

Conductive Properties of $\text{ReO}_3/\text{SrCuO}_2$ Bilayered Films

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We studied bilayered films with infinite layer SrCuO_2 and ReO_3 as a charge reservoir block in order to obtain novel high- T_c superconductors. The SrCuO_2 thin films and the ReO_3 thin films were prepared individually by RF sputtering. The SrCuO_2 thin films which had good crystallinity were obtained by substrate heating during deposition and showed semiconducting properties. The ReO_3 thin films which had (100) preferential orientation were obtained by in-situ post-annealing after deposition and showed metallic conductivity. The $\text{ReO}_3/\text{SrCuO}_2$ bilayered films were prepared. The resistivity of the films revealed curious temperature dependences though superconductivity was not observed.

Key words: Re oxide, infinite layer, sputtering, resistivity

1. INTRODUCTION

The structure of an infinite layer (IL) is a fundamental crystal unit included in the most of superconducting cuprates. This structure is composed with two-dimensional CuO_2 layers sandwiched by alkaline earth metal ions. The SrCuO_2 films with an IL structure were semiconductive and did not show superconductivity [1]. However, electron type of superconductivity was observed in the IL compound $\text{Sr}_{1-y}\text{Nd}_y\text{CuO}_2$ at $T_c=40\text{K}$ [2], and hole type of superconductivity in $(\text{Sr}_{1-x}\text{Ca}_x)_{1-y}\text{CuO}_2$ at $T_c=110\text{K}$ [3]. If adequate carriers are doped to the CuO_2 planes from a charge reservoir block (CRB), high temperature superconductivity is expected to take place.

We adopt rhenium (Re) oxides as a material of CRB. As Re has multi-valences (+2~+7), Re oxides are oxidized or reduced easily. Moreover, as ReO_3 reveals extremely high conductivity comparable to that of Ag [4], carriers in ReO_3 move easily. We expect a new type of superconductivity when chemical redox reactions take place at the interface between ReO_3 and IL. The lattice constant of ReO_3 and SrCuO_2 was similar, and a lattice mismatch in ab-planes is about 4.5%. The ReO_3 is suitable for the bilayer grown on SrCuO_2 . We propose the bilayered films with ReO_3 and SrCuO_2 in order to develop novel high- T_c superconductors.

In this work, we discuss the crystallinity and the resistivity of SrCuO_2 , ReO_3 and $\text{ReO}_3/\text{SrCuO}_2$ bilayered thin films.

2. EXPERIMENTALS

2.1 Preparation of SrCuO_2 thin films

The SrCuO_2 thin films were prepared by 90° off-axis RF magnetron sputtering. The SrCuO_2 target was prepared by a sintering process. The starting materials were powders of SrCO_3 and CuO . They were mixed, pre-sintered three times, crushed, pressed into a disc (52mm in diameter) and sintered at 900°C for 50 hours. The substrate of $\text{SrTiO}_3(100)$ was fixed by Pt sheet on a substrate holder. The substrate-target configuration is shown in Fig.1.

The sputtering gas was a mixture of Ar and O_2 . The total gas pressure was 14Pa. The flow rates of Ar and O_2 were 50ccm and 50ccm, respectively. The RF power was 60W (2.8W/cm²). The films were grown for 60min with substrate heating in the range of 530-600°C. After deposition, films were cooled down to room temperature for about 1h in the atmosphere same to the deposition.

2.2 Preparation of ReO_3 thin films

The Re oxides thin films were prepared by 90° off-axis RF magnetron sputtering. The target was a metal Re disc (80mm in diameter), and the substrate was quartz. The substrates were glued on the substrate holder by silver paste and were baked at about 200°C in air to evaporate solution of the paste. A substrate-target configuration is shown in Fig.2.

The sputtering gas was a mixture of Ar and O_2 . The pressure of the gas was $\text{Ar}/\text{O}_2 = 2/0.4\text{Pa}$. The RF power was 20W (0.4W/cm²). The films were grown at ambient substrate temperature for 60min, and then in-situ post-annealing was carried out in Ar atmosphere at the temperature range from 200°C to 270°C for 30min.

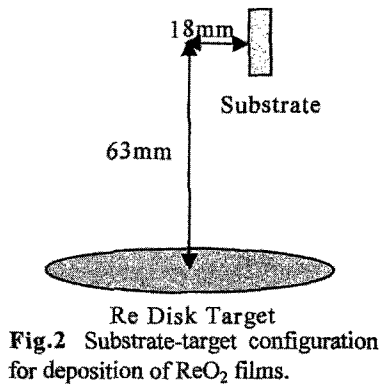
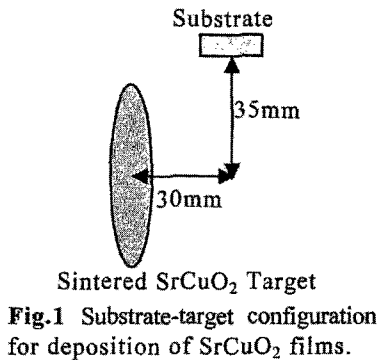
2.3 Preparation of $\text{ReO}_3/\text{SrCuO}_2$ bilayered films

The SrCuO_2 thin films were prepared in condition of 2.1. The substrate temperature was about 560°C.

