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Influence of Post Annealing Treatment on Fixed Charge State and Chemical Bonding State of Sr-silicate Film

Shota Taniwaki, Mitsuhiro Umano, Haruhiko Yoshida,
Koji Arafune, Shin-ichi Satoh, and Yasushi Hotta

Univ. of Hyogo, 2167 Shosha, Himeji, Hyogo, 671-2201, Japan
Phone: +81-79-267-4963 E-mail: eu15m002@steng.u-hyogo.ac.jp

Abstract

We investigated chemical bonding (CB) states and fixed charge (FC) states of Sr_2SiO_4/Si(100) for various annealing conditions. Sr_2SiO_4 films were fabricated by pulsed laser deposition using a Sr_2SiO_4 polycrystalline target. The CB state and the FC state were measured by XPS and C-V measurements, respectively. The CB state was estimated from areal ratio of the Si-O-Sr bond peak to the total O 1s core-level peak. On the other hand, the effective FC density was estimated from the flat band voltage shift in the C-V curve. The Sr_2SiO_4/Si(100) sample annealed at 400°C for 6 hours maintained the maximum contents of the effective FCs density and Si-O-Sr bond.

1. Introduction

In field effect devices represented by metal-insulator-semiconductor field effect transistor (MIS-FET), the charging layer (or gate insulator) materials have been studied as alternatives for SiO_2. In a typical MIS-FETs, since the field effect arise from the charges accumulated on the gate capacitor, we should continuously energize the capacitor to keep the field effect. On the other hand, another type of field effect using statically charged insulator layers have been studied. In this case, although the magnitude of field effect is uncontrollable in real time, we obtaine static field effect (SFE) without connecting to an external voltage source. For example, this type of field effect has been used for the surface passivation of silicon solar cells[1]. The magnitude of the field effect is propotional to the amount of the fixed charge (FC) included in the insulator layer. Hence, to tune the field effect, the FC state of the insulator layer needs to controlle. Furthremore, a higher FC density is demanded in order to obtain a larger magnitude of field effect. As SFE layers, high-k dielectric layer such as Al_2O_3 and HfO_2 have been usually used[2].

Sr-silicate (Sr_xSiO_{x+2}) thin film is one of candidates to be the SFE layer. The thin film which is grown on Si substrate includes 10^{12} cm^{-2} order of FCs[3]. This FC value is enough to be the SFE layer. Sr-silicate has some advantages for the other materials. For one thing, the thin film is directrly grown on Si surface without any interface layer such as SiO_x, and we avoid loss of the field effect due to the interface layer.

Up to now, we have studied on the correlation between the FC state and the chemical bonding (CB) state of the Sr_xSiO_{x+2} thin films grown on Si substrates. As a result, we found that the FC density strongly depends on the amount of Sr silicate bonding (Sr-O-Si) species including in the Sr_2SiO_4 film[3]. This result indicates that, the SFE of the Sr_2SiO_4 film can be tuned by controlling the containing of Sr-O-Si bonding.

In this study, we investigated the influence of post annealing treatment (PAT) on the CB state of the Sr_2SiO_4 film. Furthermore, we measured the FC density of the different CB state samples. From the causal link between the CB state and the FC state, we found out better PAT condition of increasing FC density. The CB state and FC state were estimated by X-ray photoelectron spectroscopy (XPS) measurements and capacitance-voltage (C-V) measurements, respectively.

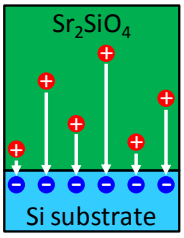

Fig. 1. Schematic illustration of the Sr_2SiO_4/Si(100) sample structure with the FC location and image of SFE on Si surface

2. Experiments

p-type c-Si(100) wafers (CZ, ρ=1-10Ωcm) were used as the substrates. All of the Si(100) wafers (size of 0.8×0.8 cm^2) were cleaned by the conventional RCA method and were immersed in 5 % HF solution for 1min to remove native oxide layers at the surface. Sr_2SiO_4/Si samples were fabricated by pulsed laser deposition (PLD) using a Sr_2SiO_4 polycrystalline target in a ultra-high vacuum of < 1×10^{-6} Pa at room temperature (RT). The thicknesses were from 5nm to 25nm. PAT were done in oxygen atmosphere using a tube furnace. The annealing temperature was 400°C and 600°C. The annealing time was 240 min and 360min. XPS measurements were performed using an Al Kα hν=1486.6 eV X-ray source in a vacuum below 10^{-7} Pa at RT. Au thin films were deposited as the top electrodes with 400μm square using a metal etching mask at RT. C-V characteristics were measured using an LCR meter.

3. Results and discussion

Figure 2 shows Si 2p, Sr 3d, and O 1s core-level spectra of the Sr_2SiO_4(10nm)/Si(100) sample annealed at 600°C for 4 hours. We determined the composition ratio of Sr to Si

(Si/Sr) for each thickness film from the RSF-normalized intensity of Si 2p and Sr 3d core-level spectra. Since the ratio of each sample was almost 0.5, the chemical composition of the obtained Sr-silicate layer films was Sr_2SiO_4.

