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Study on Structural, Optical and Electrical Properties of 
CuScO₂ Thin Films 
as p-type Transparent Oxide Semiconductors

Yoshiharu Kakehi

November 2009

Doctoral Thesis at Osaka Prefecture University
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Chapter 1. General Introduction

Some wide gap oxides such as In$_2$O$_3$, ZnO, and SnO$_2$ are n-type transparent oxide semiconductors (TOSs) with unique features of high optical transparency in the visible region and controllable electrical conductivity through extrinsic doping. They can be changed to transparent conductors by higher extrinsic doping, whose electrical conductivities are almost equivalent to those of typical metals. Therefore, they are termed transparent conducting oxides and have been widely used for a long time in optoelectronics applications as well as in various research fields. The first report of a transparent conducting oxide film was published in 1907 when the first cadmium oxide films were prepared by thermally oxidizing sputtered films of cadmium [1]. Since then, extensive works have been done in the field of transparent conducting oxide technology to prepare new types of transparent conducting oxides with wide ranging applications. These include binary and ternary compounds and new materials such as Sn-doped In$_2$O$_3$ [2,3], B,Al,Ga,In-doped ZnO [4,5], Sb,F-doped SnO$_2$ [6,7], Nb,Ta-doped TiO$_2$ [8,9], Zn$_2$SnO$_4$ [10-12], ZnSnO$_3$ [13], In$_2$O$_3$-ZnO(IZO) [14], Cd$_2$SnO$_4$ [15], MgIn$_2$O$_4$ [16], Zn$_2$In$_2$O$_5$ [17], Sn-doped Ga$_2$O$_3$ [18], and 12CaO-7Al$_2$O$_3$ [19]. The important applications in which transparent conducting oxides are used are transparent electrodes for solar cells and flat panel displays, low-emissivity windows, oven windows, touch-sensitive control panels, defrosting windows in refrigerators and airplanes, invisible security circuits, gas sensors, and antistatic coatings [2,20-26]. However, only a limited number of studies have been done on these materials as TOSs. This is because the above-mentioned transparent conducting oxides are n-type TOSs and there has been little possibility of realizing transparent pn-junctions essential for the electron activity of
semiconductors due to the lack of p-type TOSs.

With regard to p-type TOSs, CuAlO$_2$ was first shown to be a p-type transparent semiconductor by Benko and Koffyberg in 1984 [27]. A sintered pellet of CuAlO$_2$ with no intentional doping showed a p-type electrical conductivity of $1.7 \times 10^{-3}$ S cm$^{-1}$ at room temperature. Undoped CuFeO$_2$ exhibited a p-type electrical conductivity, and substituting 2% Mg for Fe increased p-type electrical conductivity [28]. On the other hand, substituting 5% Sn for Fe in CuFeO$_2$ showed n-type electrical conductivity. This indicates that the bipolar doping is achieved in CuFeO$_2$ through extrinsic dopants [28]. CuCrO$_2$ and CuYO$_2$ were doping by substituting Ca for the trivalent cation [29,30]. However, the carrier concentration and Hall mobility for these pellets were not determined by Hall effect measurements probably due to very low Hall mobility. Moreover, the first report of a p-type TOS film was published in 1993 [31]. The electrical conductivity of a 110-nm-thick NiO polycrystalline film with no intentional doping was 7.1 S cm$^{-1}$ at room temperature, but the transmittance of the film was as low as 40% in the visible region. Therefore, there has been considerable interest in finding new p-type TOSs.

In 1997, Kawazoe et al. argued that it was very difficult to prepare binary metallic oxides with p-type electrical conductivity because holes introduced at oxygen 2p levels were strongly localized due to the high electronegative nature of oxygen based on the electronic structure of the metallic oxides. Therefore, they showed the chemical design concept to explore new p-type TOSs called “chemical modulation of the valence band (CMVB)” to delocalize the holes introduced at oxygen 2p levels and proposed the delafossite structure (CuFeO$_2$) as the structural requirement for designing p-type TOSs [32]. Furthermore, they also reported that a 500-nm-thick CuAlO$_{2-x}$ thin film with a delafossite structure showed 70% transmittance in the visible region and a p-type
Fig. 1-1 Crystal structures of (a) 2H and (b) 3R phases of Cu-based delafossites (Cu$^{+}\text{M}^{3+}\text{O}_2$) with hexagonal c-axis vertical. Large spheres are Cu atoms, and small spheres are O atoms. Orientation of MO$_6$ octahedra is same for all layers in 3R phase, but switches back and forth in 2H phase [41].
electrical conductivity of $9.5 \times 10^{-1}$ S cm$^{-1}$ at room temperature [32]. This has opened up a new field in transparent electronics device technology, the so-called “Transparent Electronics” or “Invisible Electronics” [33]. However, the results of the later study for CuAlO$_2$ showed that it was very difficult to control the carrier concentration in CuAlO$_2$ by intercalating with excess oxygen near the Cu-planes or by substituting divalent species for the octahedral Al-sites [34]. Therefore, other Cu-based delafossites isostructural with CuAlO$_2$ have attracted much attention not only as thermoelectric, catalytic, and luminescent materials [35-37] but also as new p-type TOSs.

Cu-based delafossites are expressed by the general formula Cu$^+\text{M}^{3+}\text{O}_2$, and the M$^{3+}$ trivalent cation can range in size from Al to lanthanides [38]. They have two crystalline phases that depend on the stacking periods of Cu$^+$ layers and (MO$_2$)$^-$ octahedral layers along the c-axis termed the 2H (hexagonal) and 3R (rhombohedral) phases, as shown in Fig. 1-1. With increasing the M$^{3+}$-site ionic radius, the magnitude of the a-axis lattice constant expressed as the hexagonal system increases from 0.28567 nm to 0.38311 nm and that of the c-axis lattice constant is almost constant [39]. The Cu-Cu distances (a-axis lattice constant) have been known to significantly influence the Cu-Cu interactions, that is, electrical conductivity, because holes predominantly pass through the Cu-planes [40].

Copper-scandium oxide (CuScO$_2$) is a p-type Cu-based delafossite. CuScO$_2$ also has two crystalline phases: rhombohedral (CuScO$_2$[3R]) and hexagonal (CuScO$_2$[2H]) [34,41,42]. The a- and c-axis lattice constants of each phase are 0.3216 nm and 1.7089 nm for CuScO$_2$[3R] [43] and 0.3215 nm and 1.1386 nm for CuScO$_2$[2H] [44]. Most of the powder preparations have been reported to yield a mixture of the two phases [40]. Unlike CuAlO$_2$ and CuGaO$_2$, holes in CuScO$_2$ can be introduced by intercalating with excess oxygen near the Cu-planes and by substituting divalent species for the octahedral
CuScO$_2$ potentially has a relatively high Hall mobility, because CuScO$_2$ is a Cu-based delafossite with the smallest Cu-Cu distance for which excess oxygen intercalation near the Cu-planes is possible [41]. Consequently, CuScO$_2$ is expected to be a new p-type TOS with the controllable carrier concentration through extrinsic doping.

In previous studies for CuScO$_2$, a 110-nm-thick CuScO$_{2+X}$ polycrystalline film was first reported to show a maximum electrical conductivity of 30 Scm$^{-1}$ at room temperature in Cu-based delafossites by Duan et al. in 2000 [45]. After that, a lot of reports have been published on the new synthesis method to obtain single-phase CuScO$_2$[3R] and CuScO$_2$[2H] powders [34,46], the analysis of strong negative thermal expansion along the O-Cu-O linkage in CuScO$_2$ [44,47], the structural and transport properties of Mg-doped CuScO$_{2+X}$ polycrystalline films and pellets [34,41,42,48-50], the interstitial oxygen site in CuScO$_2$[3R] and CuScO$_2$[2H] pellets intercalated with excess oxygen [51], the electronic structure of CuScO$_2$ and the discovery of the intense excitonic peak [52,53], and the first principle study of extrinsic defects in CuScO$_2$ [54]. However, the carrier concentration and Hall mobility of CuScO$_2$ have not been determined by Hall effect measurements using CuScO$_2$ polycrystalline films and pellets. This is due to the anisotropic electrical conductivity between parallel and perpendicular to the c-axis direction owing to the delafossite structure, thus CuScO$_2$ epitaxial films must be prepared. However, the epitaxial growth of CuScO$_2$ thin films has not been reported until now.

We succeeded in fabricating a 50-nm-thick CuScO$_2$[3R](0001) epitaxial film on an a-plane sapphire substrate using a pulsed laser deposition (PLD) method (Chapter 2). However, by increasing the film thickness using a high laser repetition frequency, grains with different orientations can easily be grown in the deposited films, as shown in Fig.
Fig. 1-2 XRD 2θ-ω patterns of CuScO₂ thin films prepared at different laser repetition frequencies. Laser repetition frequency and deposition rate of each film are as follows: (a) 2 h, 1 Hz, and 25 nm h⁻¹ (epitaxial film); and (b) 2 h, 10 Hz, and 244 nm h⁻¹. Other deposition parameters are a substrate temperature of 925 °C, an oxygen pressure of 1.5 Pa, an rf forward power of the oxygen radical source of 200 W, and a laser fluence of 2.6 Jcm⁻².
1-2. Although the deposition at a relatively high substrate temperature is very useful to solve this problem, the chemical composition of the films easily deviates due to the difference in the vapor pressure between elements during deposition in conventional vapor phase deposition methods. Therefore, a solid-phase epitaxy method was used to obtain CuScO\textsubscript{2} epitaxial thick films. In this method, a bilayer laminate composed of a thin epitaxial layer is grown on a single-crystal substrate and a thicker polycrystalline or amorphous layer of a target, deposited at room temperature, is thermally annealed at high temperature (> 1000 °C). The solid-state reaction at high temperature leads to the formation of a thin, single-crystalline layer on the substrate, which may work as an epitaxial template for successive homoepitaxial growth of the film [55]. This method is very effective when growing complex compounds that have both a high vapor pressure and a high melting point, because the deposition process of the film is separated from the epitaxial growth process.

In this thesis, the deposition and post-annealing conditions of CuScO\textsubscript{2} thin films are investigated to obtain single-phase CuScO\textsubscript{2}[3R](0001) epitaxial thick films using a solid-phase epitaxy method. The structural, optical, and electrical transport properties of the undoped and extrinsic doped films are then discussed to obtain transparent p-type CuScO\textsubscript{2}[3R](0001) epitaxial thick films with the controllable carrier concentration through extrinsic doping. This thesis is composed of seven chapters.

In chapter 2, CuScO\textsubscript{2} thin films are deposited on a-plane sapphire substrates by PLD using a single-phase Cu\textsubscript{2}Sc\textsubscript{2}O\textsubscript{5} target. The effects of the substrate temperature, oxygen pressure, and laser fluence on the film quality are investigated to obtain CuScO\textsubscript{2}(0001) epitaxial films to be used as thin epitaxial layers in a solid-phase epitaxy method. The crystallographic characteristics of the deposited films are evaluated by X-ray diffraction (XRD) measurements, and the in-plane orientation relationship
(1) Preparation of CuScO$_2$[3R](0001) epitaxial thin film by PLD

[Chapter 2]
CuScO$_2$[3R](0001) epitaxial film (thickness < 10nm)

(2) Preparation of CuScO$_2$[3R] polycrystalline thick film by PLD

[Chapter 3]
CuScO$_2$[3R] polycrystalline film (thickness = 200 ∼ 300nm)

(3) Post-annealing treatment under controlling oxygen pressure

[Chapter 3]
Post-annealing treatment using electric furnace (Oxygen pressure = 100 ∼ 1 kPa)

Electric furnace (Ta ≥ 1050 °C)

(4) Fabrication of CuScO$_2$[3R](0001) epitaxial thick film

[Chapter 3]
CuScO$_2$[3R](0001) epitaxial film (thickness = 200 ∼ 300nm)

Fig. 1-3 Schematic illustration of fabrication of CuScO$_2$[3R](0001) epitaxial thick films by solid-phase epitaxy method used in this study
between the substrates and the films is also discussed.

Chapter 3 focuses on the fabrication of single-phase CuScO$_2$(0001) epitaxial thick films using a solid-phase epitaxy method. By converting CuScO$_2$ amorphous films into CuScO$_2[3R]$ polycrystalline films in the fabrication process, single-phase CuScO$_2[3R]$(0001) epitaxial thick films are successfully obtained on a-plane sapphire substrates, as shown in Fig. 1-3. The electrical transport property of the films is first estimated using Hall effect measurements.

In chapter 4, the excess oxygen intercalation is investigated as the control method of the carrier concentration in CuScO$_2[3R]$(0001) epitaxial thick films. However, a number of holes generated by the excess oxygen intercalation exist near the film surface, thus a 40-nm-thick CuScO$_2[3R]$(0001) epitaxial film prepared using the fabrication method described in chapter 3 is used as the sample to intercalate with excess oxygen in the whole film. The effects of the excess oxygen intercalation on the structural, optical, and electrical transport properties of the film are studied. The conduction mechanism of the film is also investigated using the temperature dependences of the electrical conductivity and Seebeck coefficient.

In chapter 5, the control of the carrier concentration in CuScO$_2[3R]$(0001) epitaxial thick films by the Mg doping in the Sc-site is discussed. Mg-doped CuScO$_2$ thin films with different Mg concentrations are prepared using the fabrication method described in chapter 3, and the effects of Mg doping in the Sc-site on the structural, optical, and electrical transport properties of CuScO$_2$ thin films are investigated by comparing them with those of the undoped epitaxial film obtained in chapter 3.

Chapter 6 focuses on controlling the carrier concentration in CuScO$_2[3R]$(0001) epitaxial thick films through extrinsic doping. Based on the results obtained in chapters 4 and 5, undoped and 1-at% Mg-doped CuScO$_2[3R]$ thin films are prepared by
changing the oxygen pressure during deposition of the polycrystalline thick layer in the two-step deposition process, followed by post-annealing treatment. The structural, optical, and electrical transport properties of the films are investigated. The films show optical transparency in the visible region, and the carrier concentration of CuScO$_2$[3R](0001) epitaxial thick films at room temperature is successfully controlled from $1.6 \times 10^{16}$ cm$^{-3}$ to $9.2 \times 10^{17}$ cm$^{-3}$ by adjusting the excess oxygen and Mg co-doping for the first time.

Chapter 7 summarizes the main results and describes the conclusion obtained in this thesis.

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Chapter 2. Crystallographic Analysis of CuScO$_2$ Thin Films Deposited on A-plane Sapphire Substrates

2.1 Introduction

A solid-phase epitaxy method is used to prepare high quality CuScO$_2$ epitaxial thick films for evaluating the carrier concentration and Hall mobility of CuScO$_2$. Although this method needs thin epitaxial layers grown on single-crystal substrates, the epitaxial growth of CuScO$_2$ thin films has not been reported. As described in chapter 1, CuScO$_2$ has two crystalline phases: rhombohedral (CuScO$_2$[3R]) and hexagonal (CuScO$_2$[2H]). The close-packed plane of both phases in CuScO$_2$ is the (0001) plane and this plane has the lowest surface free energy. Therefore, it is presumed that CuScO$_2$ thin films grow preferentially with the c-axis perpendicular to the substrates.

In this chapter, CuScO$_2$ thin films are prepared on a-plane sapphire substrates by PLD using a single-phase Cu$_2$Sc$_2$O$_5$ target. The effects of the substrate temperature, oxygen pressure, and laser fluence on the film quality of CuScO$_2$ thin films are investigated to obtain CuScO$_2$(0001) epitaxial films to be used as thin epitaxial layers in a solid-phase epitaxy method. The crystallographic characteristics of the deposited films are evaluated by XRD measurements, and the in-plane orientation relationship between the substrates and the films is also discussed.

