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Metalorganic Chemical Vapor Deposition of High-Dielectric-Constant Praseodymium Oxide Films Using a Liquid Cyclopentadienyl Precursor

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1. Introduction

Further scaling of ultra-large-scale-integrated circuits (ULSI) devices requires gate dielectrics with a subnanometer-order equivalent oxide thickness (EOT) and, therefore, higher-k oxide films such as lanthanum (La) oxides and praseodymium (Pr) oxides are expected as a gate dielectric of the next generation. A Pr-oxide film is one of promising candidates to have a dielectric constant more than 30 [1]. In addition, it has been reported that Pr oxide is substantially an excellent insulator, which is attributed to the fact that f-electrons in a narrow sub-band forming the conduction band bottom have very heavy electron masses and very low mobilities [2]. However, chemical vapor deposition (CVD) and atomic layer deposition (ALD) techniques for Pr oxide films with a high dielectric constant has not been established yet. Although composite oxides such as PrSiO and PrAlO were reported in several papers, fabrication of pure Pr oxides by CVD or ALD has been hardly reported, [3-4].

The selection of source gases in CVD and ALD growth is a crucial issue for their practical application to ULSI processes. Because most of rare-earth metal (Re) β -diketonate precursors ($\text{Re}(\text{DPM})_x$), which is conventionally used for the CVD and ALD of Re oxides, have melting points more than 200°C, they are usually supplied by sublimation [5-6]. However, the amount of supplies sublimated from solid precursors is unstable and it is difficult to control that. Furthermore, interfacial reactions with substrates are easy to occur since $\text{Re}(\text{DPM})_x$ includes oxygen in itself. Based on such perspectives, we focused on an oxygen-free cyclopentadienyl precursor with a low melting point. The melting point of tris[ethyl-cyclopentadienyl]Pr ($\text{Pr}(\text{EtCp})_3$) is 72°C and the Pr precursor can be stably delivered by a conventional bubbling system. In this study, CVD growth of Pr oxides using $\text{Pr}(\text{EtCp})_3$ was investigated and, the structural and electrical properties of CVD-Pr oxide films were evaluated. In the experiment, O_2 gases and H_2O vapors are compared as an oxidant.

2. Experimental

The substrates used were n-type Si(100), which were subjected with conventional chemical cleaning using RCA solutions. After dilute HF treatments to remove native oxides, Pr oxide films were deposited by CVD using

$\text{Pr}(\text{EtCp})_3$. The $\text{Pr}(\text{EtCp})_3$ gas was introduced into the deposition chamber by a bubbling system using a carrier gas of N_2 . O_2 and H_2O gasses were independently supplied to the chamber as an oxidant, where H_2O was also delivered by the bubbling method using N_2 . The $\text{Pr}(\text{EtCp})_3$ and H_2O were stored in the bottles set to 120°C and 40°C, and the carrier gas flows of N_2 were 10 and 5 sccm, respectively. The O_2 gas flow was 10 sccm. The CVD growth were carried out at 300°C for 60 min. Cross-sectional film structures were observed by transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were used to analyze the chemical bonding and composition. MOS capacitors with Pt top electrodes were fabricated to measure capacitance-voltage (C-V) and leakage current density-electric field (J-E) characteristics.

3. Results and discussions

Figure 1 shows O1s photoelectron spectra of Pr oxide films after the sputtering by Ar ions for 500 s. Peaks at the binding energy of 530.5 and 529.0 eV are attributed to Pr_2O_3 and PrO_2 , respectively. Peaks observed at around 531.5 eV are considered to be due to PrSiO in interfacial regions or H_2O in Pr oxide films. AES depth profiles of CVD-Pr oxide/Si samples are shown in Fig. 2. The C concentration of CVD-Pr oxide films formed using O_2 is about 20 % and, on the other hand, that is less than 2 % in the case of H_2O . Therefore, the C concentration in the CVD-Pr

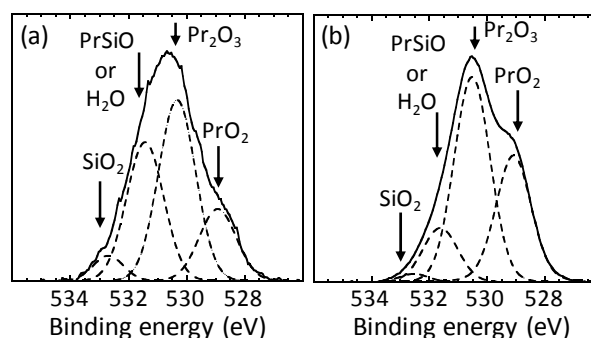


Figure 1. O1s photoelectron spectra of Pr oxide films deposited using (a) O_2 and (b) H_2O . The take-off angle of photoelectrons is 90°.

oxide can be drastically reduced using H₂O as an oxidant. It is suggested that hydrogen atoms effectively suppress polymerization of EtCp-ligands decomposed from the precursors and consequently enhance their detachment from the sample surfaces.

Figure 3 is TEM images and transmission electron diffraction (TED) patterns of CVD-Pr oxide/Si samples. It is found that a uniform Pr oxide film with columnar structures is successfully formed by the CVD using H₂O. In the case of O₂, the film surface is rough and the film is partially crystallized as observed in Fig. 1 (a) and (b). According to the TED pattern, a hexagonal Pr₂O₃ is oriented onto the Si(001) surface; Pr₂O₃(002)||Si(001). Considering the TEM and XPS results, it is considered that the polycrystalline Pr₂O₃ film is formed using H₂O, although a small amount of PrO₂ exists on the surface region. The interlayer thickness of the films formed using H₂O is 0.9 nm, the value of which is smaller than the case using O₂. This fact suggests that the CVD growth of Pr oxide films using Pr(EtCp)₃ and H₂O has low reactivity at the Pr oxide/Si interface.

