Structural, Electrical and Optical Characterization of SrIrO$_3$ Thin Films Prepared by Laser-Ablation

Yuxue Liu, Hiroshi Masumoto and Takashi Goto

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

SrIrO$_3$ thin films were prepared by laser ablating a monoclinic SrIrO$_3$ 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 SrIrO$_3$ thin films were obtained. The resistivities and transmittance of SrIrO$_3$ thin films at room temperature were in the range from 0.93 to $4 \times 10^5 \Omega \cdot \text{cm}$ and from 0.20 to 0.30 in the wavelength range of 600–800 nm, respectively. The electrical property of SrIrO$_3$ thin films changed from semiconductive to metallic with increasing the ablation oxygen pressure.

(Received August 19, 2004; Accepted November 12, 2004)

Keywords: SrIrO$_3$ films, glancing angle incidence X-ray diffraction, X-ray photoelectron spectra, atomic force microscopy, resistivity, transmittance

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. 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. 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 SrIrO$_3$, Sr$_3$Ir$_2$O$_7$, Sr$_4$Ir$_3$O$_{10}$, Sr$_2$IrO$_4$ and Sr$_4$IrO$_6$ are stable phases in the Sr-Ir-O system. 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, SrIrO$_3$ 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 SrIrO$_3$ thin films were investigated.

2. Experiment

SrIrO$_3$ thin films were prepared by laser ablating a monoclinic SrIrO$_3$ target (Furiya metal Co.: 99.9%, 2 cm in diameter) on silica substrates at substrate temperatures ($T_{\text{sub}}$) 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 $1.8 \times 10^5$ J/m$^2$, pulse width: 15 ns and repetition rate: 10 Hz) was focused onto the SrIrO$_3$ target at an angle of 45$^\circ$. The substrates were placed parallel to the SrIrO$_3$ target at a distance of 6 cm. The thickness of SrIrO$_3$ 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 ($\alpha$) of 2$^\circ$. The chemical binding state was investigated by micro-X-ray photoelectron spectroscopy (micro-XPS) using Al K$_\alpha$ radiation (Surface Science Instruments SSI-100). No Ar ion sputtering was conducted to avoid the decomposition of SrIrO$_3$ 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 SrIrO$_3$ thin films prepared at $T_{\text{sub}}$ = RT to 973 K and $P_{O_2}$ = 4 Pa. SrIrO$_3$ thin
films showed good adherence to the substrates. At \( T_{\text{sub}} \) lower than 873 K, a broad SrIrO\(_3\) diffraction peak around \( 32^\circ \) appeared suggesting amorphous structure. At \( T_{\text{sub}} = 973 \) K, other SrIrO\(_3\) diffraction peaks with monoclinic structure were also observed.\(^7\)

Figure 2 depicts the GIXRD patterns of SrIrO\(_3\) thin films prepared at \( T_{\text{sub}} = 973 \) K and \( P_{\text{O}_2} \) = 4 to 67 Pa. At \( P_{\text{O}_2} \) lower than 40 Pa, the intensity of SrIrO\(_3\) (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 SrIrO\(_3\) (114) diffraction peak was observed at \( 31^\circ \). With increasing oxygen pressure from 40 to 67 Pa, a narrow SrIrO\(_3\) diffraction peak at \( 32^\circ \) appeared. It can be indexed as the superposition of SrIrO\(_3\) (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 O\(_2\) 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 SrTiO\(_3\) films prepared on Si(001) substrate by laser ablation.\(^9\) They reported that polycrystalline presenting a structure similar to cubic bulk SrTiO\(_3\) 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 SrIrO\(_3\) 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 SrIrO\(_3\) 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 IrO\(_2\) thin films prepared at \( T_{\text{sub}} = 873 \) K and \( P_{\text{O}_2} = 13 \) Pa (d) by laser ablation.\(^{10,11}\) The binding 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, IrO\(_2\) and SrIrO\(_3\) 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 SrIrO\(_3\) thin films were almost consistent with the value of IrO\(_2\) and reported IrO\(_2\) value (62.2 eV).\(^{15}\)

Figure 4 represents schematic crystal structures of IrO\(_2\) (a unit cell) and SrIrO\(_3\) (1/2 of a unit cell). IrO\(_2\) (\( a = 0.4498 \) 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 IrO\(_2\) octahedron is 0.1982 nm.\(^{17}\) SrIrO\(_3\) 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 IrO\(_2\) octahedra (IrO\(_2\)-type I and IrO\(_2\)-type II) as shown in Fig. 4(b). The average Ir-O distance in these IrO\(_2\) octahedra is calculated to be 0.1992 nm,\(^{18}\) which is close to that of IrO\(_2\). 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 IrO\(_2\) and SrIrO\(_3\). 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 SrIrO\(_3\) thin films than that of Ir thin films suggested that the SrIrO\(_3\) thin film may not contain an Ir metal phase.

