

## Investigation of chemical-bonding state and fixed charge state of $\text{Sr}_2\text{SiO}_4$ film on Si(100) substrate

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### Abstract

We investigated chemical bonding (CB) states and fixed charge (FC) states for various thicknesses of  $\text{Sr}_2\text{SiO}_4$  films which were fabricated on Si substrates by the silicate reaction of SrO films with Si atoms diffusing from the substrates. The CB state and the FC state were measured by XPS and C-V measurements, respectively. With increasing thickness, the CB state of the  $\text{Sr}_2\text{SiO}_4$  film surface varies from Sr-silicate character to SrO character. Correspondingly, the effective FC density of the  $\text{Sr}_2\text{SiO}_4$  film decreases. This result indicates that the CB of Sr-silicate character plays important roles in the FC generation.

### 1. Introduction

Recently, crystalline silicon (c-Si) solar cells have been studied for use of a thin c-Si wafer below 100  $\mu\text{m}$  to reduce the cell production cost. To use the thin wafer, however, presents an emerging issue that the conversion efficiency of the solar cells was limited by surface recombination losses at the semiconductor interfaces. Surface passivation becomes more important to improve the efficiency of the thin c-Si solar cell. Field-effect passivation (FEP) is one of promising technique to solve the problem. [1] In the FEP, an internal electric field arising from presence of fixed charges (FCs) in the passivation layer repels the repulsive polarity of the minority carriers from the semiconductor interface. As a result, the carrier concentration decreases at the interface, and the surface recombination loss decrease. Recently, the FEP has been intensively studied for  $\text{AlO}_x$ . [2] Meanwhile, the generation mechanism of the FCs has been also investigated. [3]

We have studied Sr-silicate (or  $\text{Sr}_x\text{SiO}_{x+2}$ ) as a candidate of the passivation materials. Previously, we have reported that there exists a FC of  $\sim 10^{-12}\text{cm}^{-2}$  in  $\text{Sr}_2\text{SiO}_4/\text{Si}$  structure.[3] Since this material can be directly grown on Si substrate without interfacial  $\text{SiO}_x$  layer, the sample structure is simplified to single layer model as shown Fig.1. (In the  $\text{AlO}_x$  case,  $\text{SiO}_x$  layer is formed at the interface and the structure is represented by bilayer model.) Furthermore, the influence of the  $\text{SiO}_x$  layer which gives uncertainties for the generation mechanism of FC is negligible. Judging on the above advantages, we considered that Sr-silicate is suitable material to investigate the detail mechanism of FEP.

In this study, we investigated the chemical bonding (CB) state and the FC state of  $\text{Sr}_2\text{SiO}_4$  ( $x = 2$ ) films. The  $\text{Sr}_2\text{SiO}_4/\text{Si}$  samples were fabricated by silicate reaction of SrO films with Si atom (diffusing from Si substrate) via post-deposition annealing treatment (PAT). The CB state and FC state of the  $\text{Sr}_2\text{SiO}_4$  film were estimated by X-ray photoemission spectroscopy (XPS) measurements and capacitance-voltage (C-V) measurements, respectively. The obtained data were analyzed using three kinds of charge distribution models to figure out the relation between the CB state and the FC state.

### 2. Experiments

$\text{Sr}_2\text{SiO}_4$  layers were fabricated to grow SrO layers on Si substrates and to anneal the SrO/Si structure. We used p-type c-Si(100) wafers (CZ,  $\rho=1-10\Omega\text{cm}$ ) as the substrate. The Si(100) wafer (size of  $0.8\times 0.8\text{cm}^2$ ) was cleaned using the conventional RCA method and immersed in 10 % HF solution for 1min to remove native oxide layers at the surface. The SrO layers were grown on the Si substrate in a vacuum of  $< 1\times 10^{-6}\text{Pa}$  at room temperature (RT) by PLD using a SrO single crystal target. KrF excimer laser with a 248nm wavelength was used at repetition rate of 5Hz and energy density of  $\sim 1\text{J}/\text{cm}^2$ . The growth rate of SrO layers were kept at 0.031 nm/sec. The thickness is form 2.5nm to 75nm. PATs were done in oxygen atmosphere using a tube furnace. The annealing temperature was 600 $^\circ\text{C}$  and annealing time was 360 min. After PAT, the sample was cut into two pieces. One was used for XPS measurement, and another was used for C-V measurement. XPS measurements were performed using an Al K $\alpha$   $h\nu=1486.6\text{eV}$  x-ray source in a vacuum below  $10^{-7}\text{Pa}$  at RT. Au thin films were deposited as the top electrodes with 400 $\mu\text{m}$  square using a metal etching mask at RT. C-V characteristics were measured using an LCR meter.

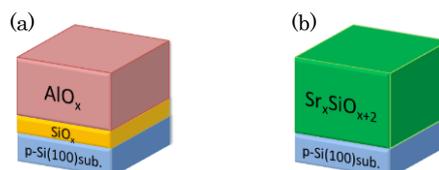


Fig. 1 Schematic illustrations of each interface structure for (a)  $\text{AlO}_x/\text{Si}$  interface and (b)  $\text{Sr}_x\text{SiO}_{x+2}/\text{Si}$  interface.