2.2 Experimental

CuScO$_2$ thin films were deposited using a PLD apparatus with an oxygen radical
source and an *in-situ* reflection high-energy electron diffraction (RHEED) (ULVAC: MB95-5005), as shown in Fig. 2-1. The helicon wave plasma gun (helicon gun) was adopted as the oxygen radical source [1]. A schematic diagram of the helicon gun and a schematic cross sectional view of the substrate and the helicon gun arrangement in our PLD apparatus are shown in Figs. 2-2(a) and 2-2(b), respectively. The gun mainly consists of a discharge room made of an Al₂O₃ crucible, a Sm-Co magnet for applying a magnetic field to the discharge room, a radio frequency [(rf): 13.56 MHz] coil for generating an rf plasma and an oxygen molecular gas inlet. The oxygen plasma is generated in the discharge room when the rf power is supplied to the rf coil. In this gun, the maximum rf forward power is 200 W, and a Sm-Co magnet put just below the center of the discharge room enhances the plasma density of the oxygen plasma. The beam of the excited oxygen species is then ejected towards the substrate through an orifice, as shown in Figs. 2-2(a) and 2-2(b).

To evaluate the characterization of the beam, the optical emission spectra from the beam were measured through a quartz window equipped with the chamber by an optical multi-channel spectral analyzer (Hamamatsu: PMA-11). Figure 2-3 shows the typical optical emission spectrum from oxygen plasma generated at an oxygen pressure of 1.5 Pa and an rf forward power of 200 W. The emission peaks were identified according to standard tables of spectral lines [2,3], and those corresponding to the oxygen radical (O*) and singly ionized molecular oxygen (O₂⁺) were detected. The emission intensities of typical peaks for the oxygen radical (λ = 777 nm) and singly ionized molecular oxygen (λ = 563 nm) as a function of oxygen pressure are shown in Fig. 2-4. They decreased with increasing oxygen pressure, and that for the singly ionized molecular oxygen was almost zero at an oxygen pressure of 13 Pa.

The target was not a CuScO₂ pellet but a Cu₂Sc₂O₅ pellet, because Cu₂Sc₂O₅ has
Fig. 2-1 Schematic illustration of the pulsed laser deposition (PLD) apparatus.

T.M.P. and R.P. are a turbo molecular pump and a rotary pump, respectively.
Fig. 2-2 (a) Schematic diagram of the helicon wave plasma gun.

(b) Schematic cross-sectional view of the substrate and the helicon wave plasma gun arrangement in the PLD apparatus.
Fig. 2-3 Typical optical emission spectrum from oxygen plasma generated by the helicon wave plasma gun. Symbols “O∗” and “O₂⁺” indicate the oxygen radical and the singly ionized molecular oxygen, respectively. Oxygen pressure and rf forward power of the helicon wave plasma gun are 1.5 Pa and 200 W, respectively.
Fig. 2-4 Oxygen pressure dependence of the emission intensities of typical peaks for the oxygen radical ($\lambda = 777$nm) and the singly ionized molecular oxygen ($\lambda = 563$ nm) generated by the helicon wave plasma gun. The rf forward power of the helicon wave plasma gun is 200 W.
the cationic concentration ratio (Cu/Sc) equal to CuScO₂ and can be easily synthesized in air and oxygen atmosphere. The Cu₂Sc₂O₅ powder was prepared via an ordinary solid state reaction. A mixture powder of CuO(99.999%) and Sc₂O₃(99.99%) was ground and heated at 1000 °C for 24 hours in an oxygen flow. After being reground, the sintered mass was pressed into pellet form and sintered at 1050 °C for 50 hours in an oxygen flow. XRD patterns proved that the target was a single phase of orthorhombic Cu₂Sc₂O₅. The target, whose nominal composition was Cu:Sc = 1.00:1.00, was confirmed by inductively coupled plasma atomic emission spectrometry. A KrF excimer laser beam (λ = 248 nm, pulse duration = 30 ns) was used for the ablation. The substrates were a-plane sapphire, because the sapphire c-axis lattice constant (1.2991 nm) matched the fourfold longer constants of the CuScO₂ a-axis lattice constant with less than a 1.01 % misfit. Therefore, it is expected that CuScO₂ thin films are epitaxially grown on a-plane sapphire substrates based on the uniaxial locked epitaxy mechanism [4]. The sapphire substrates were previously annealed in oxygen at 1150°C for 14 h to obtain atomically flat surfaces. The distance from the target to the substrate was fixed at 40 mm.

The crystallographic structure, crystallinity and orientations along the out-of-plane and in-plane directions against the substrate were characterized with an X-ray diffractometer using Cu Kα₁ radiation (PANalytical: X’pert PRO MRD) and using Cu Kα radiation (Rigaku: RINT-2500). The optical transmission spectra were measured by a spectrophotometer (Shimadzu: UV-3100). The film thickness was determined by a surface profilometer (KLA Tencor: P-15). The film composition was measured by an X-ray photoelectron spectroscopy employing Mg Kα radiation (Shimadzu, Model ESCA3300s) and a Rutherford backscattering spectroscopy (RBS) at an acceleration voltage of 950 keV of He⁺ ions (KOBELOCO: MB-1010-EW). The surface morphology was observed with scanning electron microscopy (SEM) (JEOL:
2.3 Results and Discussion

2.3.1 Thermal decomposition reaction of Cu$_2$Sc$_2$O$_5$ bulk

The thermogravimetric analysis (TGA) was carried out to study the thermal characteristics of bulk Cu$_2$Sc$_2$O$_5$. Figure 2-5 shows the TGA profiles of bulk Cu$_2$Sc$_2$O$_5$ under different gas atmospheres. No weight change of the bulk was observed in oxygen; however, significant weight changes were detected in reducing gases such as argon and nitrogen above approximately 300°C. This large weight loss agreed closely with the theoretical value expected for the decomposition reaction that forms Cu and Sc$_2$O$_3$ from Cu$_2$Sc$_2$O$_5$. XRD 2θ-ω patterns of the reaction samples are shown in Fig. 2-6. Several Cu and Sc$_2$O$_3$ peaks were detected only for the sample heated in nitrogen gas, indicating that Cu$_2$Sc$_2$O$_5$ decomposes into Cu and Sc$_2$O$_3$. It has been well documented that copper metal oxidized into Cu$_2$O and CuO in that order under increasing oxygen pressure [5]. Consequently, we concluded that it was possible to prepare a CuScO$_2$ thin film by using a single-phase Cu$_2$Sc$_2$O$_5$ target while controlling oxygen pressure and substrate temperature.

2.3.2 Substrate temperature dependence of film quality

Figure 2-7 shows the XRD 2θ-ω patterns of CuScO$_2$ thin films prepared at various substrate temperatures. Other deposition parameters are as follows: an oxygen pressure of 0.5 Pa, an rf forward power of the oxygen radical source of 0 W, a laser fluence of 2.6 Jcm$^{-2}$, a laser repetition frequency of 1 Hz, and a deposition time of 1 h.
Theoretical value: 10.8 wt%

Fig. 2-5 TGA profiles of bulk Cu$_2$Sc$_2$O$_5$ samples under different gas atmospheres.

Gases are oxygen, nitrogen and argon, respectively.
Fig. 2-6 XRD 2θ-ω patterns of reaction samples after TGA measurements in nitrogen and oxygen atmospheres. Several peaks for Cu (●) and Sc$_2$O$_3$ (○) were detected for the sample obtained in nitrogen gas.
Only diffraction peaks corresponding to CuScO$_2$ 000$\ell$ were observed at substrate temperatures of 800 °C and 850 °C, where the $\ell$ values corresponded to 3,6,9,12 if the structure of the film supposed to be 3R and to 2,4,6,8 if it supposed to be 2H. The intensities for their diffraction peaks increased with increasing substrate temperature, but became weaker at a substrate temperature of 950 °C. Additional diffraction peaks corresponding to Cu$_2$O 110, 220 and CuScO$_2$[3R] 1011 also appeared when the substrate temperature exceeded 850 °C.

The in-plane orientation relationship of the film with respect to the substrate for the film deposited at a substrate temperature of 850 °C was investigated using XRD $\phi$-scan measurements. The results using 3030 diffractions of the substrate, 1014 diffractions of the CuScO$_2$[3R] phase, and 1013 diffractions of the CuScO$_2$[2H] phase of the film are shown in Fig. 2-8. Peaks with two-fold rotational symmetry were observed for 3030 diffractions of the substrate. On the other hand, no peaks for the 1014 diffractions of the CuScO$_2$[3R] phase and 1013 diffractions of the CuScO$_2$[2H] phase of the film were observed, indicating that the film has no in-plane orientations.

The substrate temperature dependence of the deposition rate and the concentration ratio of Cu/(Cu+Sc) in deposited films are shown in Fig. 2-9. All concentration ratios of Cu/(Cu+Sc) were normalized by that of the film deposited at a substrate temperature of 900 °C. The deposition rate increased when the substrate temperature exceeded 850 °C. On the other hand, the concentration of Cu was almost constant within a substrate temperatures ranging from 800 °C to 900 °C, and slightly decreased at a substrate temperature of 950 °C.

The surface morphologies of the deposited films were examined using SEM observation. The images are illustrated in Fig. 2-10. There were few precipitates on the
Fig. 2-7 XRD 2θ-ω patterns of CuScO₂ thin films deposited on a-plane sapphire substrates at various substrate temperatures. (a) 800 °C, (b) 850 °C, (c) 900 °C, and (d) 950 °C.
Fig. 2-8 XRD φ-scans of a-plane sapphire substrate and CuScO$_2$(0001) thin film deposited at a substrate temperature of 850 °C. (a) $\{0\overline{3}0\}$ plane of substrate, (b) $\{0\overline{1}4\}$ plane of CuScO$_2$[3R] phase of film, (c) $\{0\overline{1}3\}$ plane of CuScO$_2$[2H] phase of film.
Fig. 2-9 Substrate temperature dependences of deposition rate and concentration ratio of Cu/(Cu+Sc) on CuScO$_2$ thin films. All concentration ratios of Cu/(Cu+Sc) were normalized by that of the film deposited at a substrate temperature of 900 °C.
Fig. 2-10 SEM images of CuScO$_2$ thin films prepared on a-plane sapphire substrates under substrate temperatures of (a) 800 °C, (b) 850 °C, (c) 900 °C, and (d) 950 °C.
film surface when the film was prepared below a substrate temperature of 850 °C, as shown in Fig. 2-10(a) and 2-10(b). A small amount of precipitates was observed on the film surface prepared at a substrate temperature of 900 °C [Fig. 2-10(c)], and a substrate temperature of 950 °C caused a large number of precipitates with a size of about 50-200 nm to form on the whole surface, as shown in Fig. 2-10(d).

Consequently, the increase in the deposition rate is because the film surface becomes rougher due to a large number of precipitations generated by the thermal decomposition reaction in deposited films.

### 2.3.3 Oxygen pressure dependence of film quality

Figure 2-11 shows the XRD 2θ-ω patterns of CuScO$_2$ thin films deposited under various oxygen pressures. Other deposition parameters are as follows: a substrate temperature of 900 °C, an rf forward power of the oxygen radical source of 0 W, a laser fluence of 2.6 Jcm$^{-2}$, a laser repetition frequency of 1 Hz, and a deposition time of 1 h. Diffraction peaks corresponding to CuScO$_2$ 000$\ell$ and 10$\bar{1}$1, Cu$_2$O 110 and 220 were observed at an oxygen pressure of 1.0×10$^{-1}$ Pa. With increasing oxygen pressure, the intensities for the diffraction peaks corresponding to CuScO$_2$ 000$\ell$ increased and those for the diffraction peaks corresponding to CuScO$_2$ 10$\bar{1}$1, Cu$_2$O 110, 220 peaks became smaller. Only diffraction peaks corresponding to CuScO$_2$ 000$\ell$ was identified at an oxygen pressure of 1.5 Pa, indicating that a strongly c-axis oriented CuScO$_2$ thin film can be grown on an a-plane sapphire substrate. The intensities from CuScO$_2$ 000$\ell$ diffraction peaks decreased, and Cu$_2$O 110, 220 and CuO 002 peaks appeared when the oxygen pressure exceeded 1.5 Pa.

The XRD $\phi$-scans using 30$\bar{3}$0 diffractions of the substrate, 10$\bar{1}$4 diffractions of the CuScO$_2$[3R] phase and 10$\bar{1}$3 diffractions of the CuScO$_2$[2H] phase of the film
Fig. 2-11 XRD 2θ-ω patterns of CuScO$_2$ thin films deposited on a-plane sapphire substrates at various oxygen pressures. (a) 1.0×10$^{-1}$ Pa, (b) 5.0×10$^{-1}$ Pa, (c) 1.0 Pa, (d) 1.5 Pa, (e) 2.0 Pa, and (f) 5.0 Pa.
Fig. 2-12 XRD $\phi$-scans of a-plane sapphire substrate and CuScO$_2$(0001) thin film prepared at an oxygen pressure of 1.5 Pa. (a) $\{0\overline{3}0\}$ plane of substrate, (b) $\{10\overline{4}\}$ plane of CuScO$_2$[3R] phase of film, (c) $\{10\overline{3}\}$ plane of CuScO$_2$[2H] phase of film.
prepared at an oxygen pressure of 1.5 Pa are shown in Fig. 2-12. For the 10\(\bar{1}\)4 diffractions of the CuScO\(_2\)[3R] phase of the film, the mixture of two types of six-fold rotational symmetry components were observed, as shown in Fig. 2-12(b). On the other hand, no peaks for the 10\(\bar{1}\)3 diffractions of the CuScO\(_2\)[2H] phase of the film were detected.

The deposition rate and the concentration ratio of Cu/(Cu+Sc) in deposited films are shown in Fig. 2-13 as a function of the oxygen pressure. All concentration ratios of Cu/(Cu+Sc) were normalized by that of the film deposited at an oxygen pressure of 1.5 Pa. The deposition rate decreased and the concentration of Cu showed no distinct dependence on oxygen pressures ranging from 1.0\(\times\)10\(^{-1}\) Pa to 1.5 Pa. In the case of relatively low oxygen pressures and/or high substrate temperatures during the deposition, we consider that the thermal decomposition reaction (2CuScO\(_2\) → Cu\(_2\)O + Sc\(_2\)O\(_3\)) does proceed in deposited films. This reaction generates grains with different orientations and phases, as shown in Fig. 2-11. The grains may have different growth speeds, causing the film surface to become rough. However, the average composition of the film must be kept constant. Consequently, a decrease in the deposition rate occurs because the thermal decomposition reaction in deposited films is suppressed by increasing oxygen pressure. With further increases in oxygen pressure, both the deposition rate and the concentration of Cu increased. It is well known that excess elements in deposited films are separated as impurity phases on the film surface at higher deposition temperatures [6].

The SEM observation was carried out to examine the surface morphologies of the deposited films. The images are illustrated in Fig. 2-14. With increasing oxygen pressure, the precipitates on the film surface decreased, and there were few precipitates on the film surface when the film was prepared at an oxygen pressure of 1.5 Pa, as
Fig. 2-13 Deposition rate and concentration ratio of Cu/(Cu+Sc) on CuScO$_2$ thin films as a function of the oxygen pressure. All concentration ratios of Cu/(Cu+Sc) were normalized by that of the film deposited at an oxygen pressure of 1.5 Pa.
Fig. 2-14 SEM images of CuScO$_2$ thin films prepared on a-plane sapphire substrates under oxygen pressures of (a) $1.0 \times 10^{-1}$ Pa, (b) $5.0 \times 10^{-1}$ Pa, (c) 1.0 Pa, (d) 1.5 Pa, (e) 2.0 Pa, and (f) 5.0 Pa.
shown in Fig. 2-14(d). With further increases in oxygen pressure, the precipitates on the film surface increased, and an oxygen pressure of 5.0 Pa caused a large number of precipitates with a size of about 50-300 nm to form on the whole surface, as shown in Fig. 2-14(f). In summary, the increase in the deposition rate at an oxygen pressures above 1.5 Pa is caused by the generation of the precipitates on the film surface due to deviations in the stoichiometry of the film’s composition.