The $\text{SrCuO}_2/\text{SrTiO}_3$ was fixed by Cu sheet on a substrate holder. The ReO_3 thin films were prepared in condition of 2.2. The prepared film was annealed in-situ at the temperature of 260°C for 10min.

2.4 Measurements

The ReO_3 , SrCuO_2 and bilayered films were examined about crystal structures by reflected X-ray diffraction (XRD) in $2\theta - \theta$ scans from 5°-90° and a rocking curve. The resistivity measurement by a four-probe technique was proceeded for specimen films directly cooled by liquid nitrogen. Each electrodes of silver paste were typically in the size of 1mm×4mm and distance between electrodes was about 1mm. The



value of measurement current was adjusted so that fluctuation of voltage by noises was within about 1% of the measurement voltage.

3. RESULTS AND DISCUSSION

3.1 SrCuO_2 films

The XRD patterns of SrCuO_2 films are shown in Fig.3. The pattern of film prepared at substrate temperature (T_{sub}) of 530°C shows weak peaks of tetragonal SrCuO_2 . Increasing T_{sub} up to 560°C , the intensities of (001) and (002) peak increased. At T_{sub} of 600°C , peak intensities of tetragonal SrCuO_2 decreased, and those of orthorhombic SrCuO_2 increased. The lattice mismatch of SrCuO_2 and SrTiO_3 is little, and tetragonal SrCuO_2 grew as a metastable phase at low temperature. At the higher temperature, orthorhombic SrCuO_2 which was a stable phase grew in prior in a thermal equilibrium state.

Figure 4 shows the XRD peak intensity ratio, $I(001)/I(002)$. It is reported that the $I(001)/I(002)$ increased as increasing defects of Sr [5]. $I(001)/I(002)$ of prepared films were larger than that (about 0.07) of the film with less Sr defects. We thought that prepared films have many Sr-vacancies.

The lattice constant c of the tetragonal thin films was $0.3455\text{nm} \sim 0.3466\text{nm}$, larger than the reported value (0.3432nm). Repulsive forces between CuO_2 layers may be enforced because of the decrease of electrostatic forces from Sr^{2+} layers.

Figure 6 shows the typical XRD rocking curve of the (002) peak of the tetragonal SrCuO_2 . The full width of half maximum intensity (FWHM) was 0.06° . The FWHM of the substrate was about 0.06° and the prepared film grew with a very high preferential

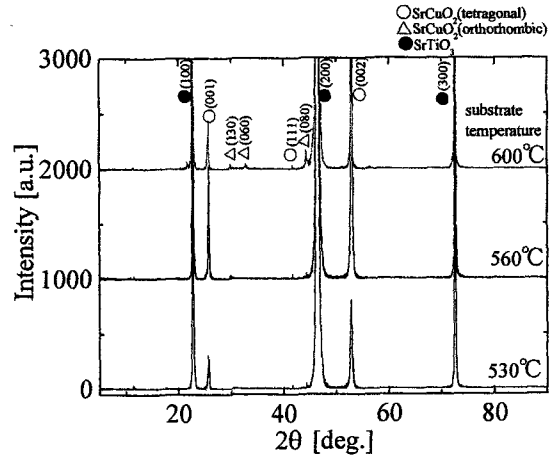


Fig.3 XRD pattern of SrCuO_2 thin films.

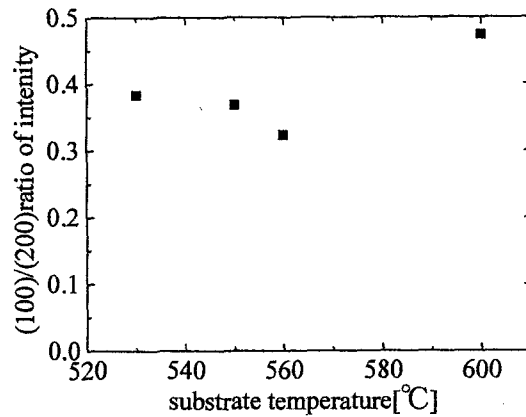


Fig.4 XRD peak ratio, $I(001)/I(002)$ of tetragonal SrCuO_2 thin films.

