Formation of Pr oxide films by atomic layer deposition using Pr(EtCp)\textsubscript{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 (Pr(EtCp)\textsubscript{3}) precursor. Since the melting point of Pr(EtCp)\textsubscript{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 Pr(EtCp)\textsubscript{3} and H\textsubscript{2}O 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). Pr(EtCp)\textsubscript{3} precursor was set to 130°C and, Pr(EtCp)\textsubscript{3} and H\textsubscript{2}O vapors were introduced to the deposition chamber using N\textsubscript{2} as a carrier gas. The standard condition of the ALD process is as follows; 1.0 and 0.1 s of pulsing and purge times of Pr(EtCp)\textsubscript{3} and H\textsubscript{2}O, 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 Pr(EtCp)\textsubscript{3} and H\textsubscript{2}O. Pr(EtCp)\textsubscript{3} and H\textsubscript{2}O supplying cycles are 200. Thickness variations of Pr oxides are less than 2% on whole area of 3-inch wafer under the standard condition of the ALD process. 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 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\textsubscript{2}O\textsubscript{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 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\textsubscript{2}O\textsubscript{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$_2$O$_3$. 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$_2$O$_3$ on the Si(111) surface; Si(111) || Pr$_2$O$_3$(111) and Si $\langle 110 \rangle$ || Pr$_2$O$_3$$\langle 110 \rangle$.

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$_2$ (ε~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$_2$O$_3$. 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 Pr(EtCp)$_3$ and H$_2$O, and ALD (this study) are plotted as functions of the growth temperature and, partial pressures of O$_2$ and H$_2$O [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$_2$O partial pressure enable us to form the hexagonal-Pr$_2$O$_3$ with a dielectric constant larger than 30.

4. Conclusions

ALD growth of Pr oxides with thickness variation less than 2% was achieved using the Pr(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$_2$O partial pressure. This result makes a rare-earth metal oxide as a gate dielectric film realistic.

References