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Formation of UO_2 Thin Film by Laser Ablation and Its Electrical Properties

Nobuaki SATO*, Migaku ARATA and Takeo FUJINO
Institute for Advanced Materials Processing, Tohoku University
**Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
dragon@tagen.tohoku.ac.jp

Uranium dioxide thin films were deposited on quartz substrates by laser ablation of UO_2 target using Nd:YAG pulsed laser. The thickness of the film increased with increasing energy, repetition time and irradiation time of laser. The crystallinity of the films was studied by X-ray diffractometry, which showed only a small broad peak at around $2\theta = 28°$ corresponding to the strongest peak of UO_2. After the heat treatment of the film in H_2 at 1273K, however, more peaks for UO_2 phase were observed: the crystallinity of the film was improved by the heat treatment. The specific resistivity of the UO_2 thin films measured by the four-probe van der Pauw method was of the order of 10^{-4} Ωm at temperatures between 40 to 300 K and it decreased with increasing temperature. In case of the H_2-treated film, the resistivity was comparable with that of bulk UO_2.

KEYWORDS: uranium dioxide, laser, ablation, thin film, electrical conductivity

I. Introduction

Uranium compounds expected to show excellent behavior in electrical, magnetic and/or optical properties because of the special bonding nature of its f-electrons. When such compounds are prepared in the form of thin film, the material properties would become more desirable one or new characters different from bulk materials would appear. The laser ablation method is one of the most convenient techniques for the formation of thin films from their compounds, such as oxides. Plumes occurred by the laser irradiation onto the target deposit on the surface of substrate forming thin film. By the laser ablation method, the ratio of metal constituents of the starting materials would not be changed in the obtained thin film[1], while non-metallic constituents, such as oxygen, would change; namely, oxygen or metal deficiency may appear in the obtained uranium oxide thin film when the uranium dioxide target is laser-ablated. Furthermore this uranium oxide thin film possibly shows different behavior compared with bulk materials. We have been doing the laser ablation studies to form thin films[2]. In this paper, we report the formation of UO_2 thin film by laser ablation of UO_2. The morphology and electrical conductivity of the UO_2 film were also studied and compared with that of bulk UO_2.

II. Experimental

For preparing UO_2, ammonium diuranate purified by the TBP extraction method[3] was first obtained, which was changed to UO_3 by heating in air at 773 K. Stoichiometric UO_2 was prepared by heating the UO_3 in a stream of H_2 at 1273 K for 6 h. The UO_2 powder was pelletized into disks of 10-mm diameter and about 1-mm thickness by using a uniaxial press at 20 MPa. The UO_2 targets were obtained by sintering UO_2 pellets at 1473 K for 4 h in a stream of H_2 gas. The UO_2 target was set in a high vacuum (10^{-8} mmHg) reaction chamber and irradiated by Nd:YAG pulse laser (λ= 1064 nm, 400 mJ, 50 Hz) which was introduced on the target with a direction of 60° from the outside of the chamber through the ZnSe window. The uranium oxide thin film was deposited on a quartz substrate faced to the target by laser ablation. The distance between target and substrate was 70 mm. For comparison, the heat-treated uranium oxide films were also prepared by heating the original films in H_2 gas at 1273 K for 1 h.

X-ray diffraction measurements of thin films were carried out using a Rigaku RAD-IC diffractometer equipped with a Rigaku MJ20ML2 thin film holder. A Cu$K\alpha$ radiation (40 kV, 20 mA) monochromatized with flat-type pyrolytic graphite was introduced on the thin film with θ=2°. The slit system was 1°-1°-0.05mm-0.6mm. The average film thickness was determined by a ULVAC DEKTAK^{3}ST surface profile measuring apparatus. The surface compositions of the films were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI model 5600 XPS system with a concentric hemispherical analyzer. The sputtering of Ar^+ ion was carried out with a beam of 5 kV and 100 μA/cm^2.

The electrical conductivity and the Hall effect were measured by the four-probe van der Pauw method. A controlled current of 30 mA (Advantest TR-6143) was applied to the sample, and the potential drop was measured by a Keithley Model 182 voltmeter of which

the input impedance was >10 GΩ. The Hall effect measurement was made by applying a constant current of 30 mA and a magnetic filed of 0.58 T, and by reversing the magnetic field and current to eliminate misalignment and thermal voltage effects.

