Effect of Post-Deposition Annealing on the Electrical Properties of MOCVD-grown Praseodymium Silicate MIS Diode

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1 Introduction
Some lanthanide oxides/silicates are worth studying as high-k gate dielectrics toward the post Hf oxide/silicate era because of their higher dielectric constants [1-3]. We have been focusing on praseodymium-based materials since the excellent high dielectric constant of beyond 30 in Pr2O3 thin film was reported in Ref. [2]. We showed that Pr-silicate was formed at the interface during deposition and that the band offset at the Si-Pr silicate interface could be controlled by the deposition temperature [4]. However, on the analogy of Hf-silicate system, there is a trade-off between k and the band offset, so that further process optimization is needed. Another important issue that must be considered in high-k dielectrics is the reduction of defect in the film. This is closely related to the mechanism of electrical properties degradation. Post-deposition annealing (PDA) is one of the fundamental techniques to improve material properties in the film. Though, effects of PDA on the MOCVD-grown Pr-silicate have not been studied in detail.

In this paper, effects of PDA on the electrical properties of MOCVD-grown Pr-silicate are discussed.

2 Experimental
We used p-type Si(100) substrates on which a 1-nm-thick chemical oxide layer was prepared. Pr-silicate thin films were deposited by metal-organic chemical vapor deposition (MOCVD) using Pr(DPM)3 as a precursor. We did not use any oxidizing agent since oxygen atoms are contained in the precursor, i.e. the source was continuously supplied to the chamber. Figure 1 shows schematics of the chamber. All films used in this study were grown at 700 °C. We performed PDA of samples in the chamber, where N2/Ar (1:1) mixed gas was introduced and the pressure was kept at 1.5 Torr. We fabricated Au/Pr-silicate/Si metal-insulator-semiconductor (MIS) diode structure for capacitance-voltage(C-V) and the leakage current densities-voltage (Jg-V) characterizations.

3 Results and Discussion
Figure 2 shows C-V and Jg-V characteristics of as-deposited films with different thicknesses. The thicknesses depicted in figures are evaluated by ellipsometry measurement using refractive index of 1.8. Even though sample B is thicker than sample A, similar accumulation capacitances were obtained from both samples. This result means that the material with higher k-value was deposited on the top of sample B. According to previous reports [4,5], the material with higher k-value is Pr-oxide.

Figure 3 shows C-V and Jg-V characteristics of films with two different thicknesses (samples C and D) after PDA of as-deposited samples A and B, respectively. Note that Jg in both samples decreases clearly after PDA, which indicates that leakage current paths tend to be passivated by the PDA treatment. From the C-V curve, we identified that the accumulation capacitance of thicker sample D was clearly reduced after PDA. This reduction might be due to the formation of materials with rather lower dielectric constant after PDA, which corresponds to formation of Pr-silicate. In cases of Pr-oxide films on Si grown by electron-beam evaporation, similar results were obtained [6].
Note that the hysteresis in $C-V$ curve becomes larger after the PDA in sample D. The result indicates that during the formation of Pr-silicate by annealing, Si around the interface region diffuses into Pr-silicate due to the good thermal stability of Pr-silicate. As a consequence, interface traps became introduced after the PDA.

On the other hand, in the $C-V$ curve of sample C, a slightly larger accumulation capacitance than in sample A was obtained after the PDA. Figure 4 shows the surface roughnesses of the 6-nm-thick films before and after the PDA. Smoother surface was identified in the sample after the PDA. As a result, the PDA improved electrical properties of the film with the thickness of around 6 nm.

4 Conclusions

We have investigated the effects of the PDA on the electrical properties of MOCVD-grown Pr-silicate. Low-pressure PDA using N$_2$/Ar gas is effective to improve the electrical properties of the thin MOCVD-grown Pr-silicate film below ~6 nm.

References