Effect of Heat Treatment Using CO₂ Laser on Ta₂O₅ Film Formation by Electrostatic Spray Deposition

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静電噴霧法を用いた Ta₂O₅ 薄膜作製における CO₂ レーザーによる熱処理の効果

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Introduction

A wide variety of transition metal oxides have been used for electronic, optical, or magnetic applications. In the development of these application devices it is important to investigate the properties of these compounds having the various forms as well as the bulk specimen. Especially, the material in the form of thin film is attractive for the miniaturized electronic devices.

Generally, it is difficult to fabricate the transition metal oxides in the form of thin film, since many inorganic materials have high melting points due to their crystalline nature. The thin film preparation has been usually performed by way of chemical vapor deposition, RF-sputtering, sol-gel method, electrolysis and so on. We have been studying the electrostatic spray deposition (ESD), which is characteristic in simpler experimental procedure and apparatus in comparison with other techniques^{1)~3)}. This technique is usually used for the materials synthesized at lower temperatures (<500°C)^{4)~6)}. However, it often becomes necessary to heat precursor materials on substrates at high temperature in order to make many kinds of thin films. In the present study, the ESD was combined with heating treatment of CO₂ laser irradiation, and the formation of Ta₂O₅ film was carried out. The crystal structure and morphology of the film were also examined.

Experimental

The experimental setup is schematically shown in Fig. 1. This method consists of generation of an aerosol by applying a high voltage between a substrate and a desired precursor solution, and chemical reaction of

deposited precursor materials by irradiation of CO₂ laser.

A gold flag type disk (6mm ϕ , 0.1mm^t) was used as a substrate to avoid interaction with oxygen under oxidizing condition. The substrate was put on a carbon plate on an aluminum hot plate (15 $\times$ 15 $\times$ 1.5^t cm), and grounded via the plate. The temperature of the hot plate was controlled at 150 $\pm$ 3°C. The ethanol solution of 0.025 mol/dm³ of purified tantalum buth-oxide was prepared as the precursor solution prior to each experiment. The precursor solution was flowed through a stainless needle (i.d. 0.3mm ϕ , o.d. 0.5mm ϕ) using a syringe pump (Kd scientific type 100) at a rate of 4.0 mL/h.

To generate an aerosol of precursor materials, a positive high voltage of 10-12 kV was applied to the needle using a high voltage power supply (Matsusada Precision, HVR-12 P) with flowing precursor solution. The needle-substrate distance was fixed at 5.0 cm. The spraying was conducted for 30-90 min. The sample deposited on the substrate by spraying was heated up rapidly in air by the irradiation of CO₂ laser (λ = 10.6 μ m, beam diameter = ca. 6 mm ϕ) with the power of 105-177 W/cm² for a period in a range of 10 sec to 10 min.

Fig. 1 Schematic representation of experimental apparatus.

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Fig. 2 X-ray diffraction pattern of Ta_2O_5 film on Au substrate. Spraying: $4.0 \text{ mL/h} \times 60 \text{ min}$, Irradiation: 177 W/cm^2 , 10 s. Crystal system: pseudo-hexagonal.

The phase of the product was identified by X-ray diffractometry (Rigaku, RAD-IC diffractometer). The morphology of product was observed by scanning electron microscope (Hitachi, S-4100 L). The average film thickness was determined by a surface profile measuring system (ULVAC Dektak³ST).

Results and Discussion

Fig. 2 shows the X-ray diffraction pattern of Ta_2O_5 thin film on Au substrate. The spraying period was 60 min and the substrate was irradiated by CO_2 laser of 177 W/cm^2 for 10 sec. The product was assigned to the $\delta\text{-Ta}_2\text{O}_5$ phase ($\text{Ta}_2\text{O}_{5-x}$) having pseudo-hexagonal crystal system. This indicates that the oxidation state of tantalum was slightly smaller than +5 for stoichiometric Ta_2O_5 compound⁷⁾. The lattice parameters were calculated to be $a/\text{\AA} = 3.634$, $c/\text{\AA} = 3.882$. The films prepared with irradiation time of 1 and 10 min were also assigned to the $\delta\text{-Ta}_2\text{O}_5$ phase, and the change of the lattice parameters with irradiation time was small, i.e. $a/\text{\AA} = 3.627$, $c/\text{\AA} = 3.887$ and $a/\text{\AA} = 3.619$, $c/\text{\AA} = 3.880$, respectively. The observation of SEM images revealed that the grain boundary was not clear, indicating the solid quickly sintered under laser irradiation.

In the case of irradiation of 105 W/cm^2 , the X-ray diffraction pattern showed only the peaks of Au substrate. The SEM observation showed the surface product having the morphology of branch like. These results suggest that the product was amorphous. In the case of preparation of Ta_2O_5 film using CVD technique, crystallization of the film started at around 660°C of thermal treatment temperature⁸⁾. Therefore, at the laser power of 105 W/cm^2 , the temperature of the substrate could be less than 660°C . From these results, the laser power is seen to be a key factor to

Fig. 3 Effect of spraying time on Ta_2O_5 film thickness. Flow rate: 4.0 mL/h , Irradiation: 1 min.

determine the crystallinity of Ta_2O_5 film.

Fig. 3 shows the effect of spraying time on the film thickness (irradiation period: 1 min). For both of 177 and 105 W/cm^2 , the film thickness increased almost linearly with spraying time, and was independent of irradiation period. It is possible to control the film thickness by changing the spraying time.

Conclusion

The synthesis of Ta_2O_5 film on Au substrate was carried out by using an electrostatic spray deposition combined with CO_2 laser irradiation. The irradiation of CO_2 laser enabled us to heat up to high temperature rapidly. The crystallinity was strongly dependent on the laser power. It was found that the product at a laser power of 177 W/cm^2 was $\delta\text{-Ta}_2\text{O}_5$ phase, while that of 105 W/cm^2 was amorphous.

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