III. Results and Discussion

1. Effects of laser energy and repetition rate

When the UO_2 target was irradiated by the laser light of 400 mJ and 50 Hz for 6 s, a white plume occurred from the surface of the target. After the ablation reaction, a dark gray film (UO_2 film) was deposited on a quartz substrate in a high vacuum chamber at the oxygen pressure of 10^{-8} Torr. On the other hand, no deposition took place when the laser energy was as low as 100 mJ. The laser energy higher than 200 mJ and repetition rates higher than 25 Hz are needed for the deposition of thin film: Power of the laser light is essential for the ablation of UO_2 target. After the ablation reaction, the surface of the target became darkened at high laser power, while no change was observed at low laser power. The effect of ablation time on the film thickness of UO_2 film deposited on SiO_2 substrate at room temperature is shown in Fig.1, where the laser light of 400mJ and 50Hz was irradiated to UO_2 target.

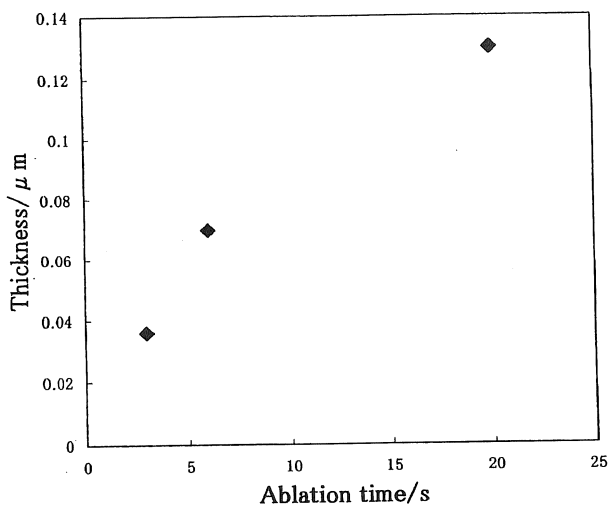

Fig. 1 Effect of ablation time on the film thickness of UO_2 film deposited on SiO_2 substrate.

From this figure, it is seen that the film thickness was increased with increasing ablation time. The film growth rate of 0.7 μm/min was obtained in the first 10s. However the growth rate decreased gradually after 10 s. This may be caused by the loss of the materials near the ablated area. The growth rate of the ablation method is faster than that of CVD method (10^{-2} to 10^{-3} μm/min), but slower than that of sputtering method (a few μm/min).

2. Effect of substrate temperature

The X-ray diffraction patterns for UO_2 films deposited on a quarts substrate at different temperatures were given in Fig. 2. The irradiation was conducted with a laser light of 400 mJ and 50 Hz for 6s. It is seen that a strong peak appears at around 2θ=28.0[3] which corresponds to the (111) peak of UO_2, and is in all the patterns except for the case of 300°C. The other peaks for UO_2 structure were unclear, namely the crystallinity of the UO_2 thin film was not well. Though the substrate temperature was increased, there seems to be no significant difference between these samples obtained at different substrate temperatures. The laser-ablated UO_2 film seems to consist of the micro crystalline assembly of the oxides rather than an amorphous structure comparing with the cases, such as Ta_2O_5. Other uranium oxides phases, such as U_4O_9, U_3O_8 and UO_3, were not observed[3].

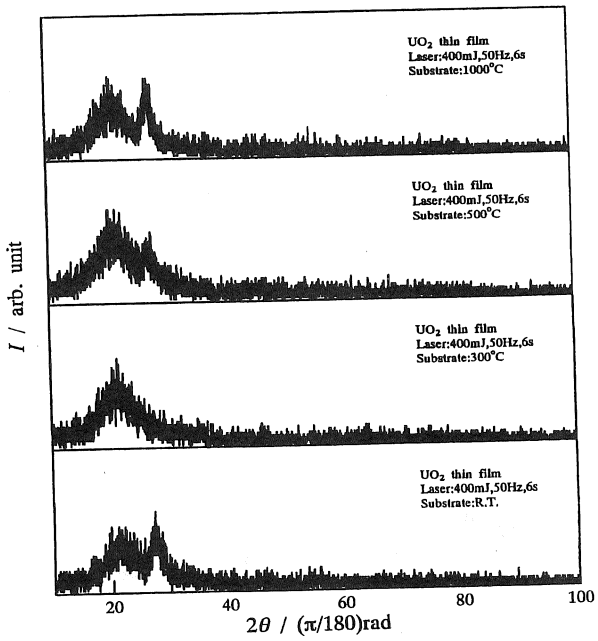

Fig. 2 X-ray diffraction patterns for UO_2 thin films deposited at different substrate temperatures.

