Electrical and Optical Properties of IrO\textsubscript{2} Thin Films Prepared by Laser-ablation

Yuxue Liu, Hiroshi Masumoto and Takashi Goto

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

IrO\textsubscript{2} thin films were prepared by laser ablation using an Ir target at substrate temperatures (T\textsubscript{sub}) from room temperature (RT) to 873 K in an oxygen atmosphere. A small amount of Ir metal was contained in IrO\textsubscript{2} films prepared at T\textsubscript{sub} = RT. The lattice parameters particularly a-axis values decreased with increasing T\textsubscript{sub}, and the values were a = 0.452 nm, c = 0.315 nm at T\textsubscript{sub} = 873 K in agreement with those of bulk IrO\textsubscript{2}. The surface roughness increased from 1.2 to 5.2 nm with increasing T\textsubscript{sub}. These values imply that the IrO\textsubscript{2} films were far smoother than those prepared by MOCVD and sputtering. The electrical conductivity of IrO\textsubscript{2} films prepared at T\textsubscript{sub} = RT changed from semiconductor-like to metallic behavior after a heat-treatment; on the other hand, those prepared at T\textsubscript{sub} > 573 K were metallic without changing after heat-treatment. The IrO\textsubscript{2} films prepared at T\textsubscript{sub} = 873 K showed the highest electrical conductivity of 37 \times 10^{-8} \, \Omega \text{m} at RT. The optical transmittance of IrO\textsubscript{2} thin films were mainly dependent on thickness and surface roughness, and were around 10% at a wavelength range from 300 to 800 nm.

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1. Introduction

Iridium oxide thin films have attracted attentions as an excellent bottom electrode and a good thermal barrier layer between Si wafers and capacitor dielectrics such as (Ba,Sr)TiO\textsubscript{3} or (Pb,Zr)TiO\textsubscript{3} thin films in memory devices.\textsuperscript{1,2} IrO\textsubscript{2} thin films can be formed by oxidation of Ir thin films in O\textsubscript{2} at above 773 K. Since Ir was not easily oxidized to form pure IrO\textsubscript{2} below 973 K, Ir phase may exist in IrO\textsubscript{2} thin films. However, at high oxidation temperature over 973 K, Ir may easily evaporate to form IrO\textsubscript{3} vapor. We have reported that pure IrO\textsubscript{2} thin films with low resistivity and high transmittance were prepared by oxidation of Ir thin films with embedding in IrO\textsubscript{2} powder.\textsuperscript{3} In the oxidation process, the thickness and surface morphology of IrO\textsubscript{2} thin films can be hardly controlled. Therefore, it is necessary to prepare IrO\textsubscript{2} thin films without post heat-treatment, i.e., as-deposited highly pure IrO\textsubscript{2} thin films. Although as-deposited IrO\textsubscript{2} thin films have been prepared by using several methods, such as sputtering and laser ablation,\textsuperscript{4,5} the performance, particularly, electrical resistivity and optical transmittance of IrO\textsubscript{2} thin films have not been well characterized. In this paper, the effect of substrate temperature on structure, electrical resistivity and optical transmittance of IrO\textsubscript{2} thin films prepared by laser ablation were investigated.

2. Experiment

IrO\textsubscript{2} thin films were deposited on silica substrates in oxygen ambient at an oxygen pressure of 13.3 Pa and the substrate temperatures (T\textsubscript{sub}) of room temperature (RT) to 873 K by ablating an Ir target (2 cm in diameter) using a pulsed Nd:YAG laser at a wavelength of 355 nm. A laser beam (pulse energy: 170 mJ, pulse width: 15 ns and repetition rate: 10 Hz) was focused onto the Ir target at a distance of 6 cm. The thicknesses of IrO\textsubscript{2} thin films deposited on silica substrates were determined by a talystep profiler (Rank Taylor Hobson). The X-ray diffraction (XRD, Rigaku RAD-C) and the glancing angle incidence X-ray diffraction (GIXRD, Rigaku Rotaflex RU-200B) were used to analyze the structure of IrO\textsubscript{2} thin films at incidence angles (α) of 2°. The chemical binding state of IrO\textsubscript{2} thin films was investigated by micro-X-ray photoelectron spectroscopy (micro-XPS) using Al K\textsubscript{α} radiation (Surface Science Instruments SSI-100). No Ar ion sputtering was conducted to avoid the decomposition of IrO\textsubscript{2} thin films during the sputtering. The tapping mode AFM images were taken using a Digital Instruments Nanoscope III, multimode atomic force microscope. An Si tip with end tip diameter of 5–10 nm and 300 kHz resonant oscillating frequency were used for the tapping mode imaging. The resistivity was measured in the temperature range from 100 to 773 K by a van der Pauw method. The optical transmission was studied by using a UV-VIS-NIR spectrophotometer (Shimadzu UV-3101PC).

