P-1-6

Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp195-196

Effects of Al Incorporation into Pr-oxides Formed by Atomic Layer Deposition

Kazuya Furuta, Wakana Takeuchi, Mitsuo Sakashita, Kimihiko Kato,
Hiroki Kondo, Osamu Nakatsuka, and Shigeaki Zaima

Graduate school of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
Phone: +81-52-789-3819 E-mail: wtakeuti@alice.xtal.nagoya-u.ac.jp

1. Introduction

The thickness of silicon dioxide (SiO_2) layers for gate insulator decreases to nanometer scale with shrinking of complementary metal-oxide-semiconductor (CMOS) transistors, and its leakage current seriously increases. The gate insulator materials (higher-k materials) having a higher dielectric constant than Hf-oxides are required. Rare-earth metal oxides such as Pr- and La-oxides are promising because of their bulk dielectric constants as high as 30. However, formation of an interfacial SiO_x (IF) layer often occurs between high-k and a Si substrate, when high-k materials are deposited on Si. It reduces the effective dielectric constant. Furthermore, a dielectric constant of high-k oxides film is decreased due to diffusion of SiO into high-k materials. It is important to prevent the formation of an IF layer.

It is well-known that the diffusion coefficient of oxygen in Al oxide thin films is lower than those of the majority of oxides. In order to prevent formation of the IF layer, we focus the incorporation of Al into Pr oxide layers. It is known that $PrAlO_x$ (PAO) has a high dielectric constant (ε_r=18~25) [1]. However, atomic layer deposition (ALD) techniques for PAO thin layers has not been established yet, while it is important for application to ultra large scale integrated circuit (ULSI) devices.

In this study, we examined the formation of PAO films by ALD using $Pr(EtCp)_3$, trimethylaluminum (TMA), and H_2O and investigated the crystalline and electrical properties of PAO gate insulators.

2. Experiments

PAO films were grown by ALD on hydrogen terminated n-type Si substrates. Pulse supplies of $Pr(EtCp)_3$ and TMA were repeated alternately in an ALD chamber. The compositions of Pr and Al were controlled by changing duration of their pulse supplies. The conditions of the ALD process were as follows: the pulsing times of $Pr(EtCp)_3$, TMA, and H_2O were 1.0, 0.1, and 0.1 s, respectively. The N_2 purging time for each gas was 15 s. The ALD process was performed at 130 and 250°C. After the ALD, top and back Al electrodes were formed with vacuum evaporation. Crystalline structures were observed with transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) was carried out to analyze the chemical bonding states and elemental composition. Capacitance-voltage (C-V) and deep level transient spectroscopy (DLTS) were performed for Al/ALD-Pr oxide/Si MOS structures.

3. Results and Discussion

Figures 1 (a) and 1(b) show the C-V characteristics of Al/PAO/Si MOS capacitors with various Al ratios, in which the PAO films were grown with ALD at (a) 130°C and (b) 250°C. In the case of 130°C, the width of hysteresis for the PAO sample with an Al composition of 60% is smaller than the pure Pr oxide sample. This result indicates that the trap density of oxide film decreases by the incorporation of Al. In the case of 250°C, the hump of C-V characteristics can be observed at approximately -1.0 V in the Pr-oxide sample without Al, which indicates the increase in the interface state density. On the other hand, in PAO samples, the hump are not observed in the C-V curves.

Figure 2 shows the interface state density measured by conductance method and DLTS. The energy distribution of the interface state density shows general U-shape as shown in DLTS results. The interface state densities of PAO samples were smaller than that of Pr-oxide sample, especially for the sample with an Al composition of 10%. This result indicates that the interface state density can be decreased by the incorporation of Al into Pr oxide.

Figure 3 shows Si2p photoemission spectra of the Pr oxide sample without Al for various sputtering time. PAO samples were sputtered with Ar ions at acceleration energy of 3 keV. In the case of sputtering time were 1000 s to 4000 s, the peak was observed at 102.5 eV. It indicates that $PrSiO_x$ and SiO_x are formed. On the other hand, in the case of sputtering time were after 5000 s, it was not observed.

$Pr3d_{5/2}$, O1s, Si2p, and Al2p spectra were obtained by XPS. Figures 4(a) and 4(b) show depth profiles of the area intensity of XPS spectra for each element of PAO samples with the ratio of Al to Pr of (a) 0% and (b) 10%, respectively. The existence of the SiO_x component is observed near the surface region in both samples. This result indicates that Pr silicate ($PrSiO_x$) is formed near the surface region. In other words, SiO diffuse to the surface region during the ALD process. On the other hand, in the case of 10%-Al, the area intensity of the SiO_x component is smaller than that of without Al. Thus, it is considered that the diffusion of SiO from a IF layer is suppressed by incorporation of Al into Pr oxide. As shown in Fig. 4(b), the Al component is observed near the surface region. This result indicates that Al atoms diffuse to the surface side during the ALD process.

It is considered that the interface state density is decrease to prevent formation of SiO_x by Al introduction. The Al incorporation into Pr-oxides effectively improves on the

electrical properties of Pr oxide MOS capacitors.

4. Conclusions

We examined PAO layers on Si substrates with ALD method and investigated the crystalline and electric properties of PAO/Si MOS structures. The oxide trap density and interface state density decrease by incorporation of Al into Pr oxide. Silicon diffusion into oxide films can be controlled by Al incorporation.

