Structural, Electrical and Optical Characterization of SrIrO₃ Thin Films Prepared by Laser-Ablation

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SrIrO₃ thin films were prepared by laser ablating a monoclinic SrIrO₃ target at the substrate temperature of 973 K with oxygen pressure ranging from 4 to 67 Pa. The glancing angle incidence X-ray diffraction (GIXRD) and micro-X-ray photoelectron spectroscopy (XPS) results suggested that SrIrO₃ thin films were obtained. The resistivities and transmittance of SrIrO₃ thin films at room temperature were in the range from 0.93 to $4.8 \times 10^{-5} \Omega\text{m}$ and from 0.20 to 0.30 in the wavelength range of 600–800 nm, respectively. The electrical property of SrIrO₃ thin films changed from semiconductive to metallic with increasing the ablation oxygen pressure.

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1. Introduction

Although 4d-electron based ruthenates have drawn much attention in recent years, the 4d and 5d-electron transition-metal oxides are mostly still unexplored and rich in novel physical phenomena often deviating from conventional expectation.^{1,2)} Many of the iridates, 5d transition metal oxides, could be much more conducting than their 3d counterparts because of the more extended 5d orbitals that significantly reduce the coulomb interaction.³⁾ Among the iridates, the Sr-Ir-O system has potential application in catalysis, electrochemistry and microelectronic devices. It is known that several ternary compounds such as SrIrO₃, Sr₃Ir₂O₇, Sr₄Ir₃O₁₀, Sr₂IrO₄ and Sr₄IrO₆ are stable phases in the Sr-Ir-O system.^{4–7)} These iridates were usually in the form of bulk crystalline prepared by fluxing or sintering. Although Sr-Ru-O films have been widely studied mainly for the application as electrodes, no Sr-Ir-O films have been well synthesized and characterized. In this paper, SrIrO₃ thin films have been first prepared by laser ablation on silica substrates. In particular, the effect of oxygen pressure on structural, electrical and optical properties of SrIrO₃ thin films were investigated.

2. Experiment

SrIrO₃ thin films were prepared by laser ablating a monoclinic SrIrO₃ target (Furiya metal Co.: 99.9%, 2 cm in diameter) on silica substrates at substrate temperatures (T_{sub}) from room temperature (RT) to 973 K and oxygen pressures (P_{O_2}) ranging from 4 to 67 Pa. A pulsed Nd:YAG laser with a wavelength of 355 nm was employed. A laser beam (pulse energy: 170 mJ, energy density: about $1.8 \times 10^5 \text{ J/m}^2$, pulse width: 15 ns and repetition rate: 10 Hz) was focused onto the SrIrO₃ target at an angle of 45°. The substrates were placed parallel to the SrIrO₃ target at a distance of 6 cm. The thickness of SrIrO₃ thin films was determined by a talystep profiler (Rank Taylor Hobson).

The glancing angle incidence X-ray diffractometer (GIXRD) (Rigaku Rotaflex RU-200B) was used to analyze the crystal structure at an incidence angle (α) of 2°. The

chemical binding state was investigated by micro-X-ray photoelectron spectroscopy (micro-XPS) using Al K α radiation (Surface Science Instruments SSI-100). No Ar ion sputtering was conducted to avoid the decomposition of SrIrO₃ thin films during the sputtering. The tapping mode atomic force microscopy (AFM) images were taken using a Digital Instruments Nanoscope III operating in air. A silicon tip with the end tip diameter of 5–10 nm and 300 kHz resonant oscillating frequency were applied to the observation of surface roughness. The electrical resistivity was measured in the temperature range from 100 to 773 K by a van der Pauw method. The optical transmittance was measured by using a UV-VIS-NIR spectrophotometer (Shimadzu UV-3101PC).

3. Results and Discussion

Figure 1 shows the GIXRD patterns of SrIrO₃ thin films prepared at $T_{\text{sub}} = \text{RT to } 973 \text{ K}$ and $P_{\text{O}_2} = 4 \text{ Pa}$. SrIrO₃ thin

Fig. 1 GIXRD patterns of SrIrO₃ thin films prepared at $T_{\text{sub}} = \text{RT to } 973 \text{ K}$ and $P_{\text{O}_2} = 4 \text{ Pa}$. (a) RT, (b) 673 K, (c) 873 K and (d) 973 K.