3. Results and Discussion

Figure 1 shows the conventional XRD patterns of IrO\textsubscript{2} thin films prepared in O\textsubscript{2} at T\textsubscript{sub} = RT to 873 K. All IrO\textsubscript{2} thin films showed excellent adherence to the substrates. At T\textsubscript{sub} = RT, a broad diffraction peak at around 34° can be observed. This broad diffraction peak can be attributed to the formation of amorphous IrO\textsubscript{2} thin films.\textsuperscript{6} At T\textsubscript{sub} > 573 K, IrO\textsubscript{2} diffraction peaks with tetragonal structure appeared. The diffraction peaks shifted to higher angle and the line width of the diffraction peaks narrowed as the substrate temperature increased. The shift to higher angles of XRD peak and the narrowing of diffraction peaks were attributed to the improvement of crystallinity and local disorder.\textsuperscript{5} The angle positions of the IrO\textsubscript{2} (110), (101) and (211) diffraction peaks were insensitive to the substrate temperature. On the other hand, the (200) diffraction peaks greatly shifted to higher angles compared with that powder IrO\textsubscript{2} as the substrate temperature increased. The lattice parameters of a- and c-axis for IrO\textsubscript{2} thin films prepared at T\textsubscript{sub} = 873 K were calculated as 0.452 and 0.315 nm, respectively. These
values were in agreement with those of bulk IrO$_2$ ($a = 0.450$ nm and $c = 0.315$ nm). The shift of IrO$_2$ (200) diffraction peaks from its normal powder IrO$_2$ value could be associated with the change in the lattice parameter of IrO$_2$ thin films. By the calculation from IrO$_2$ (200) diffraction peak, the lengths of a-axis for IrO$_2$ thin films prepared at $T_{\text{sub}} = 573$, 723 and 873 K were 0.469, 0.462 and 0.452 nm, respectively. The lattice parameter of a-axis of IrO$_2$ thin films might decrease with increasing the substrate temperature. The distortion of lattice along the a-axis could be attributed to the lattice strain between IrO$_2$ thin films and the substrates and a relatively large amount of lattice defects such as oxide vacancy particularly at lower substrate temperature. This result was consistent with that of the sputtered IrO$_2$ films.

Figure 2 shows the GIXRD patterns ($\alpha = 2\theta$) of IrO$_2$ thin films prepared in O$_2$ at the substrate temperature of room temperature (a), 573 K (b), 723 K (c) and 873 K (d).

![Fig. 2 GIXRD patterns of IrO$_2$ thin films prepared in O$_2$ at the substrate temperature of room temperature (a), 573 K (b), 723 K (c) and 873 K (d).](image)

For IrO$_2$ thin films prepared in O$_2$ at $T_{\text{sub}} = RT$ to 873 K. For IrO$_2$ thin films prepared at $T_{\text{sub}} = 873$ K, the intensity ratio of the conventional XRD and GIXRD patterns was similar. This result suggested that the orientation and grain size of IrO$_2$ were not changed from the surface to inside the film. For IrO$_2$ thin films prepared at $T_{\text{sub}} = 573$ and 723 K, the intensity ratio of IrO$_2$ (101) diffraction peak to that of IrO$_2$ (200) was significantly different between conventional XRD and GIXRD. Since the GIXRD indicates the information near the surface, (101) oriented IrO$_2$ grains mainly distributed near the surface of the IrO$_2$ thin films.

Figure 3 demonstrates the micro-XPS spectra from Ir 4f core levels for the Ir (Fig. 3(a)) and IrO$_2$ thin films prepared in O$_2$ at the substrate temperature of room temperature (b), 573 K (c), 723 K (d) and 873 K (e).

