

# Characterization of SrRuO<sub>3</sub> Conducting Thin Films Grown on p-Si (100) Substrates by Metalorganic Chemical Vapor Deposition

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The SrRuO<sub>3</sub> films for application of the bottom electrode were deposited on p-Si (001) substrates by metalorganic chemical vapor deposition (MOCVD). The films are characterized by various deposition parameters. The optimum deposition condition for SRO films is the deposition temperature of 500 °C, Sr/Ru input mol ratio of 1.0, and a flow rate of precursors of 15 ml/h. The films deposited by an optimum condition exhibited a single phase of SrRuO<sub>3</sub>, an rms roughness of 8 nm, and a resistivity of approximately 900 μΩ·cm. The high resistivity of the films for application of a bottom electrode should be improved through a characterization of an interface.

**Keywords :** SrRuO<sub>3</sub> thin films, Resistivity, MOCVD

## 1. INTRODUCTION

In recent years, SrRuO<sub>3</sub> (SRO) materials were known as promising candidate conductive oxide for application in many different fields such as a bottom electrode for ferroelectric random access memory (FeRAM), a buffer layer in the fabrication of high temperature superconductor, and etc, because of its thermal and chemical stability and relatively high conductivity[1-3]. In addition, SrRuO<sub>3</sub>, which crystallizes in the GdFeO<sub>3</sub>-type orthorhombic distorted perovskite structure with lattice constants of  $a=0.5573$  nm,  $b=0.5538$  nm, and  $c=0.7856$  nm, has a good lattice mismatch with the ferroelectric oxide materials. The structure of SRO is also described as a pseudo-cubic perovskite with a lattice constant of approximately 0.3928 nm[4-6]. Therefore, SRO films can be utilized as a seed layer for heteroepitaxial growth of the other perovskite oxide. Regarding fabrication of SRO film, SRO material easily deposits on the same perovskite structure and small lattice mismatch substrates such as SrTiO<sub>3</sub> or LaAlO<sub>3</sub>. However, it is difficult to directly deposit a SRO film on the substrates with different structure and large lattice mismatch such as Si-substrates[7]. To our best knowledge, there have been few studies concerning the direct deposition of SRO films on Si-substrates.

In this study, SRO films were deposited directly on Si substrates by metal organic chemical vapor deposition (MOCVD) method. The influences of experimental

parameters such as the flow rate of precursors, mol ratio of (Sr:Ru), and the deposition temperature on the uniformity, crystalline quality, and electric properties of the deposited films were investigated in detail.

## 2. EXPERIMENTAL PROCEDURE

For deposition of the SRO film, p-type Si (100) substrates were etched with buffered HF solution (HF: H<sub>2</sub>O=1:100) for 1 min at room temperature to remove the natural oxide layer. A schematic diagram of the MOCVD system was shown in Fig. 1.

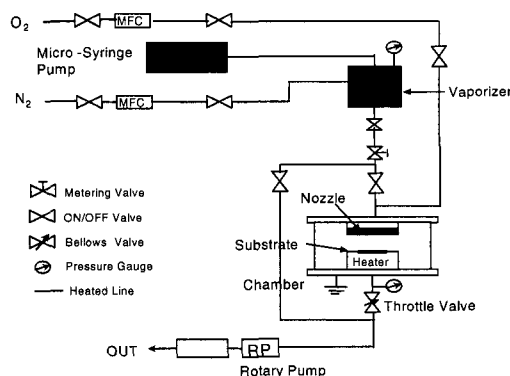


Fig. 1. Schematic diagram of MOCVD system for SrRuO<sub>3</sub> conductive thin films.

Table 1. Deposition conditions of SrRuO<sub>3</sub> film by MOCVD.

Parameters	SrRuO <sub>3</sub>
Deposition temperature	500-600 °C
Vaporizer temperature	240 °C
Ru precursor	Ru(TMHD) <sub>3</sub>
Sr precursor	Sr(thd) <sub>2</sub> (tetraglyme)
Substrate	P-type Si(001)
O <sub>2</sub> flow rate	100 sccm
N <sub>2</sub> flow rate	100 sccm
Mole ratio (Sr: Ru)	2:1, 1:1, 1:2
Solvent	Tetrahydrofuran
Flow rate of input source	5, 10, 15 ml/h

Ru(TMHD)<sub>3</sub> and Sr(thd)<sub>2</sub>(tetraglyme) precursors, dissolved in tetrahydrofuran, were selected as the source of Sr and Ru with concentration of 0.05 mol/L and 0.05 mol/L, respectively.