References

[1] P. Rouffignac and R. G. Gordon, Chem. Vap. Deposition **12** (2006) 152.

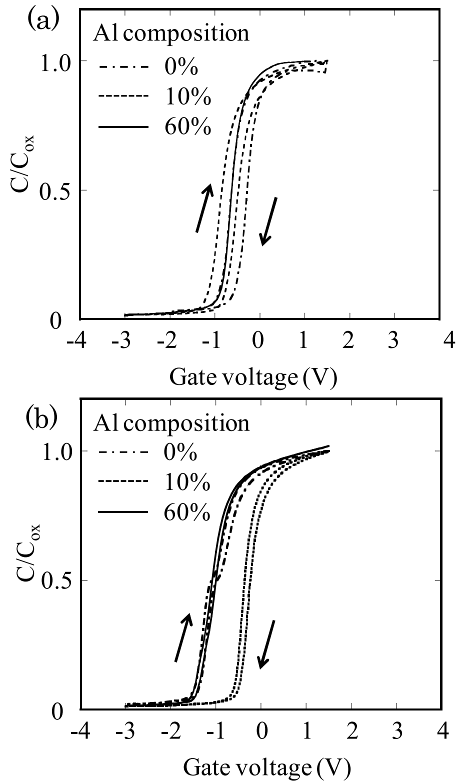

Fig. 1 Al ratio dependence of C-V characteristics of Al/PAO/Si capacitors, in which the oxide films were grown by ALD at (a) 130°C and (b) 250°C.

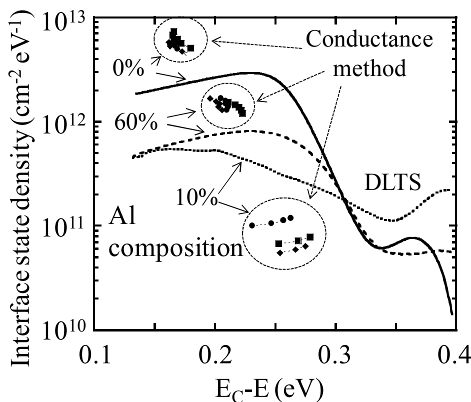

Fig. 2 Interface state density of PAO samples measured by conductance method and DLTS. PAO films were grown at 250°C.

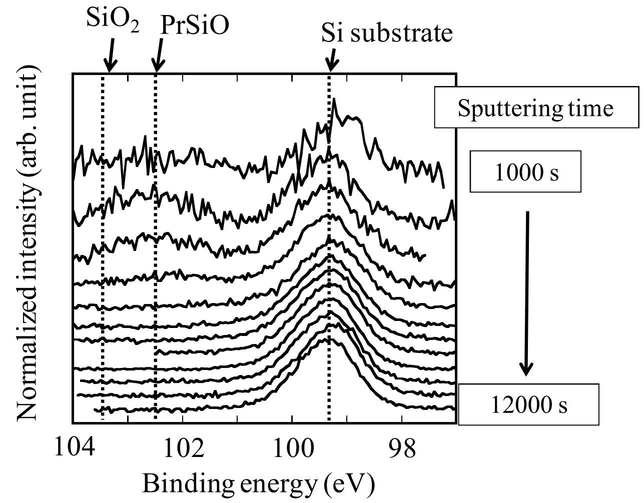

Fig. 3 . Si2p photoemission spectra of the Pr oxide sample without Al for various sputtering time. The intensity was normalized by $Si2p_{3/2}$ peak intensity.

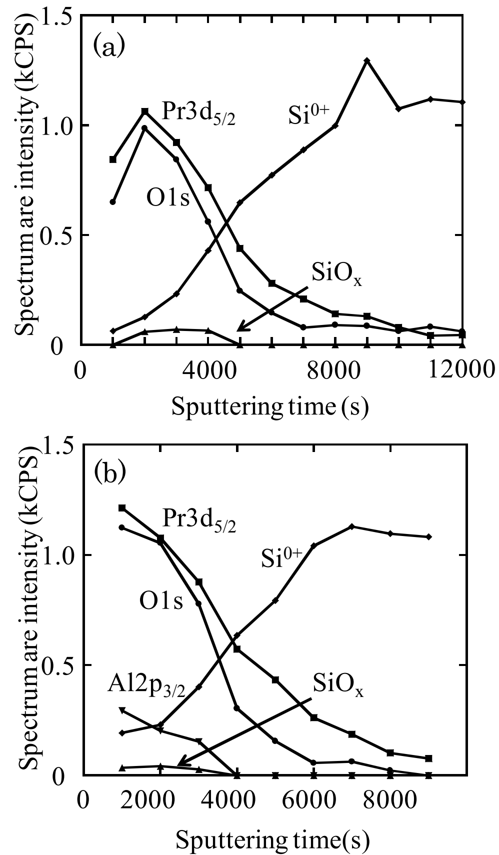

Fig. 4 $Pr3d_{5/2}$, O1s, Si2p and Al2p spectrum area intensity of the PAO films that were grown by ALD at 250°C and the ratio of Al to Pr was (a) 0% and (b) 10%, respectively.