![Fig. 3 The micro-XPS spectra from Ir 4f core levels for the Ir (a) and IrO$_2$ thin films prepared in O$_2$ at the substrate temperature of room temperature (b), 573 K (c), 723 K (d) and 873 K (e).](image)

The Ir 4f$_{7/2}$ binding energy for the IrO$_2$ thin films slightly increased with increasing the substrate temperature. The Ir 4f$_{7/2}$ binding energy of IrO$_2$ thin films prepared at $T_{\text{sub}} > 573$ K were almost identical.

For the Ir thin film, the Ir 4f$_{7/2}$ binding energy was consistent with that of pure Ir (60.9 eV). The slight higher Ir 4f$_{7/2}$ binding energy of IrO$_2$ thin films prepared at $T_{\text{sub}} = RT$ than that of Ir thin films suggested that Ir phase may exist in the IrO$_2$ thin films. The shapes of the XPS spectra for the IrO$_2$ thin films prepared at $T_{\text{sub}} > 573$ K were almost identical. The Ir 4f$_{7/2}$ binding energy for the IrO$_2$ thin films slightly increased with increasing the substrate temperature. The Ir
The binding energy of the IrO$_2$ thin films prepared at $T_{\text{sub}} = 873$ K (61.9 eV) was almost in agreement with that of reported value (62.2 eV).\textsuperscript{11)

Figure 4 depicts three-dimensional tapping mode AFM images of the surface of IrO$_2$ thin films prepared at $T_{\text{sub}} = \text{RT}$ and 873 K. The thicknesses of IrO$_2$ thin films prepared at $T_{\text{sub}} = \text{RT}$, 573, 723 and 873 K were 80, 100, 120 and 60 nm, respectively. Figure 5 demonstrates the root-mean-square roughness (Rms) and the growth rate of IrO$_2$ thin films as a function of substrate temperature. The IrO$_2$ thin films prepared at $T_{\text{sub}} = \text{RT}$ were smooth with the Rms of 0.48 nm. The surface roughness of IrO$_2$ thin films increased from 1.2 to 5.2 nm with increasing the substrate temperature from 573 to 873 K. It was reported that the surface roughnesses of IrO$_2$ thin films prepared by MOCVD and reactive sputtering methods ranged from 10–20 nm.\textsuperscript{12) Therefore, the surface of IrO$_2$ thin films prepared by laser ablation was smoother than that prepared by the other methods. The growth rate increased with increasing the substrate temperature in the range from RT to 723 K. As the substrate temperature was further increased to 873 K, the growth rate of IrO$_2$ thin films decreased. The decrease of the growth rate of IrO$_2$ thin films prepared at 873 K could be attributed to the formation of IrO$_3$ vapor at high temperatures.\textsuperscript{31) The evaporation of IrO$_2$ thin films may be also associated with the increase in the Rms at the high substrate temperatures.

Figure 6 shows the resistivity of IrO$_2$ thin films prepared at $T_{\text{sub}} = \text{RT}$ to 873 K as a function of temperature. The IrO$_2$ thin films prepared at $T_{\text{sub}} = \text{RT}$ showed semiconductor-like conduction behavior (Fig. 6(a)). Above 500 K, the resistivity greatly decreased with increasing temperature due to the annealing effect. When the resistivity of IrO$_2$ thin films prepared at $T_{\text{sub}} = \text{RT}$ was measured under decreasing temperature condition, metallic conduction behavior of IrO$_2$ thin films was observed (Fig. 6(b)). This result suggested that IrO$_2$ thin films prepared at RT were not well-stabilized probably containing a significant amount of defects. The improvement of crystallization could cause the decrease of
the resistivity at 773 K. The resistivities were measured under increasing and decreasing temperature, then the IrO$_2$ thin films prepared at $T_{\text{sub}} > 573$ K had almost the similar positive temperature coefficient of resistivity exhibiting metallic conduction behavior. At room temperature, the resistivity of IrO$_2$ thin films prepared at $T_{\text{sub}} = 573$, 723, and 873 K were 161, 87 and $37 \times 10^{-8}$ $\Omega$m, respectively. The resistivity of $37 \times 10^{-8}$ $\Omega$m was close to that reported in the literatures for bulk (110) IrO$_2$ ($34.5 \times 10^{-8}$ $\Omega$m). The decrease of the resistivity with the substrate temperature would be associated with the change of lattice parameter. The smaller lattice parameter could suggest fewer defects in the IrO$_2$ thin films yielding smaller resistivity.