The sources were mixed each other in a syringe with a desired mol ratio before being pumped into a flash vaporizer. The vaporizer temperature was maintained at 240 °C. When source chemical was pumped into the vaporizer, it was immediately vaporized and then carried into the CVD reactive chamber with N<sub>2</sub> carrier gas having flow rate of 100 sccm (standard cc/min). Oxidant of O<sub>2</sub> was supplied to showerhead with the fixed flow rate of 100 sccm through a separate gas line to minimize any premature reaction on the line during delivery. All lines and showerhead were maintained at 250 °C during deposition process to prevent the source vapor from clogging. The detailed deposition conditions were summarized in the table 1. The crystallinity of the SRO films was characterized x-ray diffraction (XRD) using CuK<sub>α</sub> radiation. The resistivity of the SRO film was measured at room temperature using the standard four-probe technique (CMT-SR 1000). The microstructure and the thickness of the SRO film were determined by scanning electron microscopy (SEM, Topcon DS-130C). The root mean square surface roughness (RMS) of the films was estimated by atomic force microscopy (AFM, AUTOPROBE CP Research) topo images over an area of 3 x 3 μm<sup>2</sup>.

### 3. RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of 60 nm thick-SRO films deposited at 500 °C with a mol ratio of Sr:Ru = 1:1 at various flow rates of the precursors. The diffraction peak showing a SRO (001) plane was only observed in the SRO film deposited with the various flow rates. As shown in Fig. 2(c), films deposited with a flow rate of 15 ml/h exhibited strong diffraction intensity, as compared with a lower flow rate of precursors. In this study, the flow

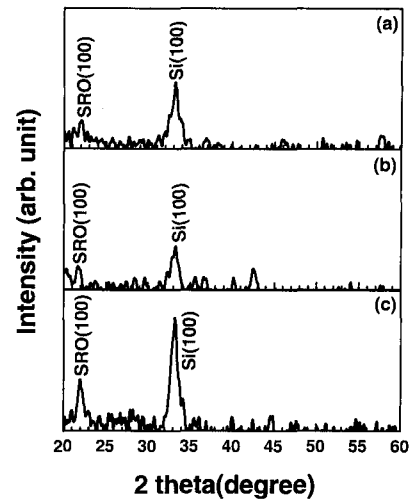


Fig. 2. XRD pattern of SRO thin film deposited with various liquid source flow rates of (a) 5 ml/h, (b) 10 ml/h, and (c) 15 ml/h.

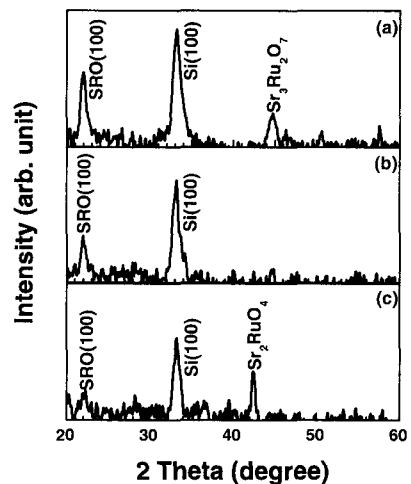


Fig. 3. XRD patterns of SRO thin films deposited with various Sr/Ru input mol ratios of (a) 2:1, (b) 1:1, and (c) 1:2.

rate of precursors was maintained constantly at 15 ml/h.

Figure 3 shows XRD patterns of the SRO films deposited at 500 °C with the different mol ratios at source flow rate of 15 ml/h. As shown in Fig. 3(b), films deposited with a mol ratio of Sr:Ru = 1:1 exhibited only a SrRuO<sub>3</sub> single phase without any second phase. On the other hand, films deposited with Sr-excess (Fig. 3(a)) and Ru-excess (Fig. 3(c)) composition exhibited a second phase of Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> and Sr<sub>2</sub>RuO<sub>4</sub>, respectively, in addition to the SrRuO<sub>3</sub> phase. The second phase in the SrRuO<sub>3</sub> films can influence on the electrical properties of SrRuO<sub>3</sub> conducting electrodes. The existence of the second phase was found in the results reported in a previous work[8].

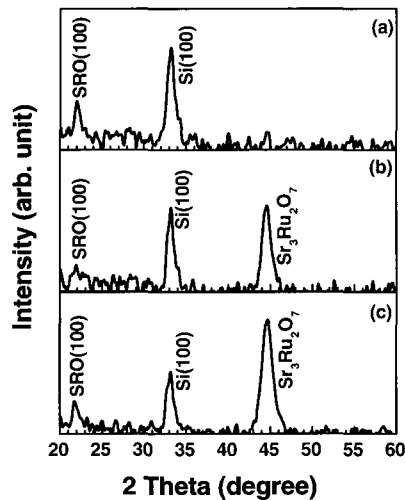


Fig. 4. XRD patterns of the SRO films deposited at (a) 500, (b) 550, and (c) 600 °C (Sr/Ru = 1.0, flow rate of precursor: 15 ml/h).