Fig. 2 GIXRD patterns of SrIrO₃ thin films prepared at $T_{\text{sub}} = 973$ K and $P_{\text{O}_2} = 4$ to 67 Pa. (a) 4, (b) 13, (c) 40 and (d) 67 Pa.

films showed good adherence to the substrates. At T_{sub} lower than 873 K, a broad SrIrO₃ diffraction peak around 32° appeared suggesting amorphous structure. At $T_{\text{sub}} = 973$ K, other SrIrO₃ diffraction peaks with monoclinic structure were also observed.⁷⁾

Figure 2 depicts the GIXRD patterns of SrIrO₃ thin films prepared at $T_{\text{sub}} = 973$ K and $P_{\text{O}_2} = 4$ to 67 Pa. At P_{O_2} lower than 40 Pa, the intensity of SrIrO₃ (023), (115), (134), (204) and (135) diffraction peaks gradually decreased and (023) and (204) diffraction peaks disappeared with increasing oxygen pressure. On the other hand, the strong intensity of SrIrO₃ (114) diffraction peak was observed at 31°. With increasing oxygen pressure from 40 to 67 Pa, a narrow SrIrO₃ diffraction peak at 32° appeared. It can be indexed as the superposition of SrIrO₃ (024), (200), (114) and (130) diffraction peaks. Kim *et al.* have studied the effect of oxygen pressure on the orientation of ZnO films prepared on Si(001) substrate by laser ablation.⁸⁾ They reported that the ZnO films grown in the O₂ pressure below 6.7 Pa are completely *c*-axis oriented in the film. The ZnO film grown at $P_{\text{O}_2} = 67$ Pa is mostly randomly oriented and shows weaker ZnO peak intensities, confirming its low crystallinity. Almeida *et al.* have studied the effect of oxygen pressure on the orientation of SrTiO₃ films prepared on Si(001) substrate by laser ablation.⁹⁾ They reported that polycrystalline presenting a structure similar to cubic bulk SrTiO₃ was obtained at low oxygen pressure (0.18 Pa). As the oxygen pressure increases to $P_{\text{O}_2} = 20$ Pa, the films start to develop a (200) preferred orientation. Both of them suggested a changing oxygen deficiency in the films. In the present study, the change in orientation of SrIrO₃ thin films with increasing oxygen pressure may be associated with the changing of oxygen deficiency.

Figure 3 gives the micro-XPS spectra of the Ir 4f core levels of SrIrO₃ thin films prepared at $T_{\text{sub}} = 973$ K and $P_{\text{O}_2} = 4$ (a) and 67 Pa (b) with comparing Ir thin film prepared at RT (c) and IrO₂ thin films prepared at $T_{\text{sub}} = 873$ K and $P_{\text{O}_2} = 13$ Pa (d) by laser ablation.^{10,11)} The binding

Fig. 3 Micro-XPS spectra of Ir 4f core levels of SrIrO₃ thin films prepared at $T_{\text{sub}} = 973$ K and $P_{\text{O}_2} = 4$ (a) and 67 Pa (b), Ir thin film prepared at RT (c) and IrO₂ thin films prepared at $T_{\text{sub}} = 873$ K and $P_{\text{O}_2} = 13$ Pa (d) by laser ablation.

energy was calibrated using the C 1s peak as reference (284.6 eV). The doublet peaks in the binding energy about 62 and 65 eV are originated from mainly Ir 4f_{7/2} and Ir 4f_{5/2} respectively.¹²⁾ By deconvoluting the spectra, the binding energies of Ir 4f_{7/2} of Ir, IrO₂ and SrIrO₃ thin films prepared at $P_{\text{O}_2} = 4$ and 67 Pa were 61.1, 61.9, 61.9 and 61.8 eV, respectively. Each spectrum was deconvoluted by the Gaussian and Lorentzian functions and the Shirley background subtraction.¹³⁾ The Ir 4f_{7/2} and Ir 4f_{5/2} peaks were fitted including the Doniac-Sunjic function.¹⁴⁾ The binding energy of Ir 4f_{7/2} for SrIrO₃ thin films were almost consistent with the value of the IrO₂ and reported IrO₂ value (62.2 eV).¹⁵⁾