### 3. Result and discussion

Figure 2 shows Si 2p, Sr 3d, and O 1s core-level spectra for the SrO(10nm)/Si(100) sample annealed at 600°C for 6 hours. From the energy position of these core-level spectra, we identified the annealed SrO film to be strontium (Sr)-silicate. [4-6] The composition ratio of Sr to Si (Sr/Si) for the Sr-silicate films was determined by 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 films was Sr<sub>2</sub>SiO<sub>4</sub>.

Next, we investigated CB states of the Sr<sub>2</sub>SiO<sub>4</sub> films for various thicknesses. Figure 3 (a) shows an O 1s core-level spectrum of the Sr<sub>2</sub>SiO<sub>4</sub> film (14 nm). To probe the special distribution of the CB state, we have fitted the core-level spectra of 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). [6] The spectral area ratios of each component to the total components were plotted as a function of thickness in Fig. 3 (b). This result indicates that the films in thinner region within 15 nm and in thick region above 15 nm consist of the Si-O-Sr bond and Sr-O bond, respectively.

We measured the C-V characteristics of the Sr<sub>2</sub>SiO<sub>4</sub> films, which the thicknesses correspond to that of the XPS samples. The effective FC density ( $Q_{\text{eff}}$ ) was estimated from the magnitude of  $V_{\text{FB}}$  shift of C-V curve. Figure 4 shows the  $Q_{\text{eff}}$  values as a function of Sr<sub>2</sub>SiO<sub>4</sub> film thickness. The  $Q_{\text{eff}}$  increases with increasing the thickness up to 15nm, and it becomes constant above 15 nm.

We considered FC distribution of the Sr<sub>2</sub>SiO<sub>4</sub> films by three different models. Figure 5 shows the schematic illustrations of the FC distribution modes. In the first model (interface charge model), all the charges exist at the interface and the  $Q_{\text{eff}}$  should be constant. In the second model (uniform distribution model), the charges are uniformly distributed from interface to surface in the layer and the  $Q_{\text{eff}}$  should be proportional to thickness. In the third model (separated-layer model), there exists two different charge state layers: uniform charge layer and no charge layer. In this case, the  $Q_{\text{eff}}$  plot has an inflection point at the layers are switched. The experimental data is well fitted by the third model curve, indicating that indicates that the Sr<sub>2</sub>SiO<sub>4</sub> films include two layers with different FC state. Considering the XPS results, the FC is located in the thinner region of the film and it would be caused by the CB state of the Sr-silicate character.

### 4. Conclusion

We investigated the CB state and the FC state of the Sr<sub>2</sub>SiO<sub>4</sub> Films on Si substrates. Sr<sub>2</sub>SiO<sub>4</sub> films which were fabricated to anneal SrO film on Si substrate consisted of the different CB states in the thinner region and the thick region. The thickness dependence of FC state was explained by the separated-layer model corresponding to the thickness dependence of the CB states. It indicates that the

FCs would arise from the CB state of the Sr-silicate character.

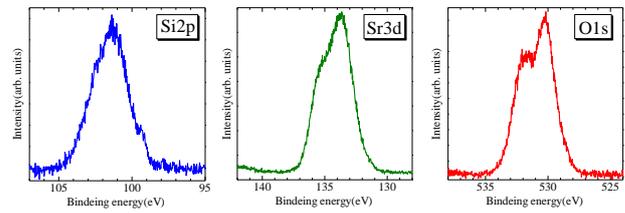


Fig. 2 Si2p, Sr3d, and O1s core-level spectra for the SrO/Si(100) sample annealed at 600°C for 6 hours.

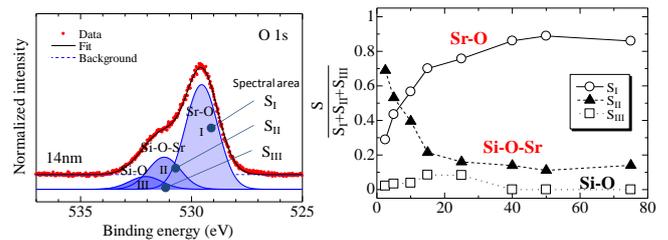


Fig. 3 (a) O1s core-level spectra of the Sr<sub>2</sub>SiO<sub>4</sub>(14nm)/Si(100) sample fitted by three components corresponding to Sr-O, Si-O-Sr, and Si-O bond. (b) Thickness dependence of spectral area ratio of each component to the total components.

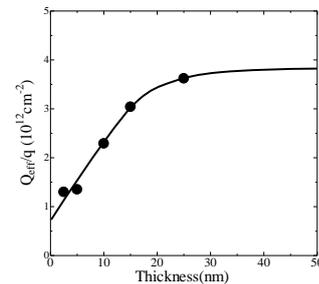


Fig. 4 Thickness dependence of the  $Q_{\text{eff}}$  of the Sr<sub>2</sub>SiO<sub>4</sub>/Si(100) structure.

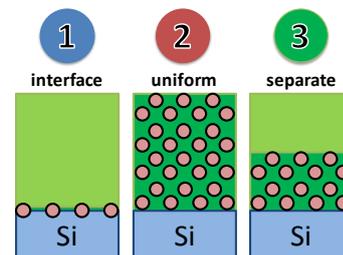


Fig. 5 Considerable charge distribution models in the Sr<sub>2</sub>SiO<sub>4</sub>/Si(100) structure.

### Reference

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