2.3.4 Fabrication of CuScO₂(0001) epitaxial films and the effect of laser fluence on the in-plane orientation of the epitaxial films

To obtain CuScO₂(0001) epitaxial films, CuScO₂ thin films were prepared at a substrate temperature of 925 °C using the oxygen radical source to suppress the thermal decomposition reaction during deposition. The XRD 2θ-ω and RHEED patterns of the CuScO₂ thin film, deposited at a substrate temperature of 925 °C, an oxygen pressure of 1.5 Pa, an rf forward power of the oxygen radical source of 200 W, a laser fluence of 2.6 Jcm⁻², a laser repetition frequency of 1 Hz, and a deposition time of 2 h, are shown in Figs. 2-15 and 2-16, respectively. Only CuScO₂ 000ℓ diffraction peaks were observed, indicating that the film is strongly oriented with the c-axis perpendicular to the substrate. Streaky RHEED patterns showing six-fold rotational symmetry were observed. However, identifying the crystallographic structure of the c-axis oriented film using conventional XRD 2θ-ω measurements was difficult because the diffraction angles of 000ℓ peaks for each phase were very close. Therefore, two-dimensional X-ray reciprocal space mapping measurements were conducted, as shown in Fig. 2-17. Diffractions corresponding to 000ℓ₀ [ℓ₀ = 6,9,12], 10ℓ₁ [ℓ₁ = 1,2,4,8,10], and 20ℓ₂ [ℓ₂ = 2] of CuScO₂ with 3R crystal structure were observed, suggesting that the film was single-phase with a rhombohedral crystal structure. The full width at half
Fig. 2-15 XRD 2θ-ω pattern of a CuScO$_2$ thin film grown on an a-plane sapphire substrate. The film was deposited at a substrate temperature of 925°C, an oxygen pressure of 1.5 Pa, an rf forward power of 200 W, a laser fluence of 2.6 Jcm$^{-2}$, a laser repetition frequency of 1 Hz, and a deposition time of 2 h.
Fig. 2-16 RHEED patterns of a CuScO$_2$ thin film deposited on an a-plane sapphire substrate. The electron beam was incidental along [10\overline{1}0] and [1\bar{1}20] azimuths.
Fig. 2-17 Two-dimensional X-ray reciprocal space mapping measurements of the c-axis oriented CuSeO\(_2\) thin film grown on an a-plane sapphire substrate. Diffractions corresponding to \(00\ell_0\) \([\ell_0 = 6,9,12]\), \(10\overline{1}\ell_1\) \([\ell_1 = 1,2,4,8,10]\), and \(20\overline{2}\ell_2\) \([\ell_2 = 2]\) of CuSeO\(_2\) with 3R crystal structure were observed. “S” denotes substrate.
Fig. 2-18 XRD φ-scans of a-plane sapphire substrate and CuScO$_2$[3R](0001) thin film.

(a) $\{30\overline{3}0\}$ plane of substrate, (b) $\{10\overline{1}4\}$ plane of film.
maximum (FWHM) value taken from a 0006-peak rocking curve measurement was 0.14°.

The XRD φ-scans using 30̅30 diffractions of the substrate and 10̅14 diffractions of the film are shown in Figs. 2-18(a) and 2-18(b), respectively. Sharp peaks with two-fold rotational symmetry were observed for 30̅30 diffractions of the substrate. On the other hand, peaks for the 10̅14 diffractions of the film exhibited six-fold rotational symmetry, indicating that the film had twin structures. However, the peaks of the film did not show agreement with those of the substrate at the φ diffraction angles of ±90°, and shifted from those of the substrate about 9°. Since it is possible that Cu⁺ layers or (ScO₂)⁻ octahedral layers form the CuScO₂[3R](0001) plane, this may be due to the atomic arrangements of the initial growth of CuScO₂[3R](0001) epitaxial films on a-plane sapphire substrates. Therefore, the effect of the laser fluence on the film quality of CuScO₂ thin films was investigated, because the in-plane orientation of ZnO thin films grown on c-plane sapphire substrates has been reported to be controlled by the laser fluence [7]. Other deposition parameters are set as follows: a substrate temperature of 925 °C, an oxygen pressure of 1.5 Pa, an rf power of the oxygen radical source of 200 W, a laser repetition frequency of 1 Hz, and a deposition time of 1–2 h.

Figure 2-19 shows the XRD 2θ-ω patterns of CuScO₂ thin films deposited at various laser fluences. Only diffraction peaks corresponding to CuScO₂ 000ℓ were identified for the film prepared at a laser fluence of 0.6 Jcm⁻². With increasing laser fluence, the intensities for CuScO₂ 000ℓ diffraction peaks became stronger and additional diffraction peaks corresponding to Cu₂O 110, 111, 200, and 220 appeared. However, the intensities for Cu₂O diffraction peaks became smaller when the laser fluence exceeded 1.0 Jcm⁻², and only CuScO₂ 000ℓ peaks were observed for the film deposited at a laser fluence of 2.6 Jcm⁻².
The in-plane orientation of the films, shown in Fig. 2-19, against the substrates was characterized using XRD $\phi$-scan measurements. The results obtained using $30\bar{3}0$ diffractions of the substrate, $10\bar{1}4$ diffractions of the CuScO$_2[3\text{R}]$ phase and $10\bar{1}3$ diffractions of the CuScO$_2[2\text{H}]$ phase of the films are shown in Figs. 2-20 and 2-21. Peaks with two-fold rotational symmetry were observed for $30\bar{3}0$ diffractions of the substrate, as shown in Figs. 2-20(a) and 2-21(a). However, peaks for $10\bar{1}4$ diffractions of the films prepared at a laser fluence of less than or equal to 1.0 Jcm$^{-2}$ exhibited six-fold rotational symmetry and were in agreement with $30\bar{3}0$ diffractions of the substrate at $\phi$ diffraction angles of $\pm90^\circ$ [Figs. 2-20(b) and 2-20(c)]. This indicates that the domain with $\text{CuScO}_2[3\text{R}][1\bar{1}20]///\text{sapphire}[0001]$ in-plane orientation grows on a-plane sapphire substrates. With increasing laser fluence, new peaks corresponding to another six-fold rotational symmetry component appeared, as shown in Figs. 2-20(d) and 2-20(e), and their intensities became stronger. This indicates that the films have two types of domain in the basal plane. Only new peaks corresponding to another six-fold rotational symmetry component were observed for the film prepared at a laser fluence of 2.6 Jcm$^{-2}$ [Fig. 2-20(f)]. On the other hand, no peaks for the $10\bar{1}3$ diffractions of the CuScO$_2[2\text{H}]$ phase of the films were observed, as shown in Fig. 2-21.

The deposition rate and the concentration ratio of Cu/(Cu+Sc) in deposited films are shown in Fig. 2-22 as a function of the laser fluence. All concentration ratios of Cu/(Cu+Sc) were normalized by that of the film deposited at a laser fluence of 2.6 Jcm$^{-2}$. The deposition rate increased with increasing laser fluence and decreased slightly when the laser fluence was 1.1 Jcm$^{-2}$. With further increases in laser fluence, the deposition rate increased again. On the other hand, the concentration of Cu in the film prepared at a laser fluence of 0.6 Jcm$^{-2}$ was almost identical to that in the film prepared at a laser fluence of 2.6 Jcm$^{-2}$. The concentration of Cu increased with increasing laser fluence,
Fig. 2-19 XRD 2θ-ω patterns of CuScO$_2$ thin films deposited on a-plane sapphire substrates at various laser fluences. (a) substrate, (b) 0.6 Jcm$^{-2}$, (c) 1.0 Jcm$^{-2}$, (d) 1.1 Jcm$^{-2}$, (e) 1.8 Jcm$^{-2}$, and (f) 2.6 Jcm$^{-2}$. Other deposition parameters are as follows: a substrate temperature of 925 °C, an oxygen pressure of 1.5 Pa, an rf forward power of the oxygen radical source of 200 W, a laser repetition frequency of 1 Hz, and a deposition time of 1~2 h.
Fig. 2-20 XRD φ-scans of \{30\overline{3}0\} plane of sapphire substrate and \{1\overline{0}1\overline{4}\} plane of CuScO$_2$[3R] phase of the films deposited at various laser fluences. (a) substrate, (b) 0.6 Jcm$^{-2}$ (c) 1.0 Jcm$^{-2}$, (d) 1.1 Jcm$^{-2}$, (e) 1.8 Jcm$^{-2}$, and (f) 2.6 Jcm$^{-2}$. Two kinds of six-fold rotational symmetry components were observed, and each component indicates using next symbols [(●) and (▲)].
Fig. 2-21 XRD φ-scans of \{0\overline{3}0\} plane of sapphire substrate and \{1\overline{0}1\} plane of CuScO$_2$[2H] phase of the films deposited at various laser fluences. (a) substrate, (b) 0.6 Jcm$^{-2}$ (c) 1.0 Jcm$^{-2}$, (d) 1.1 Jcm$^{-2}$, (e) 1.8 Jcm$^{-2}$, and (f) 2.6 Jcm$^{-2}$. No peaks for the 10\overline{1}3 diffractions of the CuScO$_2$[2H] phase of the films were observed.
Fig. 2-22 Deposition rate and concentration ratio of Cu/(Cu+Sc) on CuScO$_2$ thin films as a function of the laser fluence. All concentration ratios of Cu/(Cu+Sc) were normalized by that of the film deposited at a laser fluence of 2.6 Jcm$^{-2}$. 
but gradually decreased when the laser fluence exceeded 1.0 Jcm\(^{-2}\). Consequently, the increase in the deposition rate at a laser fluence of 1.0 Jcm\(^{-2}\) is because the film surface becomes rougher due to the precipitates generated by the compositional deviation in the film.

Optical emission spectra were measured to study the laser fluence dependence of the excited species in the plume. For example, Figure 2-23 shows the optical emission spectrum of the plume when the target was ablated at a laser fluence of 2.6 Jcm\(^{-2}\). Emission lines including radicals, and singly and molecular ionized species for each element were identified in accordance with standard tables of spectral lines [2.3]. Molecular band heads in relation to ScO were also detected. Therefore, the typical peaks for each excited species were chosen, and their emission intensities were measured as a function of the laser fluence. These peaks are a copper ion (Cu\(^{+}\); 214nm), a copper radical (Cu*; 325nm), a scandium ion (Sc\(^{+}\); 361nm), a scandium radical (Sc*; 391nm), a molecular oxygen ion (O\(_2\)^{+}; 642nm), an oxygen radical (O*; 777nm), and a molecular scandium oxide (ScO; 604nm), respectively. The results are shown in Fig. 2-24. The emission intensities for Sc*, O*, and ScO were almost zero at a laser fluence ranging from 0.6 to 1.0 Jcm\(^{-2}\), and those for another excited species showed no distinct dependence. The emission intensity for ScO began to increase when the laser fluence exceeded 1.0 Jcm\(^{-2}\). With further increasing laser fluences, the emission intensities for Cu* and Sc*, Sc\(^{+}\) and ScO abruptly increased. On the other hand, the emission intensity for Cu\(^{+}\) was almost constant, and those for O\(_2\)^{+} and O* gradually increased. By comparing these results to those shown in Fig. 2-20, we notice that another six-fold rotational symmetry component (▲ in the figure) appears when the emission intensities for Cu* and Sc*, Sc\(^{+}\) and ScO begin to increase, and that preferentially grows as their emission intensity increase.
Fig. 2-23 Optical emission spectrum of the plume from the target ablated at a laser fluence of 2.6 Jcm$^{-2}$. Emission lines including radicals, and singly and molecular ionized species for each element were identified and molecular band heads in relation to ScO were also detected.
Fig. 2-24 Intensities of typical peaks for each excited species as a function of the laser fluence. The peaks are Cu\(^+\) (214nm), Cu\(^*\) (325nm), Sc\(^+\) (361nm), Sc\(^*\) (391nm), O\(_2\)^{+} (642nm), O\(^*\) (777nm), and ScO (604nm), respectively.
Here, we consider the atomic arrangements for the CuScO$_2[3R](0001)$ and sapphire $(\overline{1}1\overline{2}0)$ planes. The CuScO$_2[3R]$ one is composed of an alternating stack of Cu$^+$ layers and (ScO$_2$)$^-$ octahedral layers along the c-axis [Fig. 1-1(b)], thus it is possible that Cu$^+$ layers or (ScO$_2$)$^-$ octahedral layers form the CuScO$_2[3R](0001)$ plane. On the other hand, both Al and O atoms exist in the sapphire $(0001)$ plane, as shown in Fig. 2-25. If Cu$^+$ layers form the CuScO$_2[3R](0001)$ plane, the Cu atoms of the layers form bonds with O atoms on the sapphire surface. The in-plane orientation relationship between the substrate and the film, shown in Fig. 2-26(a), is CuScO$_2[3R]|\overline{1}1\overline{2}0|$/sapphire[0001] and the distance between two neighboring O atoms along with sapphire [0001] direction (c-axis lattice constant of sapphire) matches the four-fold longer constants of CuScO$_2[3R]|\overline{1}1\overline{2}0|$ with less than a 0.98% misfit. On the contrary, if (ScO$_2$)$^-$ octahedral layers form the CuScO$_2[3R](0001)$ plane, the O atoms of the layers form bonds with Al atoms on the sapphire surface. In this case, the distance between two neighboring Al atoms along with sapphire $[2\overline{2}01]$ direction matches the three-fold longer constants of CuScO$_2[3R]|\overline{1}1\overline{2}0|$ with less than a 0.98% misfit when the in-plane orientation relationship between the substrate and the film is CuScO$_2[3R]|\overline{1}1\overline{2}0|$/sapphire$[2\overline{2}01]$ [Fig. 2-26(b)]. The angle between sapphire $[2\overline{2}01]$ and $[\overline{1}00]$ directions is 38.24°, as shown in Fig. 2-25. Therefore, the angle between CuScO$_2[3R]$ $|\overline{1}1\overline{2}0|$ and sapphire $[\overline{1}\overline{1}00]$ directions is 8.24°. This agrees well with the result shown in Fig. 2-18.

Consequently, it is presumed that two kinds of in-plane orientation for the epitaxial growth of CuScO$_2[3R](0001)$ thin films on a-plane sapphire substrates are influenced by the atomic arrangements (Cu$^+$ layers or (ScO$_2$)$^-$ octahedral layers) of the initial growth of the films.
Fig. 2-25 Schematic representation of sapphire \((11\bar{2}0)\) plane. Large and small dark circles represent O and Al atoms, respectively [8]. Table summarizes the length between neighboring Al atoms in a distorted hexagonal lattice.
Fig. 2-26 Schematic diagram of a lattice for CuScO$_2$[3R](0001) and sapphire ($\{1\bar{1}2\bar{0}\}$) planes. CuScO$_2$[3R](0001) epitaxial films with two kinds of in-plane orientation are possible to be grown on a-plane sapphire substrates by the atomic arrangements of the initial growth of the films, and their in-plane orientation relationships are as follows:

(a) CuScO$_2$[3R]$[1\bar{1}\bar{2}0]$ // sapphire $[0001]$

(b) CuScO$_2$[3R]$[1\bar{1}\bar{2}0]$ // sapphire $[2\bar{2}01]$
2.3.5 Chemical composition and optical property of CuScO$_2$[3R](0001) epitaxial film

The chemical composition of the film with CuScO$_2$[3R][1120]/sapphire[2201] in-plane orientation was analyzed by RBS. The following parameters were used in the simulation: density 4.050 g/cm$^3$ and compositional ratio Al:O = 2.0:3.0 for the sapphire substrate, and density 4.574 g/cm$^3$, compositional ratio Cu:Sc:O = 1.0:1.0:2.0 and film thickness 50 nm for the CuScO$_2$[3R](0001) epitaxial film. Figure 2-27 shows the simulation and experimental results. The simulation showed good agreement with the experimental data. Accordingly, the chemical composition of the epitaxial film was found to be stoichiometry; that is, Cu:Sc:O = 1.0:1.0:2.0.