Figure 4 represents schematic crystal structures of IrO₂ (a unit cell) and SrIrO₃ (1/2 of a unit cell). IrO₂ ($a = 0.4498$ nm, $c = 0.3154$ nm and space group: P42/mnm)¹⁶⁾ has a rutile structure in which O atoms octahedrally coordinated to Ir atom as shown in Fig. 4(a). The average Ir-O distance in the IrO₆ octahedron is 0.1982 nm.¹⁷⁾ SrIrO₃ has a monoclinic structure ($a = 0.5604$ nm, $b = 0.9618$ nm, $c = 1.417$ nm, $\beta = 93.26^\circ$ and space group: C2/c)⁷⁾ in which there are basically two kinds of IrO₆ octahedra (IrO₆-type I and IrO₆-type II) as shown in Fig. 4(b). The average Ir-O distance in these IrO₆ octahedra is calculated to be 0.1992 nm,¹⁸⁾ which is close to that of IrO₂. Although the binding energy of Ir 4f is not only explained by the bonding Ir-O distance, the similarity of the short-ranged Ir-O coordination may be associated with the coincidence of binding energy between IrO₂ and SrIrO₃. For the Ir thin films, the Ir 4f_{7/2} binding energy at 61.1 eV was consistent with that of pure Ir (60.9 eV).¹⁹⁾ The larger Ir 4f_{7/2} binding energy of SrIrO₃ thin films than that of Ir thin films suggested that the SrIrO₃ thin film may not contain an Ir metal phase.

Figure 5 depicts three-dimensional tapping mode AFM images of the surface of SrIrO₃ thin films prepared at $T_{\text{sub}} = 973$ K and $P_{\text{O}_2} = 4, 13, 40$ and 67 Pa. The surfaces of

Fig. 4 Schematic crystal structure of IrO₂ (a unit cell) (a) and SrIrO₃ (1/2 of a unit cell) (b).

these films have no large clusters or voids. The thicknesses of the as-deposited SrIrO₃ thin films prepared at 973 K and $P_{O_2} = 4, 13, 40$ and 67 Pa were 120, 120, 125 and 95 nm, respectively. Figure 6 gives the root-mean-square roughness and the growth rate of SrIrO₃ thin films prepared at $T_{sub} = 973$ K as a function of oxygen pressure. At P_{O_2} lower than 40 Pa, the surface roughnesses of SrIrO₃ thin films increased from 3.0 to 5.3 nm with increasing P_{O_2} , and the growth rate showed almost no change. At P_{O_2} higher than 40 Pa, the surface roughness and growth rate of SrIrO₃ thin films decreased with increasing oxygen pressure. The decrease in the growth rate of SrIrO₃ thin films might be originated from the collisional effect at high oxygen pressures.

Figure 7 shows the resistivities of SrIrO₃ thin films prepared at $T_{sub} = 973$ K and $P_{O_2} = 4$ to 67 Pa as a function of temperature. In the temperature range from 100 to 773 K, SrIrO₃ thin films prepared at $P_{O_2} = 4$ Pa showed semi-conductive behavior, and had a resistivity of $4.8 \times 10^{-5} \Omega m$ at room temperature. SrIrO₃ thin films prepared at $P_{O_2} = 13$ Pa exhibited the almost temperature independence

Fig. 5 Three-dimensional tapping mode AFM images of the surface of SrIrO₃ thin films prepared at $T_{sub} = 973$ K and $P_{O_2} = 4$ (a) and 67 Pa (b).

Fig. 6 Root-mean-square roughness and the growth rate of SrIrO₃ thin films prepared at $T_{sub} = 973$ K as a function of oxygen pressure. (a) 4, (b) 13, (c) 40 and (d) 67 Pa.

of resistivity, and a resistivity of $2.1 \times 10^{-5} \Omega m$ at room temperature. At $P_{O_2} > 40$ Pa, SrIrO₃ thin films had slightly positive temperature dependence of resistivity implying metallic conduction behavior in the temperature range from

Fig. 7 Resistivities of SrIrO₃ thin films prepared at $T_{\text{sub}} = 973$ K and $P_{\text{O}_2} = 4$ to 67 Pa as a function of temperature. (a) 4, (b) 13, (c) 40 and (d) 67 Pa.

100 to 773 K. The resistivities of SrIrO₃ thin films prepared at $P_{\text{O}_2} = 40$ and 67 Pa were 1.2 and $0.93 \times 10^{-5} \Omega m$, respectively, at room temperature. The resistivity of SrIrO₃ thin films at room temperature decreased with increasing the ablation oxygen pressure. Hiratani *et al.* reported the preparation of SrRuO₃ thin films at oxygen pressure ranging from 1.3×10^{-4} to 13 Pa.²⁰⁾ Their results also showed that the resistivity decreased and electrical property changed from semiconductive to metallic with increasing the oxygen pressure. In the present study, based on their explanation, the semiconductive behavior was attributed to oxygen deficiency in SrIrO₃ thin films prepared at low oxygen pressure. The suppressed oxygen deficiency at high oxygen pressure resulted in metallic behavior of SrIrO₃ thin films.