3. XPS of UO_2 film

For analyzing the oxidation state and composition of UO_2 film, XPS was measured out for the UO_2 films. From the result of the XPS survey scan of UO_2 film, the peaks for C1s, O1s, Si2p and U4f electrons were observed. The XPS U4f spectra recorded on a UO_2/SiO_2 films before and after heat treatment are given in Fig.3(a) and (b), respectively. The typical binding energy for $U4f_7$ electron is 380.0 eV which is shown in the figure as a

dotted line. The observed peak at 380.4eV is close to the dotted line. Since the bonding energies of $U4f_7$ for U_3O_8, U_4O_9 and UO_3 are 380.1, 379.9 and 381.7 eV, respectively, it is not clear from the XPS result where the uranium of UO_2 thin film takes a tetravalent or not.

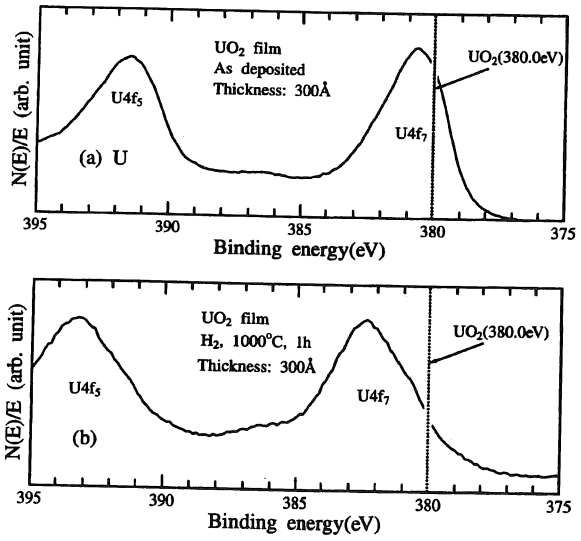

Fig.3 XPS U4f spectra recorded on a UO_2/SiO_2 films. (a)As deposited, (b) After heat treatment.

4. Effect of heat treatment

Next, the UO_2 thin films obtained at different substrate temperatures were heat-treated in H_2 atmosphere at 1273 K for 4 h. The X-ray diffraction patterns for the heat- treated films are shown in Fig.4. From the result, it is seen that the more peaks for UO_2 fluorite structure appear for the films deposited on the room temperature substrate even under the different laser irradiation conditions((a), (b)): The crystallinity of the films was improved.

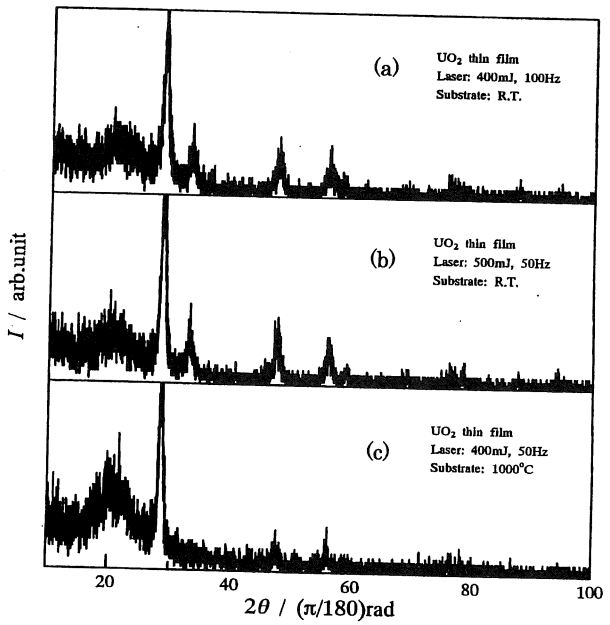

Fig.4 X-ray diffraction patterns after heat-treatment in H_2 at 1273 K for UO_2 thin films deposited at different substrate temperatures.

It is seen that the peak of the (111) plane of UO_2 structure is by far the strongest in the X-ray diffraction profile of 1273K deposited film(Fig.4(c)), suggesting that the orientation effect in the diffraction seems to be related to this UO_2 film. In Fig.3(b), the XPS U4f spectra are recorded on a UO_2/SiO_2 film which was heat-treated in H_2 at 1273 K for 1 h. Comparing the XPS U4f spectra of as deposited UO_2 film (Fig.3(a)), the peaks slightly shifted to higher energy side. From the result of the quasi-quantitative analysis of the XPS spectra, the O/U ratio of heat-treated UO_2 film was 2.40. This value is slightly larger than 2.04 of the as deposited UO_2 film. If the stoichiometric UO_2 is obtained by the heat treatment, the original UO_2 thin film seems to have an oxygen deficiency.

