Analysis of Local Leakage Current of Pr Oxide Thin Films with Conductive Atomic Force Microscopy

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1. Introduction

For the further scaling down of equivalent oxide thickness (EOT) of gate dielectric films in a metal-oxide-semiconductor field effect transistor (MOSFET) to less than 1 nm, an insulator material having a dielectric constant higher than Hf oxides is required. Rare-earth metal oxides, such as Pr and La oxides, are promising because of their dielectric constants higher than $30^{[1]}$. In addition, it has been reported that Pr oxides are superior insulator thin films^[1-4]. Previously, we demonstrated the formation of Pr oxide films by atomic layer deposition (ALD) method using Pr(EtCp)₃, and found that the crystalline structure of Pr oxide films was different depending on the surface orientation of Si substrates^[5].

Since high-k/Si gate stacks generally have complicated structures, not only measurement of macroscopic device performance but also microscopic analysis of local electrical properties is required to clarify the current leakage and degradation mechanisms of the films. Conductive atomic force microscopy (C-AFM) is a powerful tool to analyze the local electrical properties of gate dielectric films^[6, 7]. In this study, we investigated the local leakage current behavior of Pr oxide films formed on Si(001) and Si(111) substrates by using C-AFM and analyzed the leakage current caused by a defect.

2. Experiment

N-type Si(001) and Si(111) wafers were used as substrates. Firstly, conventional chemical cleaning of substrates was performed. Pr oxide films were deposited by ALD using $Pr(EtCp)_3$ and H_2O as precursors. The ALD process was performed at a temperature of 130°C.

For microscopic observation, current and topographic images with a scanning area of 1 μ m² were obtained by using C-AFM with a Pt-coated Si conductive tip. In order to estimate the current density from current image, a contact area of 2×10⁻¹² cm² for an effective C-AFM tip was employed^[8]. Current leakage properties were measured under the accumulation condition. Crystalline structures of Pr oxide films were also observed with cross-sectional transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) was carried out to analyze the chemical bonding states and elemental compositions of Pr oxide films.

3. Results and Discussion

Figures 1(a) and 1(b) show cross-sectional TEM images of Pr oxide films formed on Si(111) and Si(001) substrates, respectively. Both Pr oxide films exhibit amorphous structure. The thicknesses of not only the Pr oxide film but also the interface layer in both samples are almost same.

Figures 2(a) and 2(b) show current images of the Pr oxide film deposited on Si(111) and Si(001) substrates at a substrate voltage of -4 V as obtained with C-AFM. Several current leakage spots are observed whose current density is more than one order of magnitude larger than the average current. The spot densities of Si(111) and Si(001) samples were estimated to be 2×10^{11} and 3×10^{10} cm⁻², respectively. The average current densities of Si(111) and Si(001) samples were also estimated 6.25×10^{-2} and 1.24×10^{-3} A/cm², respectively. It is found that in the Pr oxide film formed on Si(111), many leakage spots are observed in current images compared to on Si(001).

Figures 3(a)-3(d) show O 1s photoelectron spectra of the Pr oxide film on Si(111) and Si(001). The take-off angle of Fig. 3(a) and 3(b) is 90° and that of Fig. 3(c) and 3(d) is 30°. In these Figure, O 1s spectra can be separated into three peaks. Binding energies of each peak are about 529.0, 529.7, and 531.5 eV, and those are related to PrO₂, cubic Pr_2O_3 (c- Pr_2O_3), and $Pr(OH)_3$ or Pr silicates, respectively^[5]. The relative intensity of the c-Pr₂O₃ peak in the spectra with a TOA of 90° is larger than that of 30°. This means that c-Pr₂O₃ is mainly formed near the Pr oxide/Si interface. The next, we compared the composition ratios of $c-Pr_2O_3$ to PrO_2 in the Pr oxide films on the Si(111) from the area intensity in the O 1s spectra. It is suggest that the composition ratios was larger than that on the Si(001). The crystalline structure of c-Pr₂O₃ corresponds to that of PrO₂ with vacancies of oxygen sites^[5]. Therefore, it is found that the oxygen vacancy of the Pr oxide film deposited on the Si(111) was more than on the Si(001). It is considered that the leakage spots observed in the current images is related to oxygen vacancy in the Pr oxide films.

Figures 4(a)-4(c) show current images of a same area of the Pr oxide film on Si(001) taken under consecutive scanning at a substrate voltage of -4 V. Most of leakage spots appearing in the first scanning are considered to be due to oxygen vacancies in the Pr oxide film. The density and current of leakage spots gradually decreases with increasing in scanning times. It is suggest that current flows through a defect in a Pr oxide film and an electric charge fills the ionized defect. Because defects in the Pr oxide film decrease after first scanning, current of leakage spots may have decreased.

4. Conclusions

We have investigated local leakage current in Pr oxide films films by using C-AFM. We found that the behavior of local leakage current of Pr oxide films depends on the crystalline orientation of substrates. In Pr oxide films formed on Si(111), many current leakage spots are observed in current images compared to Si(001). The XPS analysis revealed that cubic Pr_2O_3 is preferentially formed near the interface between a Pr oxide film and a Si(111) substrate compared to Si(001). This result indicates that the density of oxygen vacancy in Pr oxide films deposited on Si(111) is larger than that on Si(001). We considered that leakage spots observed in C-AFM current images is strongly related to oxygen vacancy in the Pr oxide films.



Fig. 1 Cross-sectional TEM images of Pr oxide film formed on (a) Si(111) and (b) Si(001) substrates.



Fig. 2 Current images obtained with C-AFM at a substrate voltage of -4 V (a)Pr oxide/Si(111) and (b) Pr oxide/Si(001).

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Fig. 3 O 1s photoelectron core spectra of the Pr oxide films deposited on the Si(111) [(a) and, (c)] and Si(001) [(b) and, (d)]. The take-off angle of (a) and (b) is 90° and that of (c) and (d) is 30°.



Fig. 4 Current images of an same area taken under continuous scanning at a substrate voltage of -4 V (a) the 1st, (b) 2nd, and (c) 3rd scans.