The average optical transmittance of the film, shown in Fig. 2-28, was larger than 80% in wavelengths ranging from 400 to 2500 nm. The direct energy gap calculated using $(\alpha \cdot h \nu)^2$ versus $h \nu$ plots in the inset was 3.7 eV. This value is consistent with the CuScO$_2$[3R] polycrystalline powders [9,10].

2.4 Conclusion

CuScO$_2$ thin films were deposited on a-plane sapphire substrates at various substrate temperatures, oxygen pressures, and laser fluences by PLD using a single-phase Cu$_2$Sc$_2$O$_5$ target to obtain CuScO$_2$(0001) epitaxial films to be used as thin epitaxial layers in a solid-phase epitaxy method. CuScO$_2$[3R](0001) epitaxial films with different in-plane orientations were obtained on a-plane sapphire substrates by changing laser fluences during deposition. Two kinds of in-plane orientation relationships of the films with respect to the substrates were CuScO$_2$[3R][1120]/sapphire[0001] and
Fig. 2-27 (a) RBS simulation model of a CuScO$_2$[3R](0001) epitaxial film grown on an a-plane sapphire substrate. (b) RBS simulation and experimental results of a CuScO$_2$[3R](0001) epitaxial film prepared on an a-plane sapphire substrate.
Fig. 2-28 Optical transmission spectrum of a CuScO$_2$[3R](0001) epitaxial film in the visible/near-IR region. The direct energy gap obtained from $(\alpha h \nu)^2$ versus $h \nu$ plots in the inset was 3.7 eV.
CuScO$_2$[3R]||120|| sapphire [2201], and are presumed to be influenced by the atomic arrangements (Cu$^+$ layer or (ScO$_2$)$^-$ layer) of the initial growth of the films. They showed six-fold rotational symmetry in the basal plane, indicating that the films had a twinned domain structure.

The chemical composition of a 50-nm-thick CuScO$_2$[3R](0001) epitaxial film with CuScO$_2$[3R]||120|| sapphire [2201] in-plane orientation was confirmed to be stoichiometric by RBS. The average optical transmittance of the film was greater than 80\% for wavelengths from 400 to 2500 nm, while the energy gap estimated for a direct allowed transition was 3.7 eV.

References


Chapter 3. Structural, Optical and Electrical Transport Properties of CuScO$_2$[3R](0001) Epitaxial Thick Films

3.1 Introduction

As described in chapter 2, CuScO$_2$[3R](0001) epitaxial films to be used as thin epitaxial layers were obtained. According to the solid-phase epitaxy method, a 300-nm-thick CuScO$_2$ amorphous film was deposited on the epitaxial film at room temperature, followed by the post-annealing treatment. As a result, a 300-nm-thick CuScO$_2$(0001) epitaxial film grew on an a-plane sapphire substrate, but showed intergrowth structures with stacking faults along the c-axis, as shown in Fig. 3-1. This suggests that CuScO$_2$ with intergrowth structures may be a most stable structure, because most of the powder preparations of CuScO$_2$ have been reported to yield a mixture of the two phases \cite{1}. Therefore, CuScO$_2$ amorphous thick films were converted into CuScO$_2$[3R] polycrystalline thick films to obtain single-phase CuScO$_2$[3R](0001) epitaxial thick films.

In this chapter, the effects of the oxygen pressure during post-annealing treatment and laser fluence on the film quality of CuScO$_2$[3R] polycrystalline thick films are investigated. CuScO$_2$[3R] thick films with the bilayered structure are then deposited on a-plane sapphire substrates by PLD, and are post-annealed at high temperature. The structural, optical, and electrical transport properties of the films obtained by post-annealing the films with the bilayered structure are also reported.
Fig. 3-1 (a) XRD 2θ-ω pattern and (b-1,b-2,b-3) φ-scans of a 300-nm-thick CuScO₂ thin film fabricated on an a-plane sapphire substrate using a solid-phase epitaxy method. The film with the bilayered structure was fabricated by depositing a CuScO₂ amorphous thick film at room temperature on a thin CuScO₂[3R](0001) epitaxial layer with CuScO₂[3R]l120|| sapphire[0001] in-plane orientation, followed by post-annealing at 1273 K for 1 h under an oxygen pressure of 600 Pa. (b-1) {3030} plane of substrate, (b-2) {1041} plane of CuScO₂[3R] phase, and (b-3) {1013} plane of CuScO₂[2H] phase of the film.
3.2 Experimental

CuScO$_2$[3R] polycrystalline thick films were deposited on a-plane sapphire substrates by PLD to study the effects of the oxygen pressure during post-annealing treatment on the film quality of the films. The as-deposited films with a thickness of 160 nm prepared under the deposition conditions shown in Table 3-I were used as the samples. Figure 3-2(a) shows the XRD $\theta$-$\omega$ pattern of the as-deposited film. Diffraction peaks corresponding to CuScO$_2$[3R] 0003, 0006, 10$\bar{1}$1, 0009, 00012 and 20$\bar{2}$22 were identified. On the other hand, the in-plane orientation relationship between the substrate and the film was investigated by the XRD $\phi$-scan measurements using 0330 diffractions of the substrate, and 10$\bar{1}$4 diffractions of the CuScO$_2$[3R] phase and 10$\bar{1}$3 diffractions of the CuScO$_2$[2H] phase of the film, as shown in Figs. 3-2(b-1), (b-2), and (b-3). For 10$\bar{1}$4 diffractions of the CuScO$_2$[3R] phase of the film, peaks with the mixture of three types of six-fold rotational symmetry components were observed [Fig. 3-2(b)]. Their in-plane orientation relationships are as follows: (●) CuScO$_2$[3R][1120]// sapphire[0001], (▲) CuScO$_2$[3R][1120]// sapphire[2201], and (■) CuScO$_2$[3R][1120]// sapphire[1100]. Consequently, the films are classed as

<table>
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<th>Table 3-I Deposition conditions for CuScO$_2$ thick films prepared by PLD</th>
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<tr>
<td><strong>Substrate temperature (°C)</strong></td>
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<td><strong>Oxygen pressure (Pa)</strong></td>
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<td>rf forward power of oxygen radical source (W)</td>
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<td><strong>Laser fluence (J cm$^{-2}$)</strong></td>
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<td><strong>Laser repetition frequency (Hz)</strong></td>
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Fig. 3-2 (a) XRD 2θ-ω pattern and (b-1,b-2,b-3) φ-scans of a 160-nm-thick CuScO₂[3R] as-deposited film. The film was prepared under the deposition conditions shown in Table 3-I. (b-1) {0330} plane of substrate, (b-2) {1014} plane of CuScO₂[3R] phase and (b-3) {1013} plane of CuScO₂[2H] phase of the film.
Fig. 3-3 Schematic illustration of an electric furnace to post-anneal the samples at various oxygen pressures. The oxygen pressure during the post-annealing treatment was controlled using a mass flow controller (MFC) for an oxygen gas and a conductance valve (C.V.). T.M.P. and R.P. are a turbo molecular pump and a rotary pump, respectively.
CuScO$_2$[3R] polycrystalline films with several preferential orientations along out-of-plane and in-plane directions. The Cu concentration in the films was slightly less than that in the stoichiometric composition.

After deposition, the films were post-annealed at 1423 K for 1 h in an Al$_2$O$_3$ crucible using an electric furnace, as shown in Fig. 3-3. The film surface was placed on an yttria-stabilized zirconia (YSZ) substrate to suppress the volatilization of the elements in the film during the post-annealing treatment. The oxygen pressure during the post-annealing treatment was varied from 5 Pa to 10 kPa. This is because Cu$_2$O, which is the same monovalent copper oxide as CuScO$_2$, is thermodynamically stable within this oxygen pressure range at 1423 K [2].

The electrical transport properties were measured by the van der Pauw method using an ac magnetic field modulation system from 220 to 373 K (TOYO, ResiTest 8310). Four Pt electrodes were deposited by ion beam sputtering and annealed at 773 K for 1 h under an oxygen pressure of 13 Pa to obtain ohmic contacts. The Seebeck coefficient was also measured at 280 K. The structural and optical properties and the composition of the films were evaluated by the same methods used in chapter 2.

### 3.3 Results and Discussion

#### 3.3.1 Effect of oxygen pressure during post-annealing treatment on film quality of CuScO$_2$[3R] polycrystalline thick films

The as-deposited films were post-annealed at various oxygen pressures using an electric furnace. The XRD 20-ø patterns of the as-deposited film and the films post-annealed at various oxygen pressures are shown in Fig. 3-4. The intensities for the
Fig. 3-4 XRD 2θ-ω patterns of the CuScO$_2$ as-deposited film and the films post-annealed at different oxygen pressures (P$_{O_2}$): (a) as-deposited, (b) P$_{O_2}$ = 5 Pa, (c) P$_{O_2}$ = 100 Pa, (d) P$_{O_2}$ = 1 kPa, and (e) P$_{O_2}$ = 10 kPa.
Fig. 3-5 XRD $\phi$-scan measurement of (a) $\{30\overline{3}0\}$ plane of substrate and (b,c,d,e) $\{10\overline{4}\}$ plane of CuScO$_2$[3R] phase of the as-deposited film and the films post-annealed at different oxygen pressures. (b) as-deposited, (c) $PO_2 = 5$ Pa, (d) $PO_2 = 100$ Pa, (e) $PO_2 = 1$ kPa, and (f) $PO_2 = 10$ kPa.
Fig. 3-6 XRD $\phi$-scan measurements of (a) $\{30\overline{3}0\}$ plane of substrate and (b,c,d,e) $\{10\overline{1}3\}$ plane of CuScO$_2$[2H] phase of the as-deposited film and the films post-annealed at various oxygen pressures. (b) as-deposited, (c) PO$_2$ = 5 Pa, (d) PO$_2$ = 100 Pa, (e) PO$_2$ = 1 kPa, and (f) PO$_2$ = 10 kPa.
CuScO$_2$[3R] $000\ell$ [$\ell = 3,6,9,12$] diffraction peaks decreased and a Cu 111 diffraction peak appeared when the film was post-annealed at an oxygen pressure of 5 Pa [Fig. 3-4(b)]. No peaks for 10\bar{1}4 diffractions of the CuScO$_2$[3R] phase and 10\bar{1}3 diffractions of the CuScO$_2$[2H] phase of the film were observed, as shown in Figs. 3-5(c) and 3-6(c). This suggests that the film is reduced due to the thermal decomposition reaction during the post-annealing treatment. Thus, the concentration of Cu in the film significantly decreased, because metallic copper was more volatile than copper oxide. With increasing oxygen pressure during the post-annealing treatment, only diffraction peaks corresponding to CuScO$_2$[3R] $000\ell$ were identified at oxygen pressures of 100 Pa and 1 kPa, as shown in Figs. 3-4(c) and 3-4(d). For 10\bar{1}4 diffractions of the CuScO$_2$[3R] phase of the film, the intensities for the diffraction peaks corresponding to three types of six-fold rotational symmetry components became stronger due to the post-annealing treatment, but the in-plane orientation relationship between the substrate and these films was identical to that of the as-deposited film [Figs. 3-5(d) and 3-5(e)]. On the other hand, no peaks for 10\bar{1}3 diffractions of the CuScO$_2$[2H] phase of the films were detected. The concentration of Cu in these films was still slightly less than that in the as-deposited film. By increasing the oxygen pressure above 1 kPa, the intensities for the peaks corresponding to CuScO$_2$[3R] $000\ell$ diffractions significantly decreased, and additional diffraction peaks corresponding to the CuScO$_2$[3R] 10\bar{1}1, 01\bar{1}2, and 20\bar{2}2 and the Cu$_2$Sc$_2$O$_5$ phase were observed, as shown in Fig. 3-4(e). No peaks for 10\bar{1}4 diffractions of the CuScO$_2$[3R] phase and 10\bar{1}3 diffractions of the CuScO$_2$[2H] phase of the film were detected, as shown in Figs. 3-5(f) and 3-6(f). This suggests that the film post-annealed at an oxygen pressure of 10 kPa is oxidized during the post-annealing treatment. The concentration of Cu in the film became equal to that in the as-deposited film.
The surface morphologies of the as-deposited film and the films post-annealed at various oxygen pressures were examined using SEM. The images are shown in Fig. 3-7. The grain size distribution in the as-deposited film was from 100 to 300 nm, as shown in Fig. 3-7(a). By post-annealing at an oxygen pressure of 5 Pa [Fig. 3-7(b)], the grain size increased and large precipitates with a diameter of greater than 1 µm were observed along with voids generated at the grain boundary. With increasing oxygen pressure up to 1 kPa, grain size still increased and the surface morphology of the films became smoother without any voids [Figs. 3-7(c) and 3-7(d)]. This is because grains grow to make the surface free energy of the film lower during the post-annealing treatment [3]. The close-packed plane of CuScO$_2$ is the (0001) plane and this plane has the lowest surface free energy, thus the CuScO$_2$ film post-annealed at the optimal annealing condition grows with a strong (0001) preferred orientation and a smooth surface. Upon annealing at oxygen pressures above 1 kPa, plate-shaped crystal grains with various orientations were observed [Fig. 3-7(e)]. These changes in surface morphology correspond well to the change in crystallographic results obtained by XRD 2θ-ω measurements.

The optical transmission spectra of the as-deposited film and the films post-annealed at different oxygen pressures are shown in Fig. 3-8. An interference fringe was observed in the spectrum of the as-deposited film, and the average optical transmittance was greater than 75% for the wavelength ranging from 400 to 2500 nm, as shown in Fig. 3-8(a). The interference fringe disappeared from the spectrum of the film post-annealed at an oxygen pressure of 5 Pa, and a decrease in average optical transmittance was observed for wavelengths above 400 nm [Fig. 3-8(b)]. This is because other phases such as the copper were generated in the film due to the thermal decomposition reaction during the post-annealing treatment, as shown in Fig. 3-4(b).
Fig. 3-7 SEM images of the CuScO$_2$ as-deposited film and the films post-annealed at various oxygen pressures (PO$_2$): (a) as-deposited, (b) PO$_2$ = 5 Pa, (c) PO$_2$ = 100 Pa, (d) PO$_2$=1 kPa, and (e) PO$_2$ = 10 kPa. The post-annealing temperature and the holding time were 1423 K and 1 h, respectively.
Fig. 3-8 Optical transmission spectra in the visible/near-IR regions of the CuScO$_2$ as-deposited film and the films post-annealed at different oxygen pressures: (a) as-deposited, (b) PO$_2$ = 5 Pa, (c) PO$_2$ = 100 Pa, (d) PO$_2$ = 1 kPa, and (e) PO$_2$ = 10 kPa.
The films post-annealed at oxygen pressures of 100 Pa and 1 kPa exhibited optical transmission spectra similar to that of the as-deposited film [Figs. 3-8(c) and 3-8(d)]. However, a different optical transmission spectrum, shown in Fig. 3-8(e), was also observed at an oxygen pressure of 10 kPa. This is because the Cu$_2$Sc$_2$O$_5$ phase mixed with the film owing to the oxidation during the post-annealing treatment, as shown in Fig. 3-4(e).

Consequently, the out-of-plane orientation of the as-deposited film was improved by post-annealing at oxygen pressures from 100 Pa to 1 kPa. However, the improvement of the in-plane orientation of the as-deposited film and the conversion of the phase in the as-deposited film did not observe due to the post-annealing treatment.