Figure 5 depicts three-dimensional tapping mode AFM images of the surface of SrIrO\(_3\) thin films prepared at \( T_{\text{sub}} = 973 \) K and \( P_{\text{O}_2} = 4, 13, 40 \) and 67 Pa. The surfaces of...
these films have no large clusters or voids. The thicknesses of the as-deposited SrIrO$_3$ 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 SrIrO$_3$ 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 SrIrO$_3$ 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 SrIrO$_3$ thin films decreased with increasing oxygen pressure. The decrease in the growth rate of SrIrO$_3$ thin films might be originated from the collisional effect at high oxygen pressures.

Figure 7 shows the resistivities of SrIrO$_3$ 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, SrIrO$_3$ thin films prepared at $P_{O_2} = 4$ Pa showed semiconductive behavior, and had a resistivity of $4.8 \times 10^{-5}$ $\Omega$m at room temperature. SrIrO$_3$ thin films prepared at $P_{O_2} = 13$ Pa exhibited the almost temperature independence of resistivity, and a resistivity of $2.1 \times 10^{-5}$ $\Omega$m at room temperature. At $P_{O_2} > 40$ Pa, SrIrO$_3$ thin films had slightly positive temperature dependence of resistivity implying metallic conduction behavior in the temperature range from
100 to 773 K. The resistivities of SrIrO$_3$ thin films prepared at $P_{O_2} = 40$ and 67 Pa were 1.2 and 0.93 $\Omega \cdot m$, respectively, at room temperature. The resistivity of SrIrO$_3$ thin films at room temperature decreased with increasing the ablation oxygen pressure. Hiratani et al. reported the preparation of SrRuO$_3$ thin films at oxygen pressure ranging from 1.3 $\times 10^{-4}$ to 13 Pa. 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 SrIrO$_3$ thin films prepared at low oxygen pressure. The suppressed oxygen deficiency at high oxygen pressure resulted in metallic behavior of SrIrO$_3$ thin films.

Figure 8 compares the resistivity of SrIrO$_3$ with those of Ir and IrO$_2$ prepared by laser ablation in our previous experiments. The thickness of Ir, IrO$_2$ and SrIrO$_3$ 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 IrO$_2$ thin films, the transmittance increased to 0.10. In the present study, the SrIrO$_3$ thin film showed the transmittance of 0.25. In recent years, IrO$_2$ thin films have been used as an electrode against oxygen diffusion for (Pb,Zr)TiO$_3$ thin films (PZT) memory devices, and showed from 0.3 to 0.2 with increasing oxygen pressure in the wavelength range from 600 to 800 nm. For SrIrO$_3$ thin films prepared at $P_{O_2} = 67$ Pa, relatively higher transmittance can be observed compared with that prepared at $P_{O_2} = 13$ and 40 Pa. It might be explained by change of oxygen deficiency in SrIrO$_3$ thin films.

Figure 10 compares the transmittance of SrIrO$_3$ thin films with those of Ir and IrO$_2$ prepared by laser ablation in our previous experiments. The thickness of Ir, IrO$_2$ and SrIrO$_3$ are 25, 60 and 95 nm, respectively. The transmittance of SrIrO$_3$ thin films prepared at $T_{sub} = 973$ K and $P_{O_2} = 4$ to 67 Pa as a function of temperature. (a) 4, (b) 13, (c) 40 and (d) 67 Pa.
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 $P_{O_2} = 4$ to 67 Pa by laser ablation. The Ir 4f$_{7/2}$ binding energies of SrIrO$_3$ thin films prepared at $P_{O_2} = 4$ 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 $\times$ $10^{-5}$ $\Omega$m and from 0.20 to 0.30 in the wavelength range of 600–800 nm, respectively, at room temperature.

Acknowledgements

The authors thank to Furuya metal Co. Ltd. and Lonmin PLC for financial support. Yuxue Liu is grateful to Ministry of Education of China and Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES