thicknesses of Pr oxides hardly change for different pulsing and purge times, except for 0.1 s of $\text{Pr}(\text{EtCp})_3$ pulsing time. This means that Pr oxides were formed by ALD growth, in which thicknesses of Pr oxides were limited by amounts of precursors absorbed on the sample surfaces. Figure 2 is dependence of Pr oxide thickness on

number of ALD cycle. The ALD process was performed under the standard condition. It is found that a Pr oxide thickness increases in proportion to a ALD cycle, and a

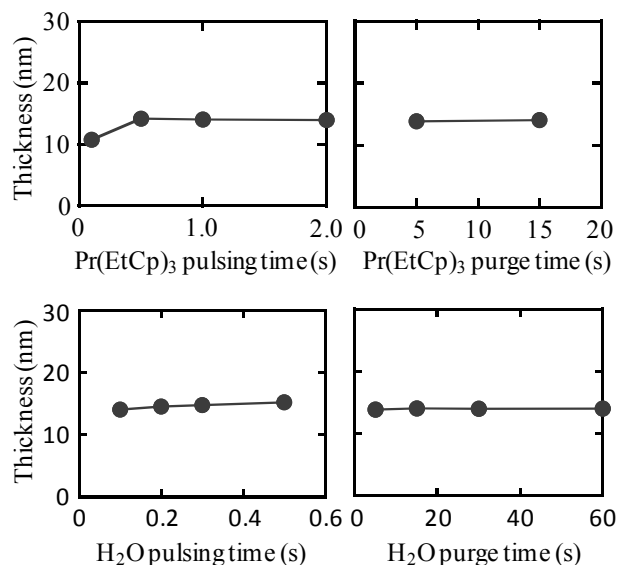


Fig. 1 Thicknesses of Pr oxides formed by ALD as functions of pulsing and purge times of $\text{Pr}(\text{EtCp})_3$ and H_2O . $\text{Pr}(\text{EtCp})_3$ and H_2O supplying cycles are 200.

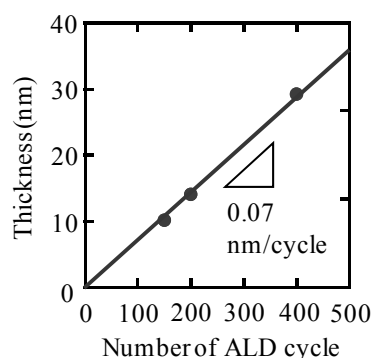


Fig. 2 Dependence of Pr oxide thickness on number of ALD cycles.

growth rate of a Pr-oxide is obtained from a slope of a fitting line to be 0.07 nm/cycle. Assuming crystalline planes of cubic- Pr_2O_3 (222) and (400), this value corresponds to 0.22 and 0.25 ML/cycle, respectively. On the other hand, thickness variations of Pr oxides are less than 2% on whole area of 3-inch wafer under the standard condition of the

ALD.

Figure 3 shows transmission electron microscopy (TEM) images and transmission electron diffraction (TED) patterns of Pr oxides grown on Si(100) ((a) and (b)) and Si(111) ((c) and (d)), respectively. ALD cycles were 150 times. In the case of the Pr oxide grown on Si(100), many diffraction spots appear in a concentric fashion (Fig. 3(b)). This indicates polycrystalline structures of cubic- Pr_2O_3 . Contrary, lattice fringes oriented in the same direction are seen in the TEM image of the Pr oxide on Si(111) (Fig. 3(c)). Additionally, the diffraction spots appear to be aligned along those of the Si substrate as shown in Fig. 3(d). These results indicate the epitaxial growth of cubic Pr_2O_3 on the Si(111) surface; $\text{Si}(111) \parallel \text{Pr}_2\text{O}_3(111)$ and $\text{Si}(110) \parallel \text{Pr}_2\text{O}_3(110)$.