Figure 8 compares the resistivity of SrIrO₃ with those of Ir and IrO₂ prepared by laser ablation in our previous experiments.^{10,11)} The thickness of Ir, IrO₂ and SrO₃ are 25, 60 and 95 nm, respectively. The resistivity of Ir thin film was almost independent of temperature, and $7.8 \times 10^{-8} \Omega m$ at room temperature, which was close to that reported value for bulk Ir ($5.3 \times 10^{-8} \Omega m$).²¹⁾ For IrO₂ thin films, the resistivity was $37 \times 10^{-8} \Omega m$ at room temperature, close to that reported value for [110] direction of single crystal IrO₂ ($35 \times 10^{-8} \Omega m$).²²⁾ The SrIrO₃ thin film shown in Fig. 6(d) had a resistivity of $0.93 \times 10^{-5} \Omega m$ at room temperature, which was smaller than that reported in the literatures for sintered disc SrIrO₃ ($4.0 \times 10^{-5} \Omega m$).⁷⁾ The resistivity of the films prepared by laser ablation (including our experimental results of Ir and IrO₂ thin films) has been shown to be close to the corresponding bulk values.²³⁾ At present, the study on the preparation of bulk SrIrO₃ have not been reported yet. The resistivity of $0.93 \times 10^{-5} \Omega m$ might be close to that of bulk SrIrO₃.

Figure 9 demonstrates the transmittance spectra of SrIrO₃ thin films prepared at $T_{\text{sub}} = 973$ K and $P_{\text{O}_2} = 4$ to 67 Pa. At $P_{\text{O}_2} < 40$ Pa, the transmittance of SrIrO₃ thin films decreased

Fig. 8 Resistivities of Ir (a), IrO₂ (b) and SrIrO₃ thin films (c) prepared by laser ablation under the optimum conditions as a function of temperature.

Fig. 9 The transmittance spectra of SrIrO₃ thin films prepared at $T_{\text{sub}} = 973$ K and $P_{\text{O}_2} = 4$ to 67 Pa. (a) 4, (b) 13, (c) 40 and (d) 67 Pa.

from 0.30 to 0.21 with increasing oxygen pressure in the wavelength range from 600 to 800 nm. For SrIrO₃ thin films prepared at $P_{\text{O}_2} = 67$ Pa, relatively higher transmittance can be observed compared with that prepared at $P_{\text{O}_2} = 13$ and 40 Pa. It might be explained by change of oxygen deficiency in SrIrO₃ thin films.

Figure 10 compares the transmittance of SrIrO₃ thin films with those of Ir and IrO₂ prepared by laser ablation in our previous experiments.^{10,11)} The thickness of Ir, IrO₂ and SrO₃ are 25, 60 and 95 nm, respectively. The transmittance of Ir thin films was about 0.01 in the wavelength range from 300–800 nm. For IrO₂ thin films, the transmittance increased to 0.10.¹¹⁾ In the present study, the SrIrO₃ thin film showed the transmittance of 0.25. In recent years, IrO₂ thin films have been used as an electrode against oxygen diffusion for (Pb,Zr)TiO₃ thin films (PZT) memory devices, and showed

Fig. 10 Transmittance spectra of Ir (a), IrO_2 (b) and SrIrO_3 thin films (c) prepared by laser ablation under the optimum conditions.

the improvement of the fatigue properties of ferroelectric thin films.²⁴⁾ However, due to relatively high vapor pressure of IrO_3 , the surface roughness of IrO_2 thin films becomes more significant at higher substrate temperature according to the decrease of growth rates and the degradation of properties. The SrIrO_3 thin films in this study showed higher transmittance than IrO_2 thin films. SrIrO_3 thin films also showed smoother surface than IrO_2 thin films under similar preparation conditions in laser ablation. SrIrO_3 thin films can become a candidate for substituting IrO_2 thin films.

4. Conclusions

SrIrO_3 thin films with semiconducting and metallic conduction behaviors were prepared at 973 K and $P_{\text{O}_2} = 4$ to 67 Pa by laser ablation. The Ir $4f_{7/2}$ binding energies of SrIrO_3 thin films prepared at $P_{\text{O}_2} = 4$ to 67 Pa ranged from 61.8 to 62.0 eV suggesting the formation of SrIrO_3 without containing Ir phase. The resistivity and transmittance of SrIrO_3 thin films were in the range from 0.93 to $4.8 \times 10^{-5} \Omega\text{m}$ and from 0.20 to 0.30 in the wavelength range of 600–800 nm, respectively, at room temperature.

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