Figure 7 depicts the transmittance spectra of IrO$_2$ thin films prepared in O$_2$ at the substrate temperature of room temperature (a), 573 K (b), 723 K (c) and 873 K (d).

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Figure 7 depicts the transmittance spectra of IrO$_2$ thin films prepared at $T_{\text{sub}} = RT$ to 873 K. The low transmittance of the IrO$_2$ thin films prepared at $T_{\text{sub}} = RT$ can be attributed to the existence of Ir phase and lattice defects in IrO$_2$ thin films. The transmittance of IrO$_2$ thin films prepared at $T_{\text{sub}} = RT$ to 723 K increased with increasing the substrate temperature probably due to the decrease in the defects in IrO$_2$ thin films. The transmittance of IrO$_2$ thin films prepared at $T_{\text{sub}} = RT$ to 723 K increased with increasing the substrate temperature probably due to the decrease in the defects in IrO$_2$ thin films. The transmittance of IrO$_2$ thin films prepared at $T_{\text{sub}} = 873$ K was smaller than that prepared at $T_{\text{sub}} = 723$ K. This might be originated from the surfacing scattering due to the larger surface roughness of IrO$_2$ thin films prepared at $T_{\text{sub}} = 873$ K.

The IrO$_2$ thin films with different thickness prepared at $T_{\text{sub}} = 723$ K in O$_2$ were used to study the thickness dependence of the resistivity and transmittance. Figure 8 shows the temperature dependence of resistivity for IrO$_2$ thin films prepared at $T_{\text{sub}} = 723$ K with the thickness of 35–120 nm. The IrO$_2$ thin films with different thickness showed metallic conduction behavior. The resistivity of IrO$_2$ thin films increased with decreasing thickness. It is the general trend that the resistivity of thin films increases with decreasing thickness, which is called as the Fuchs size effect. The resistivity of IrO$_2$ thin films was reproducible after several high temperature measurements.

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Figure 8 Resistivities of IrO$_2$ thin films prepared in O$_2$ at the substrate temperature of 723 K with the thickness of 35 nm (a), 70 nm (b) and 120 nm (c) as a function of temperature.

The figure shows the temperature dependence of resistivity for IrO$_2$ thin films prepared at $T_{\text{sub}} = 723$ K with the thickness of 35–120 nm. The IrO$_2$ thin films with different thickness showed metallic conduction behavior. The resistivity of IrO$_2$ thin films increased with decreasing thickness. It is the general trend that the resistivity of thin films increases with decreasing thickness, which is called as the Fuchs size effect. The resistivity of IrO$_2$ thin films was reproducible after several high temperature measurements.

Figure 9 Transmittance spectra of IrO$_2$ thin films prepared in O$_2$ at the substrate temperature of 723 K with the thickness of 35 nm (a), 70 nm (b) and 120 nm (c).

Figure 9 depicts the effect of thickness on the transmittance spectra of IrO$_2$ thin films prepared at $T_{\text{sub}} = 723$ K. The transmittance decreased with increasing thickness. The thinner IrO$_2$ thin films had higher transmittance in a visible light region. The absorption of IrO$_2$ thin films in wavelength range from 400 to 800 nm can be assigned to d-electrons intra-band transition.

4. Conclusions

IrO$_2$ thin films were prepared by laser ablation at substrate temperatures from RT to 873 K in an oxygen atmosphere. The XPS results suggested that Ir phase existed in IrO$_2$ thin films prepared at RT and pure IrO$_2$ thin films were prepared over 573 K. As the substrate temperature increased, the
surface roughness of IrO$_2$ thin films increased from 0.48 to 5.2 nm. IrO$_2$ thin films prepared at RT showed semiconductor-like conduction behavior. IrO$_2$ thin films prepared at the substrate temperature above 573 K exhibited metallic conduction behaviors. The room temperature resistivities of IrO$_2$ thin films decreased from 231 to $37 \times 10^{-8}$ $\Omega$m with increasing substrate temperature. As the substrate temperature increased, the transmittance of IrO$_2$ thin films increased. The increase of IrO$_2$ thin film thickness resulted in the decrease of its resistivity and transmittance.

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REFERENCES