### 3.3.2 Effect of laser fluence on the out-of-plane and in-plane orientations of CuScO$_2$[3R] polycrystalline thick films

It is very important to control the in-plane orientation of CuScO$_2$[3R] polycrystalline thick films, because the in-plane orientation of the as-deposited films was not improved due to the post-annealing treatment. Therefore, on the basis of results obtained in sub-section 2.3.4, the out-of-plane and in-plane orientations of CuScO$_2$ thick films were investigated with changing laser fluence. Other deposition parameters are as follows: a substrate temperature of 900 °C, an oxygen pressure of 4.5 Pa, an rf power of the oxygen radical source of 0 W, a laser repetition frequency of 10 Hz, and a deposition time of 2 h.

Figure 3-9 shows the XRD 20-ω patterns of CuScO$_2$ thick films deposited at various laser fluences. Additional diffraction peaks corresponding to Cu$_2$O 110 and 220 were observed when the film was deposited at a laser fluence of 1.0 Jcm$^{-2}$ [Fig. 3-9(b)]. With increasing laser fluence, peaks corresponding to Cu$_2$O 110 and 220 diffractions
Fig. 3-9 XRD 2θ-ω patterns of CuScO2 thin films deposited on a-plane sapphire substrates at various laser fluencies: (a) substrate, (b) 1.0 Jcm⁻², (c) 1.6 Jcm⁻², and (d) 2.6 Jcm⁻². Other deposition parameters are a substrate temperature of 900 °C, an oxygen pressure of 4.5 Pa, an rf forward power of the oxygen radical source of 0 W, a laser repetition frequency of 10 Hz, and a deposition time of 2 h.
Fig. 3-10 XRD $\phi$-scan measurements of $\{30\bar{3}0\}$ plane of a-plane sapphire substrate and $\{1\bar{0}14\}$ plane of CuScO$_2$[3R] thick films deposited at various laser fluences: (a) substrate, (b) 1.0 Jcm$^{-2}$, (c) 1.6 Jcm$^{-2}$, (d) 2.6 Jcm$^{-2}$. The symbols used in this figure indicate the domains with different in-plane orientation relationships:

- (●) CuScO$_2$[3R] $[1\bar{1}20]//\text{sapphire}[0001]$,  
- (▲) CuScO$_2$[3R] $[1\bar{1}20]//\text{sapphire}[2\bar{2}01]$,  
- (■) CuScO$_2$[3R] $[1\bar{1}20]//\text{sapphire}[\bar{1}1\bar{0}0]$.  

Fig. 3-11 XRD $\phi$-scan measurements of $\{30\overline{3}0\}$ plane of a-plane sapphire substrate and $\{\overline{1}0\overline{1}3\}$ plane of CuScO$_2$[2H] phase of CuScO$_2$ thick films deposited at various laser fluences: (a) substrate, (b) 1.0 Jcm$^{-2}$, (c) 1.6 Jcm$^{-2}$, and (d) 2.6 Jcm$^{-2}$.
disappeared and another additional diffraction peaks corresponding to CuScO$_2$[3R] 10\( \bar{1} \)1 and 20\( \bar{2} \)2 were detected and their intensities became stronger, as shown in Figs. 3-9(c) and 3-9(d). On the other hand, the in-plane orientation relationship between the substrate and the film was investigated by the XRD \( \phi \)-scan measurements using 3030 diffractions of the substrate, and 10\( \bar{1} \)4 diffractions of the CuScO$_2$[3R] phase and 10\( \bar{1} \)3 diffractions of the CuScO$_2$[2H] phase of the films. The mixture of three types of six-fold rotational symmetry components for 10\( \bar{1} \)4 diffractions of the CuScO$_2$[3R] phase of all films were confirmed, as shown in Fig. 3-10. Diffraction peaks corresponding to CuScO$_2$[3R]1120//sapphire[0001] in-plane orientation grew preferentially for the film deposited at a laser fluence of 1.0 Jcm$^{-2}$ [Fig. 3-10(b)]. The intensities for these diffraction peaks became smaller with increasing laser fluence and peaks corresponding to other six-fold rotational symmetry components with CuScO$_2$[3R]1120//sapphire[2\( \bar{2} \)01] and CuScO$_2$[3R]1120//sapphire[\( \bar{1} \)00] in-plane orientations started to be preferential, as shown in Figs. 3-10(c) and 3-10(d). However, only peaks with CuScO$_2$[3R]1120//sapphire[2\( \bar{2} \)01] in-plane orientation could be preferentially grown. On the other hand, peaks corresponding to CuScO$_2$[2H]1120//sapphire[0001] in-plane orientation were observed for 10\( \bar{1} \)3 diffractions of the CuScO$_2$[2H] phase of the film deposited at a laser fluence of 1.0 Jcm$^{-2}$ [Fig. 3-11(b)]. However, no peaks for 10\( \bar{1} \)3 diffractions of the CuScO$_2$[2H] phase of the films were detected with increasing laser fluence [Figs. 3-11(c) and 3-11(d)].

Consequently, we adopted the CuScO$_2$[3R]1120//sapphire[0001] in-plane orientation as the in-plane orientation of CuScO$_2$ thin films with the bilayered structure in order to obtain CuScO$_2$[3R](0001) epitaxial thick films by a solid-phase epitaxy method combining two-step deposition and post-annealing techniques.
3.3.3 Fabrication of CuScO$_2$[3R](0001) epitaxial thick films using a solid-phase epitaxy method

Based on the studies described in sub-sections 3.3.1 and 3.3.2, CuScO$_2$ thick films with the bilayered structure that had an in-plane orientation relationship of CuScO$_2$[3R][1120]/sapphire[0001] were deposited on a-plane sapphire substrates by PLD. To prevent the growth of CuScO$_2$[2H] phase in the film, the deposition of the CuScO$_2$ polycrystalline thick layer was carried out at a substrate temperature of 940 °C. The two-step deposition conditions used in this study are summarized in Table 3-II. The deposited films were post-annealed at 1423 K for 1 h in an oxygen atmosphere at 200 Pa in an Al$_2$O$_3$ crucible using an electric furnace. The surface of the film was placed on an YSZ substrate to suppress the volatilization of the elements in the film during the post-annealing treatment. CuO powder was also set into the Pt crucible during the post-annealing treatment to prevent the volatilization of copper from the film surface.

The XRD 2θ-ω pattern of a 250-nm-thick film is shown in Fig. 3-12. Only CuScO$_2$ 000ℓ diffraction peaks were observed, indicating that the film is oriented with the c-axis perpendicular to the substrate. Next, the crystallographic structure of the c-axis-oriented thick film was confirmed by two-dimensional X-ray reciprocal space mapping measurements. As shown in Fig. 3-13, diffractions corresponding to 000ℓ ($ℓ_0 = 3,6,9,12$), 101ℓ ($ℓ_1 = 1,2,4,5,7,8,10,14$), and 202ℓ ($ℓ_2 = 1,2,4,7,8$) of the CuScO$_2$[3R] phase, together with those corresponding to 1120, 2240 and 3030 of sapphire were observed, suggesting that the film is single-phase with a rhombohedral crystal structure.

The results of the XRD φ-scan measurements using 3030 diffractions of the substrate and 1014 diffractions of the c-axis-oriented CuScO$_2$[3R] thick film are shown in Fig. 3-14. A similar in-plane orientation relationship as that for a thin
Table 3-II Deposition conditions for CuScO$_2$ thick films with bilayered structure prepared by PLD.

1) CuScO$_2$[3R](0001) epitaxial layer

<table>
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<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Substrate temperature (°C)</td>
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<tr>
<td>Oxygen pressure (Pa)</td>
<td>1.5</td>
</tr>
<tr>
<td>rf forward power of oxygen radical source (W)</td>
<td>200</td>
</tr>
<tr>
<td>Laser fluence (J cm$^{-2}$)</td>
<td>0.6</td>
</tr>
<tr>
<td>Laser repetition frequency (Hz)</td>
<td>1</td>
</tr>
<tr>
<td>Deposition rate (nm h$^{-1}$)</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

2) CuScO$_2$[3R] polycrystalline thick layer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Substrate temperature (°C)</td>
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</tr>
<tr>
<td>Oxygen pressure (Pa)</td>
<td>4.5</td>
</tr>
<tr>
<td>rf forward power of oxygen radical source (W)</td>
<td>0</td>
</tr>
<tr>
<td>Laser fluence (J cm$^{-2}$)</td>
<td>1.0</td>
</tr>
<tr>
<td>Laser repetition frequency (Hz)</td>
<td>10</td>
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<tr>
<td>Deposition rate (nm h$^{-1}$)</td>
<td>80</td>
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</table>
Fig. 3-12 XRD 2θ-ω pattern of a 250-nm-thick CuScO$_2$ thin film obtained by a solid-phase epitaxy method using CuScO$_2$[3R] polycrystalline thick layers.
Fig. 3-13 Two-dimensional X-ray reciprocal space mapping measurements of a 250-nm-thick CuScO$_2$(0001) thin film. Diffractions corresponding to $000\ell_0$, $[\ell_0 = 3,6,9,12]$, $10\ell_1$, $[\ell_1 = 1,2,4,5,7,8,10,14]$, and $20\ell_2$, $[\ell_2 = 1,2,4,7,8]$ of CuScO$_2$[3R] phase were observed. “S” denotes substrate.
Fig. 3-14 XRD φ-scans of a-plane sapphire substrate and CuScO$_2$[3R](0001) thin film. (a) $\{30\overline{3}0\}$ plane of substrate, (b) $\{1\overline{0}14\}$ plane of CuScO$_2$[3R] phase of the film.
Fig. 3-15 XRD rocking curves for the as-deposited CuScO$_2$ thick film before the post-annealing treatment and the epitaxial thick film fabricated by post-annealing the as-deposited CuScO$_2$ thick film:

(a) CuScO$_2[3R]$ 0006 peak (out-of-plane crystallinity)

(b) CuScO$_2[3R]$ 1014 peak (in-plane crystallinity)
CuScO$_2$[3R](0001) epitaxial layer to be used in this study was observed for the 250-nm-thick film. This indicates that CuScO$_2$[3R](0001) thick film can be grown epitaxially on a-plane sapphire substrates by a solid-phase epitaxy method. The orientation relationships of the film with respect to the substrate were CuScO$_2$[3R](0001)//sapphire(1120) and CuScO$_2$[3R][1120]//sapphire[0001]. The crystallinity along both out-of-plane and in-plane directions of the epitaxial thick film was evaluated using XRD rocking curve of the CuScO$_2$[3R] 0006- and 1014-peaks. The results compared with those of the as-deposited thick film before the post-annealing treatment are shown in Fig. 3-15. The FWHMs corresponding to the CuScO$_2$[3R] 0006- and 1014-peaks were 0.247° and 0.508° for the as-deposited film and 0.182° and 0.272° for the epitaxial film, respectively. Consequently, the out-of-plane and in-plane crystallinity of the film was significantly improved due to the post-annealing treatment. The a- and c-axis lattice constants of the film estimated from the vicinity of the CuScO$_2$[3R] 1014 and 00012 reflections using two-dimensional X-ray reciprocal space mapping measurements were 0.3214 nm and 1.710 nm, and were almost in agreement with the ones reported in the Joint Committee for Powder Diffraction Files (JCPDF) file No. 79-0599 (CuScO$_2$[3R]: a = 0.3216 nm, c = 1.7089 nm) [4].

### 3.3.4 Optical and electrical transport properties of CuScO$_2$[3R](0001) epitaxial thick films

The optical transmission of the 250-nm-thick epitaxial film, shown in Fig. 3-16, was higher than 60% for wavelengths greater than 500 nm and 85% for wavelengths ranging from 800 to 2500 nm. The direct energy gap calculated using ($\alpha h\nu$)$^2$ versus $h\nu$ plots in the inset of Fig. 3-16 was 3.7 eV. This value is almost consistent with the ones obtained in previous reports [5].
Fig. 3-16 Optical transmission spectrum of the 250-nm-thick CuScO$_2$[3R](0001) epitaxial film in the visible/near-IR region. The direct energy gap obtained from $(\alpha h\nu)^2$ versus $h\nu$ plots in the inset was 3.7 eV.
Fig. 3-17 Temperature dependences on (a) electrical conductivity ($\sigma$), (b) carrier concentration ($n_p$), and (c) Hall mobility ($\mu$) of the 250-nm-thick CuScO$_2$[3R](0001) epitaxial film. The activation energy estimated from the temperature dependence on the carrier concentration of the film was 0.62 eV.
The Hall and Seebeck coefficients of the film were $+1.4 \times 10^2$ cm$^3$C$^{-1}$ and $+968$ µVK$^{-1}$ at room temperature, indicating p-type conduction. The origin of p-type conduction is presumed to be ionized copper vacancies or interstitial oxygen ions, such as Cu$_2$O [6]. The electrical conductivity ($\sigma$), carrier concentration ($n_p$) and Hall mobility ($\mu$) of the film were $1.0 \times 10^{-3}$ Scm$^{-1}$, $4.5 \times 10^{16}$ cm$^{-3}$, and $1.4 \times 10^{-1}$ cm$^2$V$^{-1}$s$^{-1}$ at room temperature, respectively.

The temperature dependences of the electrical conductivity, carrier concentration, and Hall mobility of the film were measured between 220 and 373 K, as shown in Fig. 3-17. The temperature dependence of the electrical transport properties of the film exhibited semiconducting characteristics, and the increase in the electrical conductivity and carrier concentration and the decrease in the Hall mobility of the film were observed with increasing temperature. The activation energy estimated from the slope as shown in Fig. 3-17(b) was as high as 0.62 eV.

3.4 Conclusion

CuScO$_2$[3R](0001) epitaxial thick films were successfully obtained by a solid-phase epitaxy method using CuScO$_2$[3R] polycrystalline thick films as CuScO$_2$ thick layers. A 250-nm-thick film was single-phase with a rhombohedral crystal structure and showed six-fold rotational symmetry in the basal plane, indicating that the film had a twinned domain structure. The orientation relationships of the film with respect to the substrate were CuScO$_2$[3R](0001)//sapphire ($\bar{1}1\bar{2}0$) and CuScO$_2$[3R]$\bar{1}1\bar{2}0$//sapphire [0001]. The a- and c-axis lattice constants of the film were 0.3214 nm and 1.710 nm, and were almost in agreement with the ones reported in
The Joint Committee for Powder Diffraction Files (JCPDF) file No. 79-0599 (CuScO$_2$[3R]: a = 0.3216 nm, c = 1.7089 nm).

The average optical transmittance of the film was greater than 60 % in the visible region and 85 % in wavelengths ranging from 800 to 2500 nm, and the energy gap for direct allowed transition was estimated to be 3.7 eV.

The electrical property of CuScO$_2$[3R] was first estimated by the Hall effect measurement. The Hall and Seebeck coefficients of the film were +1.4×10$^2$ cm$^3$C$^{-1}$ and +968 $\mu$VK$^{-1}$ at room temperature, indicating p-type conduction. The electrical conductivity, carrier concentration, and Hall mobility of the film at room temperature were 1.0×10$^{-3}$ Sm$^{-1}$, 4.5×10$^{16}$ cm$^{-3}$, and 1.4×10$^{-1}$ cm$^2$V$^{-1}$s$^{-1}$, respectively. The temperature dependences of the electrical transport properties of the film exhibited semiconducting behavior, and the activation energy estimated from the temperature dependence of the carrier concentration was 0.62 eV.

References

Chapter 4. Structural, Optical and Electrical Transport Properties of CuScO$_2$[3R](0001) Epitaxial Films Intercalated with Excess Oxygen

4.1 Introduction

As described in chapter 1, holes in CuScO$_2$ can be induced by intercalating with excess oxygen and by substituting divalent species for Sc sites [1]. Especially, the former has been reported to be a very effective method for improving the p-type electrical conductivity of CuScO$_2$ polycrystalline films and bulks in spite of increasing the Cu-Cu distance in CuScO$_2$ [1-3]. However, there are no reports on the control of the carrier concentration in CuScO$_2$ through the excess oxygen intercalation.

In this chapter, CuScO$_2$[3R](0001) epitaxial films prepared using the solid-phase epitaxy method described in chapter 3 are exposed to oxygen plasma in the PLD chamber to intercalate with excess oxygen. The structural, optical and electrical transport properties of the films intercalated with excess oxygen are investigated.