5. Electrical conductivity

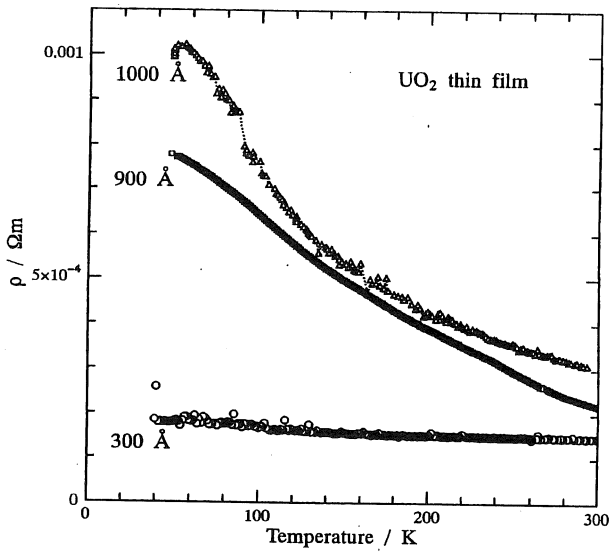

Fig.5 Specific resistivity of UO_2 thin film as a function of temperature.

The specific resistivity, ρ, of UO_2 thin film of different thickness was measured in a temperature range from 40 to 300 K as shown in Fig.5. Since the ρ value decreases with increasing temperature, these UO_2 thin films are semi-conductive. As the thickness of the film decreased, the temperature dependence of the ρ value became less independent to the temperature. It is surprising that UO_2 film is still low at lower

temperatures: Almost no temperature dependence for the 300 Å film is seen, in sharp contrast to bulk UO_2 of which the resistivity is very high at lower temperatures[4]. After the heat treatment of these films in H_2 atmosphere at 1273 K for 1 h, the resistivity of the films could not be measured by the van der Pauw method. By the two pole method using ultra high resistivity meter, it was proved that the ρ value of these films at room temperature is the order of 10^6 Ω, which is comparable with that of bulk UO_2 at room temperature. The Hall effect of these films could not be measured because the amount of the sample was so small.

Specific resistivity of UO_2 thin film as a function of film thickness is shown in Fig. 6. It is seen that the ρ value increases with increasing film thickness. Usually, in the case of size effect of conductive thin film, the ρ value decreases when the thickness increases. The higher electrical conductivity of the laser-ablated UO_2 film is thought to be ascribed to the amorphous structure and oxygen deficiency, but the reason is not clear at present.

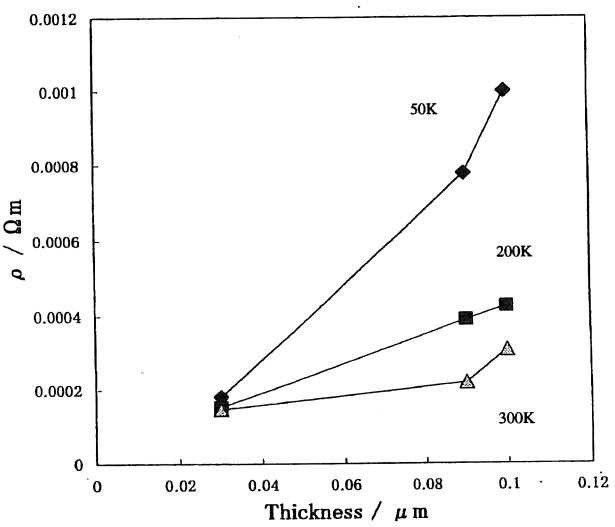

Fig.6 Specific resistivity of UO_2 thin film as a function of film thickness.

IV. Conclusion

In the present study, UO_2 thin films were deposited on quartz substrates by laser ablation of UO_2 target using Nd:YAG pulse laser. The thickness of the film increased with increasing energy, repetition time and irradiation time of the laser. By X-ray diffractometry, only a small broad peak was observed at around $2\theta = 28°$ corresponding to the strongest peak of UO_2. This shows that the crystallinity of the film was low. After the heat treatment of the film in H_2 at 1273 K, however, the crystallinity of the film was improved. The specific resistivity of the UO_2 thin films measured by the four-probe van der Pauw method was of the order of 10^{-4} Ω m at temperatures between 40 to 300 K and it decreased with increasing temperature. In case of the H_2-treated film, the resistivity was comparable with that of bulk UO_2.

Acknowledgement

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