Next, we investigated CB states of the Sr_2SiO_4 films for various thicknesses. Figure 3 shows an O 1s core-level spectra of the Sr_2SiO_4/Si(100) sample annealed at 400°C for 6 hours. To investigate the CB state in detail, we have fitted the core-level spectra for various thickness samples by Gaussian curves. The O 1s spectra obtained in this experiment were well fitted by three components, Si-O (529.8eV), Si-O-Sr (531.5eV), and Sr-O bond (533.1eV) [4,5]. At the various annealing conditions, the spectral area ratio of Si-O-Sr bond peak to the total component peak was plotted in Figure 4 as the function of thickness. The as depositon samples show the highest ratio in all the sample. However, the C-V property of the as deposition samples was too poor to define the flat band voltage shift. This indicates that the annealing treatment for the as deposition sample is indispensable to improve the C-V property. Compared with non annealed sample, the ratio of the annealed samples decreases. And, the more we adapt the long time and the high temperature annealing, the more the Si-O-Sr bond components decrease. Among the annealed samples, we obtain the highest Si-O-Sr bond containing sample at 400 °C for 6 hours in this time.

Next, we measured the C-V characteristics of the Sr_2SiO_4/Si(100) sample annealed at 400°C for 6 hours. Figure 4 shows the obtained C-V curves at the measurement frequency of 1MHz. The flat band voltage shift becomes large toward negative voltage side with increasing layer thickness. The effective FC density (Q_{eff}/q) was estimated from the flat band shift voltage of the C-V curves. The maximum value Q_{eff}/q value of $1.5\times10^{13}cm^{-2}$ was obtained for at the 15nm sample. This value is the highest recorde of the reported Q_{eff}/q value for Sr-silicate film.

4. Conclusions

We investigated the CB state and the FC state of the Sr_2SiO_4 films on Si substrates. Sr_2SiO_4 films were annealed using various conditions. The sample annealed at 400°C for 6 hours include the highest of Sr-O-Sr bond component and was the maximum effective FC density of 1.5×10^{13} cm^{-2}. This result indicates that the CB state of the Sr-silicate films is sensitive to annealing condition. Therefor, optimization of annealing condition is required to control FC state.

Acknowledgements

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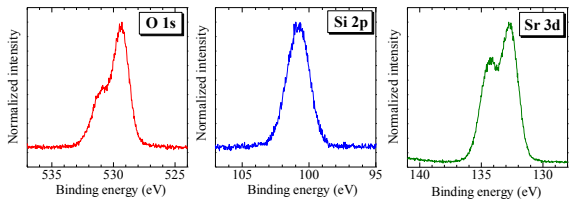

Fig.2 O 1s, Si 2p, and Sr 3d core-level spectra of Sr_2SiO_4(10nm)/Si(100) sample annealed at 600°C for 4 hours

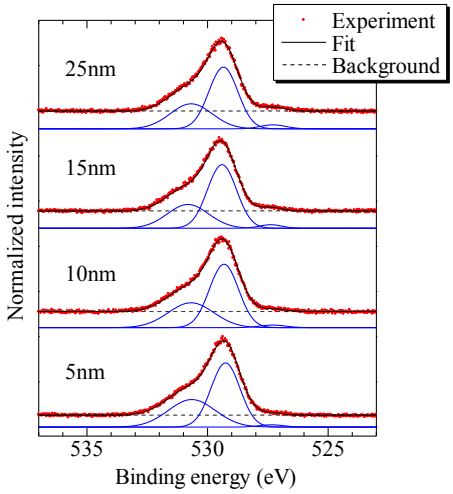

Fig. 3 O1s core-level spectra of the Sr_2SiO_4/Si(100) sample annealed at 400°C for 6 hours.

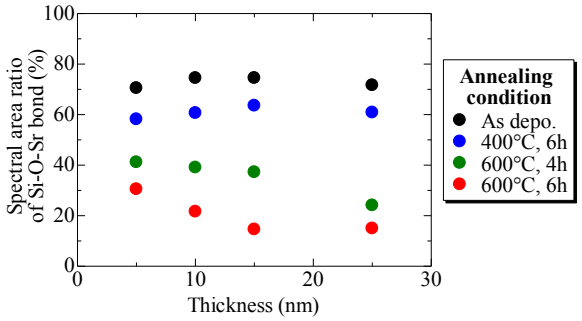

Fig. 4 Area ratio of Sr-O-Sr bond peak for various annealing conditions.

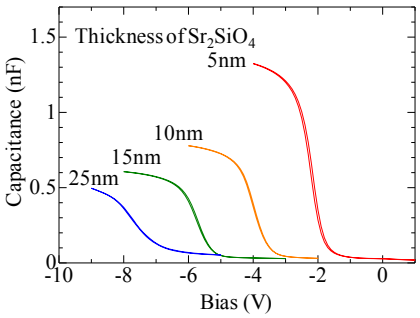

Fig. 5 The C-V curves of the Au/Sr_2SiO_4/p-Si(100)/Au samples annealed at 400°C for 6 hours. Thicknesses of the Sr_2SiO_4 layers were 5, 10, 15, and 25 nm, respectively.