4.2 Experimental

According to the fabrication method of the epitaxial films described in chapter 3, a 80-nm-thick CuScO$_2$[3R](0001) epitaxial film was prepared on an a-plane sapphire substrate to evaluate the thickness of the excess oxygen intercalation layer. The film was divided in two and one of them was then exposed to oxygen plasma in the PLD
chamber to intercalate with excess oxygen, as shown in Fig. 2-1. The oxygen plasma annealing conditions to intercalate with excess oxygen into the film is listed in Table 4-I. The depth measurement using XPS equipped with Ar ion etching (ULVAC Phi, Model 5700) was conducted for two kinds of films before and after excess oxygen intercalation treatment. Figure 4-1 shows the depth profiles of the integrated intensity of O1s peak for both films. The thickness of the excess oxygen intercalated layer from the film surface was found to be about 60 nm by comparing the depth profiles for both films. Therefore, a 40-nm-thick CuScO$_2$[3R](0001) epitaxial film was used as a sample in this study, because the whole film was intercalated with excess oxygen due to the oxygen plasma annealing conditions listed in Table 4-I.

The electrical conductivity of the film was measured using the van der Pauw method from 30 K to 300 K with sputtered Pt electrodes. Four Pt electrodes were deposited by ion beam sputtering and annealed at 773 K for 1 h under an oxygen pressure of 13 Pa to obtain ohmic contacts. The dependence on temperature of the Seebeck coefficient was also measured. A temperature gradient of about 6 K was established across the film at a given temperature, and the resulting thermoelectric voltage was measured from 140 K to 300 K (TOYO, ResiTest 8310). The structural and optical properties of the films were evaluated by the same methods used in chapter 2.

Table 4-I Oxygen plasma annealing conditions to intercalate with excess oxygen into CuScO$_2$[3R](0001) epitaxial films

<table>
<thead>
<tr>
<th>Substrate temperature (K)</th>
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<tbody>
<tr>
<td>Oxygen pressure (Pa)</td>
<td>13</td>
</tr>
<tr>
<td>rf forward power of oxygen radical source (W)</td>
<td>200</td>
</tr>
<tr>
<td>Annealing time (h)</td>
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</table>
Fig. 4-1 Depth profiles of the integrated intensity of oxygen 1s peak for CuScO$_2$[3R](0001) epitaxial films before and after excess oxygen intercalation treatment using XPS equipped with Ar ion etching.
4.3 Results and Discussion

4.3.1 Structural property of CuScO$_2$[3R](0001) epitaxial films intercalated with excess oxygen

A 40-nm-thick CuScO$_2$[3R](0001) epitaxial film was exposed to oxygen plasma in the PLD chamber to intercalate with excess oxygen. The XRD $2\theta$-$\omega$ pattern and the XRD $\phi$-scans using 3030 diffractions of the substrate and 1014 diffractions of the CuScO$_2$[3R] phase of the film are shown in Figs. 4-2 and 4-3, respectively. The out-of-plane and in-plane orientations of the film against the substrate were identical to those of the epitaxial film before excess oxygen intercalation treatment, and the orientation relationship for the film with respect to the substrate were CuScO$_2$[3R]$//$(11$ar{2}$0) and CuScO$_2$[3R]$//$(11$ar{2}$0). The FWHMs taken from the CuScO$_2$[3R] 0006- and 1014-peak rocking curve measurements for the film slightly increased compared with those for the film before excess oxygen intercalation treatment and were 0.247° and 0.348°, respectively. The a- and c-axis lattice constants of the film, shown in Fig. 4-4, were estimated from the CuScO$_2$[3R] 10$ar{1}$4 and 00012 reflections using two-dimensional X-ray reciprocal space mapping measurements, and were 0.3216 nm and 1.711 nm, respectively. The slight increase in the c-axis lattice constant was observed compared with that of the undoped epitaxial film obtained in chapter 3 (a = 0.3214 nm, c = 1.710 nm).

4.3.2 Optical property of CuScO$_2$[3R](0001) epitaxial films intercalated with excess oxygen

The optical transmission spectra of the epitaxial films before and after excess oxygen intercalation treatment are shown in Fig. 4-5. Similar optical transmission
Fig. 4-2 XRD 2θ-ω pattern of a CuScO$_2$[3R] (0001) epitaxial film intercalated with excess oxygen. The thickness of the film was about 40 nm.
Fig. 4-3 XRD φ-scans of a-plane sapphire substrate and CuScO$_2$[3R](0001) epitaxial film intercalated with excess oxygen.

(a) $\{30\bar{3}0\}$ plane of the substrate, (b) $\{10\bar{1}4\}$ plane of the film.
Fig. 4-4 Two-dimensional X-ray reciprocal space mapping measurements taken in the vicinity of the 10\overline{1}1_4 and 000\overline{1}_2 CuScO_2[3R] reflections for the CuScO_2[3R](0001) epitaxial film intercalated with excess oxygen.
Fig. 4-5 Optical transmission spectra of CuScO$_2$[3R](0001) epitaxial films before and after excess oxygen intercalation treatment in visible/near-IR regions. The direct energy gap obtained from $\alpha h \nu^2$ versus $h \nu$ plots of the film intercalated with excess oxygen in the inset was 3.7 eV.
spectra were observed for both films. The average optical transmittance of the film before excess oxygen intercalation treatment was greater than 85% for a wavelength from 400 to 2500 nm. However, a decrease in the average optical transmittance was observed for the film after excess oxygen intercalation treatment at a wavelength greater than 400 nm, and the average optical transmittance was larger than 75% for the wavelength above 400 nm. This decrease in the average optical transmittance is because the fraction of Cu$^{2+}$ cations in the film increase due to hole carriers introduced by excess oxygen. The energy gap of the film after excess oxygen intercalation treatment was 3.7 eV for direct allowed transition calculated from the plot of $(\alpha h\nu)^2$ versus $h\nu$ shown in the inset of Fig. 4-5. This value was identical to the film before excess oxygen intercalation treatment and was larger than the one obtained in CuScO$_{2+X}$ polycrystalline film [2].

### 4.3.3 Conduction mechanism of CuScO$_2$[3R](0001) epitaxial films intercalated with excess oxygen

Annealing by using oxygen radicals drastically increased the electrical conductivity ($\sigma$) of the film from $1.4\times10^{-7}$ Scm$^{-1}$ to 2.7 Scm$^{-1}$ at room temperature. The Seebeck coefficient of the film intercalated with excess oxygen was as low as +14 $\mu$VK$^{-1}$ at room temperature. This indicates that a number of holes are induced in the film by the excess oxygen intercalation. However, the dependence on temperature of the electrical conductivity of the film exhibited semiconducting behavior, as shown in Fig. 4-6. On the other hand, the Seebeck coefficient of the film did not show temperature dependence above 140 K, as shown in Fig. 4-7(a). This suggests that the dominant conduction mechanism above 140 K is a small polaron conduction, which causes the mobility to be thermally activated [4]. In this conduction mechanism, the form of the
Fig 4-6 Dependence on temperature of electrical conductivity of the CuScO$_2$[3R](0001) epitaxial film intercalated with excess oxygen.
Fig. 4-7 (a) Temperature dependences of the electrical conductivity- temperature product ($\sigma T$) and Seebeck coefficient ($Q$) of the CuScO$_2$[3R](0001) epitaxial film intercalated with excess oxygen between 140 K and 300 K.

(b) Electrical conductivity ($\sigma$) as a function of $T^{-1/4}$ of the CuScO$_2$[3R](0001) epitaxial film intercalated with excess oxygen between 30 K and 140 K.
electrical conductivity is given by

\[ \sigma = \frac{\sigma_0}{T} \exp \left( - \frac{E_H}{k_B T} \right), \tag{4-1} \]

where \( \sigma_0 \), the preexponential factor, is \( 4.2 \times 10^4 \) Scm\(^{-1} \), \( E_H \) is the hopping energy, and \( k_B \) is Boltzmann’s constant. A linear relationship between \( \log (\sigma T) \) and \( T^{-1} \), shown in Fig. 4-7(a), was observed, and the hopping energy obtained was about 0.10 eV. This value is mostly consistent with the one (0.11 eV) reported in CuScO\(_{2+x}\) polycrystalline films [2].

On the other hand, the Seebeck coefficient for small polaron conductors is given by [4]

\[ Q = \pm \frac{k_B}{e} \ln \left[ \frac{\beta(1-c)}{c} \right], \tag{4-2} \]

where \( e \) is the unit of electron charge, \( \beta \), the spin degeneracy factor, is typically 2, \( c \) is the fraction of the sites occupied by holes, and the entropy of the transport term has been neglected. In this equation, the Seebeck coefficient does not show dependence on the temperature. This is in agreement with the experimental results, as shown in Fig. 4-7(a).

With further decreases in temperature below 140 K, the electrical conductivity of the film decreased, as shown in Fig. 4-6. A linear relationship between \( \log \sigma \) and \( T^{-1/4} \), shown in Fig. 4-7(b), was observed from 30 K to 140 K. This indicates that the carrier transport of the film obeys the three-dimensional variable-range hopping conduction due to the localization of the holes below 140 K.

Consequently, a number of holes can be induced near the film surface of CuScO\(_2\)[3R](0001) epitaxial films by the excess oxygen intercalation using oxygen radical annealing, and significantly increase the electrical conductivity of the films at room temperature. However, the dominant electrical conduction of the films at room
temperature changes to the thermally activated small polaron conduction due to the strong hole-phonon interaction. This suggests that it is very difficult to control the carrier concentration in CuScO$_2$ [3R](0001) epitaxial thick films through the excess oxygen intercalation using an oxygen radical source.

### 4.4 Conclusion

Excess oxygen was intercalated in a 40-nm-thick CuScO$_2$[3R](0001) epitaxial film by annealing using oxygen radicals, and the structural, optical, and electrical transport properties of the film were investigated.

The out-of-plane and in-plane orientations of the film against the substrate were identical to those of the film before excess oxygen intercalation treatment. The a- and c-axis lattice constants of the film were 0.3216 nm and 1.711 nm. The slight increase in the c-axis lattice constant was observed compared with that of the undoped epitaxial film described in chapter 3 (a = 0.3214 nm, c = 1.710 nm).

The decrease in the average optical transmittance was observed for the film at wavelengths greater than 400 nm. This is because the fraction of Cu$^{2+}$ cations in the film increase due to hole carriers introduced by excess oxygen. The energy gap of the film was 3.7 eV for direct allowed transition calculated from the plot of $(\alpha h\nu)^2$ versus $h\nu$, and was identical to that of the film before excess oxygen intercalation treatment.

The electrical conductivity of the film significantly increased from $1.4 \times 10^{-7}$ S/cm$^{-1}$ to 2.7 S/cm$^{-1}$ at room temperature and the Seebeck coefficient was about $+14 \mu$VK$^{-1}$ at room temperature. This indicates that a number of holes are induced in the film by the excess oxygen intercalation. However, the dependence on temperature of the electrical
conductivity of the film exhibited semiconducting behavior, and the Seebeck coefficient of the film did not show temperature dependence above 140 K. This indicates that the dominant conduction mechanism of the film from 140 K to 300 K is the thermally activated small polaron conduction caused by the strong hole-phonon interaction. With decreasing temperature below 140 K, the three-dimensional variable range hopping conduction was dominant because of the localization of the holes.

Accordingly, it is very difficult to control the carrier concentration in CuScO$_2$[3R](0001) epitaxial thick films through the excess oxygen intercalation using an oxygen radical source. This is because a number of holes generated by the excess oxygen exist near the film surface and the dominant electrical conduction of the excess oxygen layers at room temperature changes to the thermally activated small polaron conduction due to the strong hole-phonon interaction. However, the excess oxygen layer intercalated near the film surface is very useful for preparing the ohmic contacts between CuScO$_2$ and metals such as Pt and Ni.

References

Chapter 5. Effect of Mg Doping in the Sc-sites on Structural, Optical and Electrical Transport Properties of CuScO$_2$[3R](0001) Epitaxial Thick Films

5.1 Introduction

There are some reports on the optical and electrical properties of Mg-doped CuScO$_2$ polycrystalline films and pellets substituting Mg ions for Sc sites [1-5]. This is because the ion radius of Mg$^{2+}$ (72 pm) is slightly smaller than that of Sc$^{3+}$ (74.5 pm) [6,7] and the Cu-Cu distance (a-axis lattice constant) in CuScO$_2$ is presumed to decrease, that is, increase the electrical conductivity. However, the p-type electrical conductivity of CuScO$_2$ polycrystalline films and pellets is slightly improved by the Mg doping in the Sc-site and the reason has been unknown yet.

In this chapter, Mg-doped CuScO$_2$ thick films with different Mg concentrations are prepared using the solid-phase epitaxy method described in chapter 3. The effects of Mg doping in the Sc-site on the structural, optical, and electrical transport properties of CuScO$_2$ thick films are investigated by comparing them with those of the undoped epitaxial thick film described in chapter 3.

5-2 Experimental

According to the fabrication method described in Section 3, the Mg-doped CuScO$_2$ thick films with a bilayered structure consisting of thin CuScO$_2$[3R](0001)
Table 5-I Deposition conditions for Mg-doped CuScO$_2$ thick films with two different layers prepared using PLD.

1) CuScO$_2$(3R)(0001) epitaxial layer

<table>
<thead>
<tr>
<th>Target</th>
<th>Cu$_2$Sc$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature (°C)</td>
<td>925</td>
</tr>
<tr>
<td>Oxygen pressure (Pa)</td>
<td>1.5</td>
</tr>
<tr>
<td>rf forward power of oxygen radical source (W)</td>
<td>200</td>
</tr>
<tr>
<td>Laser fluence (J cm$^{-2}$)</td>
<td>0.6</td>
</tr>
<tr>
<td>Laser repetition frequency (Hz)</td>
<td>1</td>
</tr>
<tr>
<td>Deposition rate (nm h$^{-1}$)</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

2) Mg-doped CuScO$_2$ polycrystalline layer

<table>
<thead>
<tr>
<th>Target</th>
<th>Cu$<em>2$(Sc$</em>{1-X,MgX}$)$_2$O$_y$ [X=0.01, 0.05, 0.10]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature (°C)</td>
<td>940</td>
</tr>
<tr>
<td>Oxygen pressure (Pa)</td>
<td>4.5</td>
</tr>
<tr>
<td>rf forward power of oxygen radical source (W)</td>
<td>0</td>
</tr>
<tr>
<td>Laser fluence (J cm$^{-2}$)</td>
<td>1.0</td>
</tr>
<tr>
<td>Laser repetition frequency (Hz)</td>
<td>10</td>
</tr>
<tr>
<td>Deposition rate (nm h$^{-1}$)</td>
<td>45</td>
</tr>
</tbody>
</table>
epitaxial layers and Mg-doped CuScO₂ polycrystalline layers with a 140-nm thickness were deposited by PLD. The deposition conditions of the as-deposited films are listed in Table 5-I. The Cu₂(Sc₁₋ₓMgₓ)₂O₅ [X=0.01, 0.05, 0.10] targets were prepared via an ordinary solid state reaction. A prescribed powder mixture of CuO(99.999%), Sc₂O₃(99.99%), and MgO(99.99%) was ground and heated at 1000°C for 24 hours in an oxygen flow. After being reground, the sintered mass was pressed into pellet form and sintered at 1050°C for 50 hours in an oxygen flow. The targets, whose nominal compositions were Cu:Sc:Mg = 1.00:0.99:0.01, 1.00:0.95:0.05, and 1.00:0.90:0.10, were confirmed using inductively coupled plasma atomic emission spectrometry.