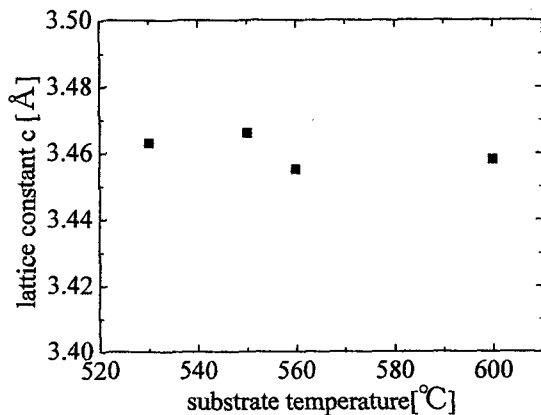


Fig.5 The value of the lattice constant c of tetragonal SrCuO_2 thin films vs. substrate temperature.

orientation of (002).

The temperature dependences of resistivity of SrCuO_2 thin films are shown in Fig.7. The resistivity was semiconductive. The film prepared at T_{sub} of 600°C showed high resistivity. Since XRD pattern of the film revealed the existence of much orthorhombic phase, the conductivity declined with increase of the orthorhombic

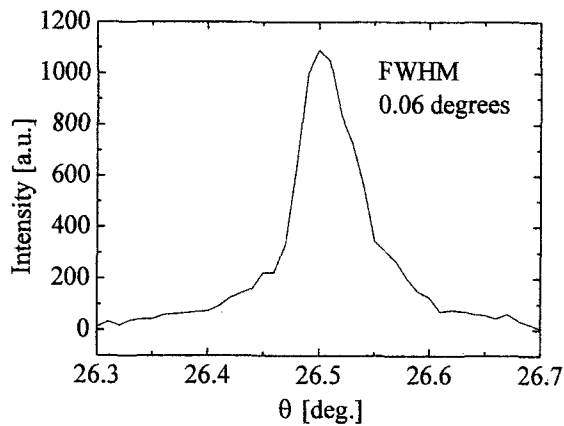


Fig.6 X-ray diffraction rocking curve of the (002) peak of the SrCu₂O₂ film.

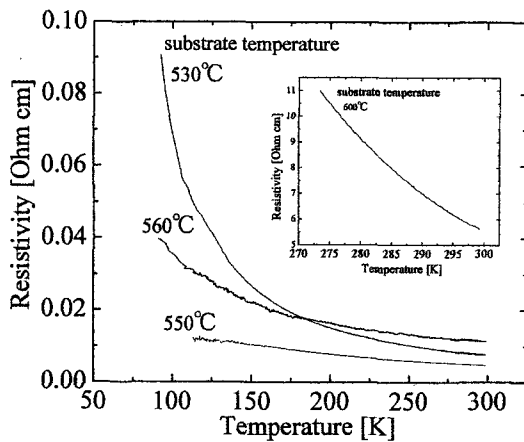


Fig.7 The temperature dependence of resistivity of SrCu₂O₂ thin films.

SrCu₂O₂ phase. The resistivity of the films prepared at other T_{sub} 's was lower than the reported value [1]. This may be caused by the much defects of Sr.

3.2 ReO₃ films

The as-deposited films deliquesced and were yellow. These properties were consistent with the features of a Re₂O₇ phase as already reported [6]. A post annealing was adopted in order to promote the crystallization and reduction of the film.

Figure 8 shows the XRD patterns of post annealed films. At the annealing temperature of 200°C, the peaks were assigned as those of a cubic ReO₃ phase and hexagonal one. At the annealing temperature of 240°C, the cubic ReO₃ phase grew strongly and a single phase was obtained. The film had the strong (100) preferential orientation. The phase of the film changed from a metastable hexagonal ReO₃ phase to a stable cubic ReO₃.

Figure 9 shows the temperature dependences of resistivity of the ReO₃ films. Most of films revealed metallic conduction and very small dependence on temperature. Abrupt increases of resistivity observed at

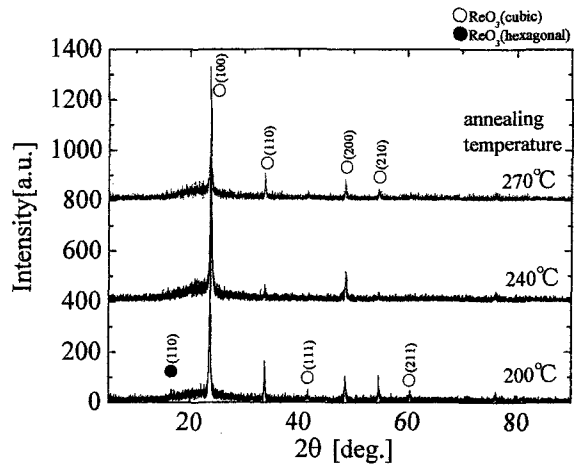


Fig.8 XRD pattern of ReO₃ thin films.