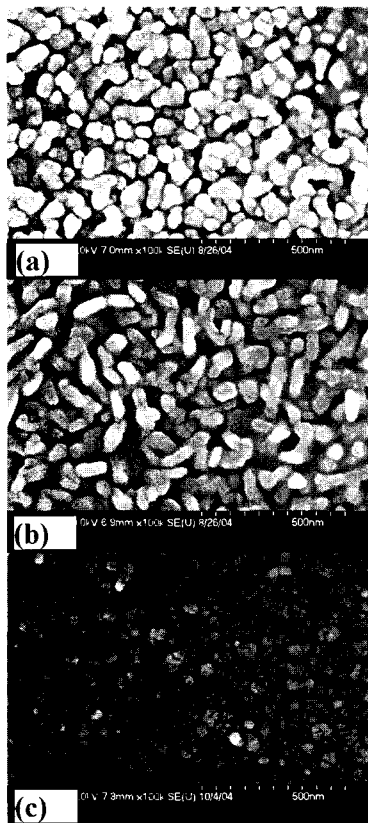


Fig. 5. SEM surface images of the SRO films deposited in (a) 1, (b) 0.76, and (c) 0.65 Torr (deposition temperature: 500 °C, Sr/Ru input mol ratio: 1.0).

Figure 4 shows XRD patterns of the SRO films grown at various deposition temperatures. As shown in Figs. 4 (b) and (c), the increase of deposition temperature above

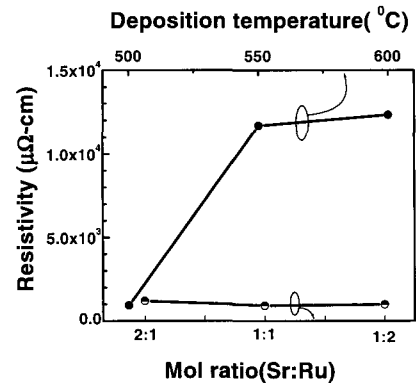


Fig. 6. The variation of resistivity of the films as a function of deposition temperature and a Sr/Ru input mol ratio.

500 °C exhibits a preferential growth of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  phase rather than the  $\text{SrRuO}_3$ . The sticking coefficient of Sr and Ru elements on Si substrates depends on the growth temperature and above a critical temperature the sticking ability of Sr element is higher than that of Ru. Therefore, Sr-excess phase is formed preferentially in the films at higher deposition temperature.

Figure 5 shows SEM surface images of the SRO films deposited at 500 °C under different system pressure. Generally, the lowering the operating pressure in deposition procedure was performed to obtain a dense microstructure of the films. The surface microstructure of the films was improved with decreasing the operating pressure. The films grown in an operating pressure of 0.65 torr exhibited a dense and smooth morphology.

Figure 6 shows the variation of resistivity as a function of deposition temperature and an input mol ratio. The resistivity of the films deposited with various Sr/Ru-input mol ratio at 500 °C was maintained at a constant value of approximately  $900 \mu\Omega\text{-cm}$  irrespective of an input mol ratio. On the other hand, films deposited above 500 °C under the condition of Sr/Ru = 1.0 exhibited a high resistivity, for application of bottom electrode, of about  $10^4 \Omega\text{-cm}$ . As shown in Fig. 4, films deposited at 550 and 600 °C included a second phase having higher intensity rather than the  $\text{SrRuO}_3$  phase. The  $\text{Sr}_3\text{Ru}_2\text{O}_7$  phase with tetragonal structure was known as an insulating material and can increase the resistivity of the films. The resistivity of the SRO films deposited at 500 °C is quite small in comparison with that of SRO films deposited at the same deposition temperature by RF sputtering[9].

#### 4. CONCLUSIONS

The  $\text{SrRuO}_3$  films for application of the bottom electrode were directly deposited on silicon substrate by

metalorganic chemical vapor deposition. The optimum deposition condition for SRO films is the deposition temperature of 500 °C, Sr/Ru input mol ratio of 1.0, and a flow rate of precursors of 15 ml/h. The films deposited by an optimum condition exhibited a single phase of SrRuO<sub>3</sub>, a rms roughness of 8 nm, and a resistivity of approximately 900 μΩ·cm. The high resistivity of the films for application of a bottom electrode is related with the Si substrate.

### ACKNOWLEDGEMENT

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