After deposition, the as-deposited films were post-annealed at 1323 K for 30 minutes under an oxygen pressure of 400 Pa in an Al₂O₃ crucible using an electric furnace to obtain the epitaxial films. To suppress the volatilization of the elements in the film during post-annealing, YSZ substrates were placed on the surface of the deposited films, and CuO and MgO powders were also set into the Pt crucible.

The structural and optical, and electrical transport properties of the films were evaluated by the same methods used in chapters 2 and 3. The Mg concentration of the target was used as the Mg concentration of the film in this study.

5.3 Results and Discussion

5.3.1 Preparation of Mg-doped CuScO₂[3R](0001) epitaxial thick films

The out-of-plane and in-plane orientations against the substrate and the a- and c-axis lattice constants of CuScO₂ thick films with different Mg concentrations were compared with those of the undoped epitaxial thick film obtained in Section 3. Figure
5-1 shows the XRD 20-ω patterns of the undoped film and the three kinds of Mg-doped films. Only diffraction peaks corresponding to CuScO$_2$[3R] 000$\ell$ [\(\ell = 3, 6, 9, 12\)] were observed for the 1-at% Mg-doped film, suggesting that the film was strongly oriented with the c-axis perpendicular to the substrate. With increasing Mg concentration in the films, additional diffraction peaks from the orthorhombic Cu$_2$MgO$_3$ 002, 004, and 006 reflections appeared, as shown in Figs. 5-1(c) and 5-1(d). This is because the excess elements, such as Cu and Mg, in the films react during post-annealing and other compounds are formed.

The in-plane orientation relationship between the substrates and the films was investigated with XRD φ-scan measurements using 3030 diffractions of the substrate and 1014 diffractions of the CuScO$_2$[3R] phase of the film. Similar in-plane orientation relationships for the films with respect to the substrates were observed in all Mg-doped films. The results obtained for the 1-at% Mg-doped film are shown in Fig. 5-2. Peaks with two-fold rotational symmetry were observed for 3030 diffractions of the substrate, as shown in Fig. 5-2(a). On the other hand, peaks for 1014 diffractions of the film exhibited six-fold rotational symmetry, indicating that the films had twin structures [Fig. 5-2(b)]. The peaks of the film were in agreement with those of the substrate at the φ diffraction angles of ±90°. Therefore, the in-plane orientation relationships for the films with respect to the substrates are Cu(Sc$_{1-X}$Mg$_X$)$_2$O$_2$[3R]11\overline{2}0]//sapphire[0001] [X=0.01, 0.05, 0.10].

The out-of-plane and in-plane crystallinity of Mg-doped thick films was estimated by the FWHMs taken from the CuScO$_2$[3R] 0006- and 1014-peak rocking curve measurements. Both FWHMs obtained for the 0006- and 1014-peaks increased with increasing Mg concentration in the films, as shown in Fig. 5-3. This indicates that the out-of-plane and in-plane crystallinity of Mg-doped films deteriorates.
Fig. 5-1 XRD 2θ-ω pattern of undoped epitaxial thick film and Mg-doped CuScO$_2$ thick films. Three kinds of Mg-doped films were grown on a-plane sapphire substrates by a solid-phase epitaxy method combining the two-step deposition and post-annealing techniques using Cu$_2$(Sc$_{1-X}$Mg$_X$)$_2$O$_y$ [X=0, 0.01, 0.05, 0.10] targets. (a) undoped (Section 3), (b) 1-at% Mg-doped, (c) 5-at% Mg-doped, and (d) 10-at% Mg-doped films.
Fig. 5-2 XRD $\phi$-scans of a-plane sapphire substrate and 1-at% Mg-doped CuScO$_2$[3R](0001) thick film. (a) $\{30\overline{3}0\}$ plane of the substrate, and (b) $\{\overline{1}0\overline{1}4\}$ plane of the film.
Fig. 5-3 Dependence of Mg concentration in CuScO$_2$[3R] films on FWHMs taken from the CuScO$_2$[3R] 0006- and 1014-peak rocking curve measurements.
Fig. 5-4 Mg concentration dependence on a- and c-axis lattice constants in CuScO$_2[3R]$ films. The a- and c-axis lattice constants in the films were measured with two-dimensional X-ray reciprocal space mapping in the vicinity of the CuScO$_2[3R]$ 10114 and 00012 reflections.
Next, two-dimensional X-ray reciprocal space mapping in the vicinity of the CuScO₂[3R] 10̅14 and 0001₂ reflections was carried out to measure the a- and c-axis lattice constants of all Mg-doped films. The results, compared with those of the undoped epitaxial film, are shown in Fig. 5-4. In all Mg-doped thick films, the slight increase in the a-axis lattice constant and the slight decrease in the c-axis lattice constant were observed, and both lattice constants were almost constant within the range of 1 to 10 at%. From Figs. 5-1 and 5-4, the Mg solubility limit of CuScO₂ thin films is presumed to be approximately 1%. This value is consistent with the results of the Mg-doped CuScO₂ polycrystalline pellets reported by Ingram et al. [2].

Consequently, the Mg-doped CuScO₂[3R](0001) epitaxial thick film was obtained at a Mg concentration of 1 at%. The orientation relationships of the film with respect to the substrate were Cu(Sc₀.₉₉Mg₀.₀₁)O₉[3R](0001)// sapphire [11̅20] and Cu(Sc₀.₉₉Mg₀.₀₁)O₉[3R][11̅20]// sapphire [0001].

5.3.2 Optical and electrical transport properties of 1-at% Mg-doped CuScO₂[3R](0001) epitaxial thick film

The optical transmission spectrum of the 1-at% Mg-doped CuScO₂[3R](0001) epitaxial thick film is shown in Fig. 5-5. The average optical transmittance of the film was higher than 60% for wavelengths greater than 400 nm and 85% for wavelengths ranging from 800 to 2500 nm. No significant increase in optical absorption was observed in the film. The direct energy gap calculated using \((\alpha h\nu)^2\) versus \(h\nu\) plots in the inset of Fig. 5-5 was 3.7 eV. This value is almost identical to the ones obtained in the undoped epitaxial film obtained in chapter 3 and the Mg-doped polycrystalline film [3].

The Hall and Seebeck coefficients of the film were \(+1.8\times10^1\) cm³C⁻¹ and \(+917\) µVK⁻¹ at room temperature, indicating p-type conduction. The electrical conductivity,
Fig. 5-5 Optical transmission spectrum of 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick film in visible/near-IR region. The direct energy gap obtained from $(\alpha h\nu)^2$ versus $h\nu$ plots for the epitaxial film in the inset was 3.7 eV.
Fig. 5-6 Temperature dependences of (a) electrical conductivity ($\sigma$), (b) carrier concentration ($n_p$), and (c) Hall mobility ($\mu$) of the undoped and 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick films. The activation energy estimated from the temperature dependence of the carrier concentration was 0.55 eV for the 1-at% Mg-doped film, and slightly decreased compared with that of the undoped film ($E_a = 0.62$ eV).
carrier concentration, and Hall mobility of the 1-at% Mg-doped epitaxial thick film were $5.1 \times 10^{-3}$ Scm$^{-1}$, $3.5 \times 10^{17}$ cm$^{-3}$, and $9.1 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ at room temperature, respectively. The increase of the carrier concentration due to the Mg doping was observed, indicating that Mg ions substituted for Sc-sites in the film work as the acceptor dopants. On the other hand, the Hall mobility slightly decreased. This is probably due to the deterioration of the in-plane crystallinity and the increase of the Cu-Cu distance (a-axis lattice constant).

The temperature dependences of the electrical conductivity, carrier concentration, and Hall mobility of the 1-at% Mg-doped epitaxial thick film were measured between 220 and 373 K, as shown in Fig. 5-6. The results for the undoped epitaxial thick film are also shown in Fig. 5-6 for comparison. The temperature dependences of the electrical transport properties of the 1-at% Mg-doped film exhibited similar semiconducting characteristics to those of the undoped film. The increase in the electrical conductivity and carrier concentration and the decrease in the Hall mobility of the film were observed with increasing temperature. The activation energy estimated from the slope, shown in Fig. 5-6(b), was 0.55 eV, and slightly decreased compared with that of the undoped epitaxial film (E$_a$ = 0.62 eV).

### 5.4 Conclusion

CuScO$_2$ thick films with different Mg concentrations were grown on a-plane sapphire substrates by a solid-phase epitaxy method using Cu$_2$(Sc$_{1-X}$Mg$_X$)$_2$O$_y$ [$X=0.01$, 0.05, 0.10] targets. The effects of Mg doping in the Sc-sites on the structural, optical, and electrical properties of the films were investigated.
A Mg-doped CuScO$_2[3R](0001)$ epitaxial thick film was obtained at a Mg concentration of 1 at%, and the orientation relationships of the film with respect to the substrate were Cu(Sc$_{0.99}$Mg$_{0.01}$)$_2$O$_7[3R] (0001)// sapphire (1120) and Cu(Sc$_{0.99}$Mg$_{0.01}$)$_2$O$_7[1120// sapphire [0001].

No significant increase in optical absorption was observed in the film. The energy gap for direct allowed transition estimated at 3.7 eV was identical with the one obtained in the undoped film.

The Hall and Seebeck coefficients of the film were $+1.8\times10^1$ cm$^3$C$^{-1}$ and $+917$ $\mu$VK$^{-1}$ at room temperature, indicating p-type conduction. The electrical conductivity, carrier concentration, and Hall mobility of the film were $5.1\times10^{-3}$ Scm$^{-1}$, $3.5\times10^{17}$ cm$^{-3}$, and $9.1\times10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ at room temperature, and the film showed an increase in the electrical conductivity and carrier concentration and a decrease in the Hall mobility compared with those of the undoped film. The increase in the carrier concentration caused by the Mg doping indicates that Mg ions substituted for Sc-sites in the film work as the acceptor dopants. On the other hand, the slight decrease in the Hall mobility is probably due to the in-plane crystallinity deteriorating and the Cu-Cu distance (a-axis lattice constant) increasing. The temperature dependences of the electrical transport properties of the film exhibited similar semiconducting characteristics to those of the undoped film. The activation energy estimated from the temperature dependence of the carrier concentration was 0.55 eV. This value slightly decreased compared with that of the undoped film (E$_a$ = 0.62 eV).
References


Chapter 6. Control of Carrier Concentration in 
CuScO$_2$[3R](0001) Epitaxial Thick Films 
through Excess Oxygen and Mg Co-doping

6.1 Introduction

The control of the carrier concentration in CuScO$_2$[3R](0001) epitaxial thick films through extrinsic doping is very important for application to transparent electronic and optoelectronic devices. As described in chapter 5, 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick films showed the slight increase of the carrier concentration of the films, indicating that Mg ions substituted for Sc-sites in the film work as the acceptor dopants. Moreover, Mg-doped CuScO$_2$ powders have been reported to easily take up excess oxygen near the Cu-planes compared with undoped CuScO$_2$ powders [1,2]. Consequently, the control of the carrier concentration in CuScO$_2$[3R](0001) epitaxial thick films through excess oxygen and Mg co-doping is expected.

In this chapter, undoped and 1-at% Mg-doped CuScO$_2$[3R] thick films are prepared by changing the oxygen pressure during deposition of the polycrystalline layer in the two-step deposition process, followed by post-annealing treatment to obtain the epitaxial films. The structural, optical, and electrical properties of all films are investigated and the control of the carrier concentration in CuScO$_2$[3R](0001) epitaxial films through excess oxygen and Mg co-doping is discussed.
6.2 Experimental

In this section, undoped or 1-at% Mg-doped CuScO$_2$[3R] polycrystalline layers prepared on thin CuScO$_2$[3R](0001) epitaxial layers in the two-step deposition process were deposited at various oxygen pressures. The deposition conditions of the as-deposited films are listed in Table 6-I.

After deposition, all as-deposited films were then post-annealed at the same conditions used in chapter 5 using an electric furnace to obtain the epitaxial films.

The structural, optical, and electrical properties of the films were evaluated by the same methods used in chapters 2 and 3. The nominal Mg composition of the target was used as the Mg concentration of the films in this study.

6.3 Results and discussion

6.3.1 Control of the carrier concentration in CuScO$_2$[3R](0001) epitaxial thick films through excess oxygen and Mg co-doping

XRD 2θ-ω and φ-scan measurements were carried out to confirm the epitaxial growth of the films. Similar out-of-plane and in-plane orientation relationships for the films with respect to the substrates were observed for all films. For example, the results obtained for the 1-at% Mg-doped film prepared at an oxygen pressure during deposition of the polycrystalline layer of 10 Pa are shown in Fig. 6-1. Only peaks corresponding to CuScO$_2$[3R] 000\(\ell\) \([\ell = 3,6,9,12]\) diffractions, shown in Fig. 6-1(a), were observed for the film, suggesting that the film is strongly oriented with the c-axis perpendicular to the substrate. On the other hand, peaks with two-fold rotational symmetry were observed
Table 6-I Deposition conditions for undoped and 1-at% Mg-doped CuScO$_2$[3R] thick films with two different layers prepared using PLD.

1) CuScO$_2$[3R](0001) epitaxial layer

<table>
<thead>
<tr>
<th>Target</th>
<th>Cu$_2$Sc$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature ($^\circ$C)</td>
<td>925</td>
</tr>
<tr>
<td>Oxygen pressure (Pa)</td>
<td>1.5</td>
</tr>
<tr>
<td>rf forward power of oxygen radical source (W)</td>
<td>200</td>
</tr>
<tr>
<td>Laser fluence (J cm$^{-2}$)</td>
<td>0.6</td>
</tr>
<tr>
<td>Laser repetition frequency (Hz)</td>
<td>1</td>
</tr>
<tr>
<td>Deposition rate (nm h$^{-1}$)</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

2) Undoped and 1-at% Mg-doped CuScO$_2$[3R] polycrystalline layer

<table>
<thead>
<tr>
<th>Target</th>
<th>Cu$<em>2$(Sc$</em>{1-X}$Mg$_X$)$_2$O$_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[X=0, 0.01]</td>
<td></td>
</tr>
<tr>
<td>Substrate temperature ($^\circ$C)</td>
<td>940</td>
</tr>
<tr>
<td>Oxygen pressure (Pa)</td>
<td>4.5, 7.5, 10, 13</td>
</tr>
<tr>
<td>rf forward power of oxygen radical source (W)</td>
<td>0</td>
</tr>
<tr>
<td>Laser fluence (J cm$^{-2}$)</td>
<td>1.0</td>
</tr>
<tr>
<td>Laser repetition frequency (Hz)</td>
<td>10</td>
</tr>
<tr>
<td>Deposition rate (nm h$^{-1}$)</td>
<td>25 ~ 80</td>
</tr>
</tbody>
</table>
for 30θ00 diffractions of the substrate, as shown in Fig. 6-1(b-1). Peaks for 1014 diffractions of the CuScO2[3R] phase of the film exhibited six-fold rotational symmetry, indicating that the films had twin structures [Fig. 6-1(b-2)]. The peaks of the film were in agreement with those of the substrate at the φ diffraction angles of ±90°. Consequently, all undoped and 1-at% Mg-doped CuScO2[3R] thick films were epitaxially grown on a-plane sapphire substrates, and the orientation relationships of the films with respect to the substrates were Cu(Sc1-xMgx)Oy[3R] (0001) // sapphire [1 1 2 0] and Cu(Sc1-xMgx)Oy[3R] [1 1 2 0] // sapphire [0 0 0 1] [X=0, 0.01].

The out-of-plane and in-plane crystallinity of the epitaxial thick films was estimated by the FWHMs taken from the CuScO2[3R] 0006- and 1014-peak rocking curve measurements. The results are shown in Fig. 6-2. In the undoped films, the FWHM obtained for the 0006-peak significantly decreased and that for the 1014-peak slightly decreased with increasing oxygen pressure during deposition of the polycrystalline layer. On the other hand, the FWHM obtained for the 0006-peak were almost constant and that for the 1014-peak significantly decreased in the 1-at% Mg-doped films with increasing oxygen pressure during deposition of the polycrystalline layer.