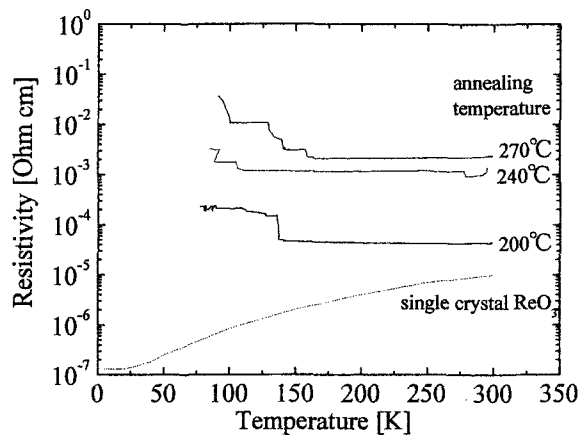


Fig.9 The temperature dependence of resistivity of ReO₃ thin films, and a single crystal.

low temperatures may be caused from the degradation of the ReO₃ phase induced by moisture during the measurement. The resistivity of the films increased as increasing the annealing temperature. The minimum resistivity was obtained at about 200°C annealing and was 4.4×10^{-5} Ohm cm of which the value was few times as large as that of the single crystal[4].

3.3 ReO₃/SrCu₂O₂ bilayered films

Figure 10 shows the XRD pattern of the ReO₃/SrCu₂O₂ bilayered film. The pattern shows peaks from the cubic ReO₃ and small amount of tetragonal and/or orthorhombic SrCu₂O₂. The crystallinity of ReO₃ was comparatively good and that of SrCu₂O₂ was inferior.

Figure 11 shows the resistivity of ReO₃/SrCu₂O₂ bilayered film as a function of temperature. The abrupt decrease of resistivity observed at about 273K may be caused from freeze of water in the film. The property of resistivity was semiconductive in the temperature range from 260K to 220K. At the temperature less than 220K, however, resistivity was metallic. The curious temperature dependence of resistivity may be interpreted by changes of current distribution in the bilayered film.

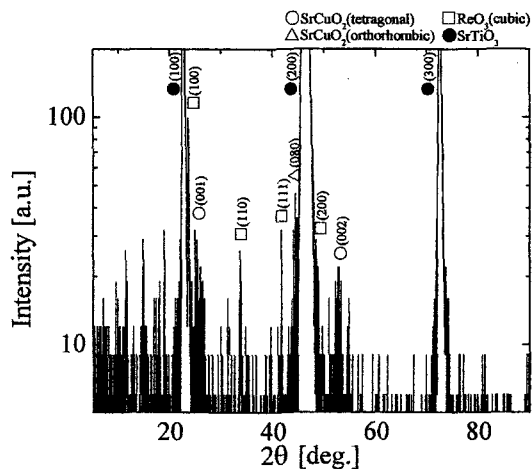


Fig.10 XRD pattern of the $\text{ReO}_3/\text{SrCuO}_2$ bilayered film.

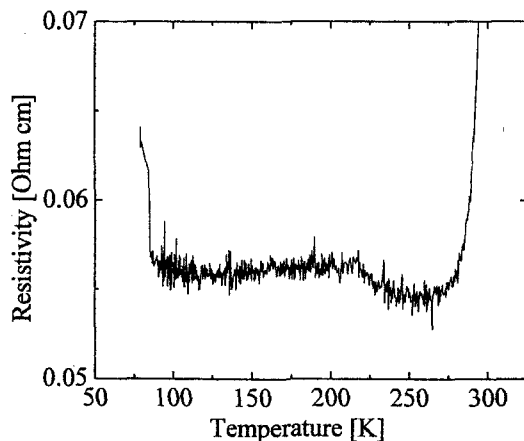


Fig.11 The temperature dependence of resistivity of the $\text{ReO}_3/\text{SrCuO}_2$ bilayered film.

4. SUMMARY

The crystal growth of tetragonal SrCuO_2 phase strongly depended on the substrate temperature. The conductivity of the SrCuO_2 thin films was semiconductive accompanying with comparatively low resistivity. The ReO_3 thin films were prepared successfully by adopting in-situ post-annealing. The crystal growth of the ReO_3 phase and the (100) preferential orientation depended on the annealing temperature. The conductivity of the films was metallic. A superconductivity expected was not observed in the bilayered $\text{ReO}_3/\text{SrCuO}_2$ thin film. The detailed investigation of conductivity at the interface between ReO_3 and SrCuO_2 is the subject for a future study.

5. REFERENCES

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