Figure 4 is capacitance-voltage (C-V) characteristics of Al/ALD-Pr oxides/Si(100) and Al/ALD-Pr oxides/Si(111) capacitors, in which ALD cycles are 150 times. EOTs and effective dielectric constants including those of interlayers are 3.4 nm and 8.7 for the Pr-oxide on Si(100) and, 3.5 nm and 10.6 for that on Si(111), respectively. Furthermore, assuming that interlayers have a dielectric constant comparable with SiO_2 ($\epsilon \sim 3.9$), dielectric constants of the ALD-Pr oxides with cubic structures are estimated to be 12.3 and 16.8 for the cases of the ALD on Si(100) and Si(111), respectively. Unfortunately, these values are smaller than reported values for hexagonal Pr_2O_3 . In figure 5, crystalline phases of Pr oxides formed on Si substrates by molecular beam epitaxy (MBE) using electron-beam evaporation, chemical vapor deposition (CVD) using $\text{Pr}(\text{EtCp})_3$ and H_2O , and ALD (this study) are plotted as functions of the growth temperature and, partial pressures of O_2 and H_2O [2-4]. These results suggest that crystalline phases of the Pr-oxides strongly depend on the partial pressure of the oxidant. Therefore, it is expected that, in this ALD process, reduction of the H_2O partial pressure enable us to form the hexagonal- Pr_2O_3 with a dielectric constant larger than 30.

4. Conclusions

ALD growth of Pr oxides with thickness variation less than 2% was achieved using the $\text{Pr}(\text{EtCp})_3$ precursor in this study. Furthermore, it is expected that the crystalline structure of the ALD-Pr oxide can be controlled by optimization of the H_2O partial pressure. This result makes a rare-earth metal oxide as a gate dielectric film realistic.

References

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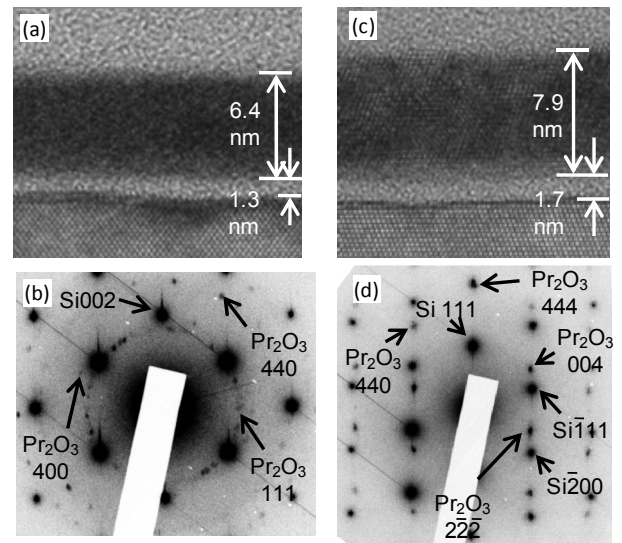


Fig. 3 TEM images and TED patterns of ALD-Pr oxides grown on Si(100) ((a), (b)) and Si(111) ((c), (d)) substrates. PDA at 400°C was also subjected.

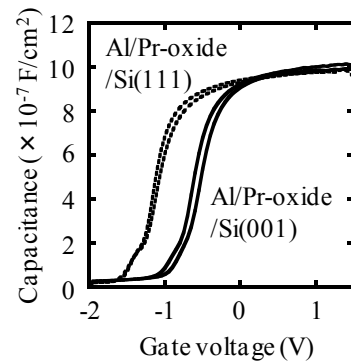


Fig. 4 C-V characteristics of Al/ALD-Pr oxides/Si(100) and Si(111) MOS capacitors.

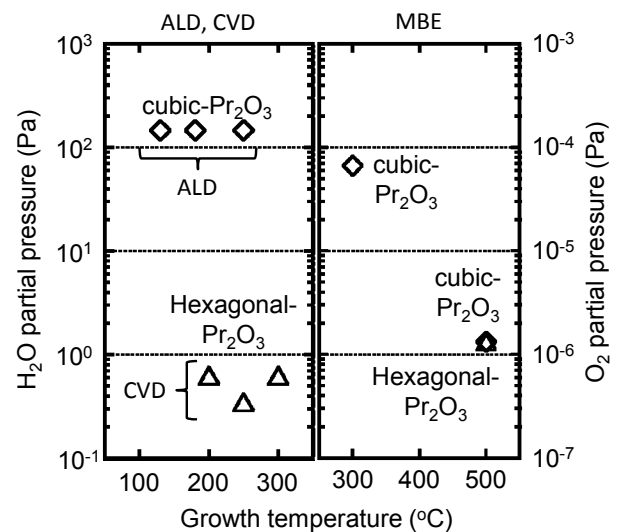


Fig. 5 Crystalline phases of Pr oxides formed on Si substrates by MBE, CVD, and ALD depending on the growth temperature and, partial pressure of O_2 and H_2O .