Next, the oxygen pressure dependences on the electrical conductivity (σ), carrier concentration (n₀) and Hall mobility (μ) of the films at room temperature are shown in Fig. 6-3. In the undoped films, the carrier concentration was almost constant and the Hall mobility slightly increased with increasing oxygen pressure during deposition of the polycrystalline layer. The increase of the Hall mobility is due to the improvement of the in-plane crystallinity for the undoped films, as shown in Fig. 6-2(a), because holes predominantly pass through the Cu⁺ planes in Cu⁺-based delafossites [2]. On the other hand, the significant improvement of the carrier concentration and Hall mobility was
Fig. 6-1. (a) XRD 2θ-ω pattern and ϕ-scans of (b-1) \( \{30\bar{3}0\} \) plane of the a-plane sapphire substrate and (b-2) \( \{10\bar{1}4\} \) plane of CuScO2[3R] phase of the film. The film was obtained by post-annealing the 1-at% Mg-doped CuScO2[3R] thick film prepared at an oxygen pressure during deposition of the polycrystalline layer of 10 Pa on a thin CuScO2[3R](0001) epitaxial layer in the two-step deposition process.
Fig. 6-2. Dependences of oxygen pressure during deposition of the polycrystalline layer on FWHMs taken from the CuScO$_2$[3R] 0006- and 1014-peak rocking curve measurements. (a) undoped and (b) 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick films.
Fig. 6-3. (a) Electrical conductivity (σ), (b) carrier concentration (n_p), and (c) Hall mobility (μ) at room temperature of the undoped and 1-at% Mg-doped CuScO_2[3R](0001) epitaxial thick films as a function of the oxygen pressure during deposition of the polycrystalline layer.
Fig. 6-4 Schematic illustration of the effect of excess oxygen and Mg co-doping on the electrical property of CuScO$_2$[3R](0001) epitaxial thick films.
observed for the 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick films with increasing oxygen pressure during deposition of the polycrystalline layer. The most conductive film was also obtained at an oxygen pressure during deposition of the polycrystalline layer of 10 Pa. Mg-doped CuScO$_2$ powders have been reported to easily take up excess oxygen close to the Cu-planes compared with undoped powders [1]. Thus the increase of the carrier concentration is caused by the generation of the holes due to the excess oxygen intercalation near the Cu-planes. The increase of the Hall mobility is due to the significant improvement of the in-plane crystallinity for the 1-at% Mg-doped films [Fig. 6-2(b)] and the Cu-O bonds newly formed in the Cu-planes by bonding Cu atoms and excess oxygen. Figure 6-4 shows the schematic illustration of the effect of excess oxygen and Mg co-doping. Accordingly, these results indicate that the carrier concentration in CuScO$_2$[3R](0001) epitaxial thick films can be controlled from $1.6 \times 10^{16}$ cm$^{-3}$ to $9.2 \times 10^{17}$ cm$^{-3}$ at room temperature by adjusting the excess oxygen and Mg co-doping.

6.3.2 Optical and electrical transport properties of excess oxygen and Mg co-doped CuScO$_2$[3R](0001) epitaxial thick film

The optical transmission spectrum of the most conductive film is shown in Fig. 6-5. The average optical transmittance of the film was higher than 70% for wavelengths greater than 400 nm and 85% for wavelengths ranging from 800 to 2500 nm. No significant increase in optical absorption was observed in the film. The direct energy gap calculated using $(\alpha h\nu)^2$ versus $h\nu$ plots in the inset of Fig. 6-5 was 3.7 eV. This value was identical to the ones obtained in the undoped (Section 3) and 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial films (Section 5).
Fig. 6-5. Optical transmission spectrum of the most conductive film in visible/near-IR region. The film was obtained by post-annealing the 1-at% Mg-doped CuScO₂[3R] thick film prepared at an oxygen pressure during deposition of 10 Pa. The direct energy gap obtained from \((\alpha h\nu)^2\) versus \(h\nu\) plots for the epitaxial film in the inset was 3.7 eV.
Fig. 6-6. Temperature dependences of (a) electrical conductivity ($\sigma$), (b) carrier concentration ($n_p$), and (c) Hall mobility ($\mu$) of undoped film (●), 1-at% Mg-doped film ($PO_2=4.5\text{Pa}$) (▲), and the most conductive film in this study ($PO_2=10\text{Pa}$) (■). The activation energy estimated from the temperature dependence of the carrier concentration in the most conductive film was 0.50 eV.
The Hall and Seebeck coefficients of the most conductive film were $+7.4 \text{ cm}^3\text{C}^{-1}$ and $+890 \mu\text{VK}^{-1}$ at room temperature, indicating p-type conduction. The electrical conductivity ($\sigma$), carrier concentration ($n_p$) and Hall mobility ($\mu$) of the film were $3.6 \times 10^{-2} \text{ Scm}^{-1}$, $8.5 \times 10^{17} \text{ cm}^{-3}$, and $2.6 \times 10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature, respectively.

The temperature dependences of the electrical conductivity, carrier concentration, and Hall mobility of the film were measured between 220 and 373 K, as shown in Fig. 6-6. The temperature dependences of the electrical transport properties of the film exhibited similar semiconducting characteristics to those of the undoped epitaxial film, and the increase in the electrical conductivity and carrier concentration and the decrease in the Hall mobility of the film were observed with increasing temperature. The activation energy estimated from the slope, shown in Fig. 6-6(b), was 0.50 eV, and decreased compared with those of the undoped epitaxial film ($E_a = 0.62 \text{ eV}$) and 1-at% Mg-doped CuScO$_2[3R](0001)$ epitaxial thick film ($E_a = 0.55 \text{ eV}$).

### 6.4 Conclusion

Undoped and 1-at% Mg-doped CuScO$_2[3R]$ thick films with a bilayered structure were prepared by changing the oxygen pressure during deposition of the polycrystalline layer in the two-step deposition, followed by post-annealing treatment. All films were epitaxially grown on a-plane sapphire substrates, and the orientation relationships of the films with respect to the substrates were $\text{Cu(Sc}_{1-x}\text{Mg}_x\text{O}_y[3R]}(0001)//\text{sapphire}[\overline{1}1\overline{2}0]$ and $\text{Cu(Sc}_{1-x}\text{Mg}_x\text{O}_y[3R]}[\overline{1}1\overline{2}0]//\text{sapphire}[0001]$ [X=0, 0.01].

No significant increase in optical absorption was observed in all epitaxial films, and the energy gap for direct allowed transition was estimated at 3.7 eV.
The significant improvements in the carrier concentration and Hall mobility were observed for the 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick films as oxygen pressure increased during deposition of the polycrystalline layer. The increase in the carrier concentration is caused by holes being generated by the excess oxygen near the Cu-planes. Moreover, the increase in the Hall mobility is due to the significant improvement of the in-plane crystallinity and the Cu-O bonds newly formed in the Cu-planes by bonding Cu atoms and excess oxygen. As a result, the carrier concentration of the epitaxial films at room temperature could be controlled from $1.6 \times 10^{16}$ cm$^{-3}$ to $9.2 \times 10^{17}$ cm$^{-3}$ at room temperature by adjusting the excess oxygen and Mg co-doping.

The 1-at% Mg-doped film prepared at an oxygen pressure during deposition of the polycrystalline layer of 10 Pa showed the maximum electrical conductivity, and the Hall and Seebeck coefficients of the film were +7.4 cm$^3$C$^{-1}$ and +890 $\mu$VK$^{-1}$ at room temperature, indicating p-type conduction. The electrical conductivity, carrier concentration, and Hall mobility of the film were $3.6 \times 10^{-2}$ Scm$^{-1}$, $8.5 \times 10^{17}$ cm$^{-3}$ and $2.6 \times 10^{-1}$ cm$^2$V$^{-1}$s$^{-1}$ at room temperature, respectively. The temperature dependences of the electrical transport properties of the film exhibited similar semiconducting characteristics to those of the undoped film, and the activation energy estimated from the temperature dependence of the carrier concentration was 0.50 eV. This value slightly decreased compared with those of the undoped (E$_a$ = 0.62 eV) and 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick films (E$_a$ = 0.55 eV).
References


Chapter 7. Conclusions

This thesis has been devoted to fundamentally studying the structural, optical, and electrical transport properties of CuScO₂ thin films as a p-type transparent oxide semiconductor. The objective is to obtain transparent p-type CuScO₂[3R](0001) epitaxial thick films with the controllable carrier concentration through extrinsic doping essential for applying to the transparent pn-junctions. The main results of this work can be summarized as follows.

In chapter 2, CuScO₂ thin films were deposited on a-plane sapphire substrates at various substrate temperatures, oxygen pressures, and laser fluences by PLD using a single-phase Cu₂Sc₂O₅ target to obtain CuScO₂(0001) epitaxial films to be used as thin epitaxial layers in a solid-phase epitaxy method. CuScO₂[3R](0001) epitaxial films with different in-plane orientations were obtained on a-plane sapphire substrates by changing laser fluences during deposition. Their in-plane orientation relationships of the films with respect to the substrates were CuScO₂[3R] \( \{1 \bar{1} 20\} \) // sapphire[0001] and CuScO₂[3R] \( \{1 \bar{1} 20\} \) // sapphire[2\( \bar{2} \)01], and are presumed to be influenced by the atomic arrangements (Cu⁺ layer or (ScO₂)- layer) of the initial growth of the films.

In chapter 3, CuScO₂[3R](0001) epitaxial thick films were successfully fabricated by a solid-phase epitaxy method using CuScO₂[3R] polycrystalline thick films as CuScO₂ thick layers. A 250-nm-thick film was single-phase with a rhombohedral crystal structure and showed six-fold rotational symmetry in the basal plane, indicating that the film had a twinned domain structure. The orientation relationships of the film with respect to the substrate were CuScO₂[3R](0001) // sapphire(1\( \bar{1} 20\)) and CuScO₂[3R] \( \{1 \bar{1} 20\} \) // sapphire[0001]. The a- and c-axis lattice constants of the film were
0.3214 nm and 1.710 nm, and were almost in agreement with the ones reported in the Joint Committee for Powder Diffraction Files (JCPDF) file No. 79-0599 (CuScO$_2$[3R]: a = 0.3216 nm, c = 1.7089 nm). The average optical transmittance of the film was greater than 60 % in the visible region and 85 % in wavelengths ranging from 800 to 2500 nm, and the energy gap for direct allowed transition was estimated to be 3.7 eV. The electrical transport property of the film was first estimated by the Hall effect measurement. The Hall and Seebeck coefficients of the film were $+1.4 \times 10^2$ cm$^3$C$^{-1}$ and $+968$ µV/K at room temperature, indicating p-type conduction. The electrical conductivity, carrier concentration, and Hall mobility of the film at room temperature were $1.0 \times 10^{-3}$ Scm$^{-1}$, $4.5 \times 10^{16}$ cm$^{-3}$, and $1.4 \times 10^{-1}$ cm$^2$V$^{-1}$s$^{-1}$, respectively. The temperature dependences of the electrical transport properties of the film exhibited semiconducting behavior, and the activation energy estimated from the temperature dependence of the carrier concentration was 0.62 eV.

In chapter 4, excess oxygen was intercalated in a 40-nm-thick CuScO$_2$[3R](0001) epitaxial film by annealing using oxygen radicals. The decrease in the average optical transmittance was observed for the film at wavelengths greater than 400 nm, because the fraction of Cu$^{2+}$ cations in the film increased due to hole carriers introduced by excess oxygen. The electrical conductivity of the film significantly increased from $1.4 \times 10^{-7}$ Scm$^{-1}$ to 2.7 Scm$^{-1}$ at room temperature and the Seebeck coefficient was about $+14$ µV/K at room temperature. This indicates that a number of holes are induced in the film by the excess oxygen intercalation. However, the dependence on temperature of the electrical conductivity of the film exhibited semiconducting behavior, and the Seebeck coefficient of the film did not show temperature dependence above 140 K. This indicates that the dominant conduction mechanism of the film from 140 K to 300 K is the thermally activated small polaron conduction caused by the strong hole-phonon
interaction. With decreasing temperature below 140 K, the three-dimensional variable range hopping conduction was dominant because of the localization of the holes.

Accordingly, it is presumed that the carrier concentration in CuScO$_2$ [3R](0001) epitaxial thick films is very difficult to be controlled by excess oxygen intercalation using an oxygen radical source. This is because a number of holes generated by the excess oxygen exist near the film surface and the dominant electrical conduction of the excess oxygen intercalation layers at room temperature change to the thermally activated small polaron conduction due to the strong electron-phonon interaction. However, the excess oxygen intercalation layer in CuScO$_2$[3R](0001) epitaxial films is very useful for preparing the ohmic contacts between CuScO$_2$ and metals such as Pt and Ni.

In chapter 5, Mg-doped CuScO$_2$[3R](0001) epitaxial thick films were obtained at a Mg concentration of 1 at%. No significant increase in optical absorption was observed in the films. The energy gap for direct allowed transition estimated at 3.7 eV was identical to that obtained in the undoped epitaxial thick film obtained in chapter 3. The Hall and Seebeck coefficients of the film were $+1.8 \times 10^{1} \text{ cm}^{3}\text{C}^{-1}$ and $+917 \text{ }\mu\text{VK}^{-1}$ at room temperature, indicating p-type conduction. The electrical conductivity, carrier concentration, and Hall mobility of the film were $5.1 \times 10^{3} \text{S} \text{cm}^{-1}$, $3.5 \times 10^{17} \text{ cm}^{-3}$, and $9.1 \times 10^{2} \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1}$ at room temperature, and the film showed an increase in the electrical conductivity and carrier concentration and a decrease in the Hall mobility compared with those of the undoped epitaxial film. This suggests that Mg ions substituted for Sc-sites in the film work as the acceptor dopants. On the other hand, the slight decrease in the Hall mobility is probably due to the in-plane crystallinity deteriorating and the Cu-Cu distance (a-axis lattice constant) increasing. The temperature dependences of the electrical transport properties of the film exhibited
similar semiconducting characteristics to those of the undoped film. The activation energy estimated from the temperature dependence of the carrier concentration was 0.55 eV, and slightly decreased compared with that of the undoped epitaxial film (Ea = 0.62 eV).

Chapter 6 focuses on the control of the carrier concentration in CuScO$_2$[3R](0001) epitaxial films through extrinsic doping. Undoped and 1-at% Mg-doped CuScO$_2$[3R] thick films with a bilayered structure were prepared by changing the oxygen pressure during deposition of the polycrystalline layer in the two-step deposition, followed by post-annealing treatment. All films were epitaxially grown on a-plane sapphire substrates. No significant increase in optical absorption was observed in any epitaxial films, and the energy gap for direct allowed transition was estimated at 3.7 eV. The carrier concentration of the epitaxial films at room temperature was successfully controlled from 1.6×10$^{16}$ cm$^{-3}$ to 9.2×10$^{17}$ cm$^{-3}$ at room temperature by adjusting the excess oxygen and Mg co-doping. The 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick film prepared at an oxygen pressure during deposition of the polycrystalline layer of 10 Pa showed the maximum electrical conductivity. The temperature dependences of the electrical transport properties of the film exhibited similar semiconducting characteristics to those of the undoped epitaxial film, and the activation energy estimated from the temperature dependence of the carrier concentration was 0.50 eV.

On the basis of the above results, the authors’ conclusions are as follows. We succeeded in fabricating undoped and 1-at% Mg-doped CuScO$_2$[3R](0001) epitaxial thick films by a solid-phase epitaxy method combining the two-step deposition and post-annealing techniques, and controlling the carrier concentration in CuScO$_2$[3R](0001) epitaxial films through excess oxygen and Mg co-doping. The films
showed optical transparency in the visible region. Consequently, CuScO$_2[3R](0001)$ epitaxial films have sufficient possibility as a p-type transparent oxide semiconductor.
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## Original Articles Regarding This Thesis

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