Figure 4 shows (a) J-E and (b) C-V characteristics in Pt/CVD-Pr oxide/Si MOS capacitors. As shown in Fig. 4(a), the leakage current density drastically decreases in the case of CVD using H₂O. According to the analysis of this J-E characteristic, a Fowler-Nordheim (F-N) tunneling current is dominant at electric field regions from 1.0 to 2.0 MV/cm, and a conduction band offset between the Pr oxide and Si substrate is obtained to be 1.0 eV, which is consistent to the previously report for the Pr₂O₃ formed by electron beam evaporation [7]. On the other hand, a Poole-Frenkel (P-F) current is dominant above 3.0 MV/cm and temperature dependence of the P-F current indicates that trap states exist at 0.22 and 0.40 eV below the conduction band edge of Pr oxide. Hysteresis of C-V characteristics hardly appeared in the case of CVD using H₂O. Assuming the 0.9-nm-thick SiO₂ interlayer with a dielectric constant of 3.9, the dielectric constant of Pr oxide films deposited by CVD using Pr(EtCp)₃ and H₂O is obtained to be 26±3. This value is comparable to the reported value of Pr₂O₃. From these results, it is concluded that, as a result of reduction of C concentration in the CVD using H₂O, the Pr₂O₃ film with low current leakage and high dielectric constants can be obtained.

3. Conclusions

CVD growth of Pr₂O₃ films using Pr(EtCp)₃ and their electrical properties were reported for the first time. The C concentration of CVD-Pr oxide films can be reduced using H₂O as an oxidant species in the CVD process and, consequently, uniform Pr₂O₃ films with columnar structures are successfully formed. This CVD-Pr₂O₃ film has a dielectric constant of 26±3, and a leakage current density is $5.8 \pm 0.9 \times 10^{-6}$ A/cm² (@V_{FB}+1V). The Pr₂O₃ film with low C concentration, small current leakage, and high dielectric constant can be formed on Si substrates by the CVD using Pr(EtCp)₃ and H₂O.

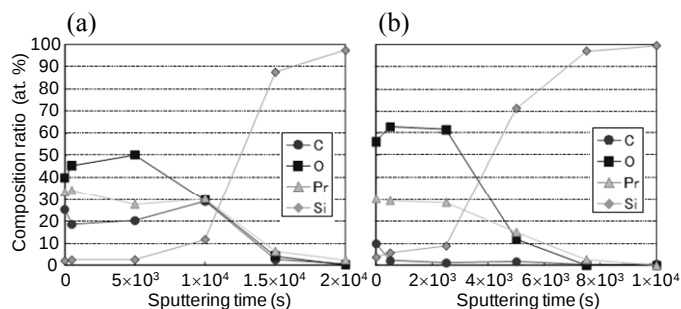


Figure 2 AES depth profiles of CVD-Pr oxide/Si samples. Pr oxide films were deposited using (a) O₂ and (b) H₂O.

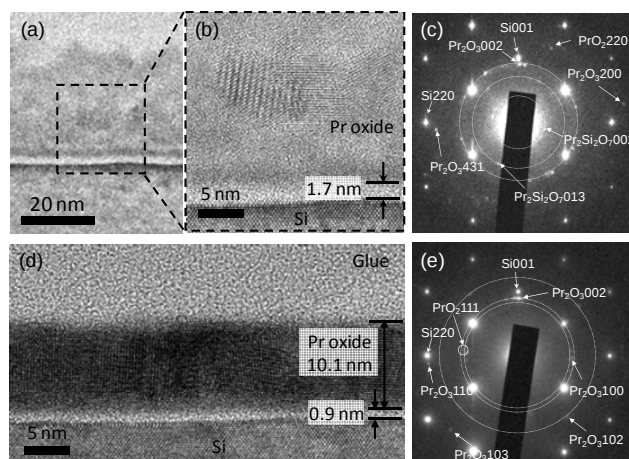


Figure 3 TEM images and TED patterns of CVD-Pr oxide/Si samples. Pr oxide films were deposited using O₂ ((a)-(c)) and H₂O ((d)-(e)).

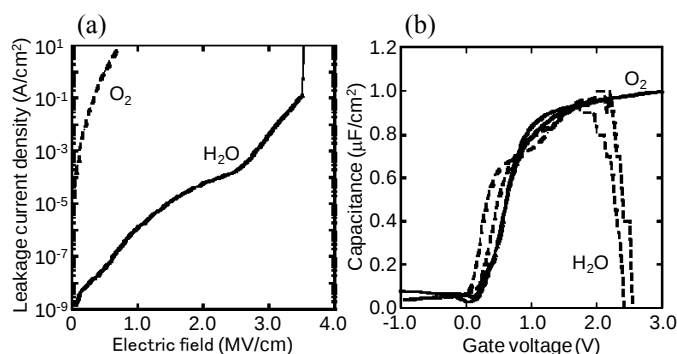


Figure 4 (a) leakage current density-electric field and (b) capacitance-voltage characteristics in Pt/CVD-Pr oxide/Si MOS capacitors. Pr oxide films were deposited using O₂ and H₂O.

Acknowledgements

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