Transmission electron microscopy (TEM) studies of the epitaxial and polycrystalline Tin oxide films prepared by the excimer laser-assisted metal organic deposition

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Abstract Epitaxial and polycrystalline SnO₂ thin films were prepared by the excimer laser annealing of amorphous SnO₂ films on TiO₂ (001) and MgO (001) substrates. The amorphous SnO₂ film was prepared by a metal organic deposition (MOD) using di-n-butylbis (2, 4-pentanedionate) tin at 300°C. The crystallinity and orientation of the product films were investigated by the XRD, pole figure and transmission electron microscopy (TEM) analyses. At 200 mJ/cm², the (002) oriented SnO₂ films were obtained by KrF laser irradiation. Using the XRD φ scanning measurement and TEM, it was found that the oriented SnO₂ films were epitaxially grown on the (001) TiO₂ substrate. On the other hand, the polycrystalline SnO₂ film was obtained on the MgO (001) substrate. It was found that the grain size of the SnO₂ film on the MgO substrate near the surface is larger than that of the near substrate based on cross-sectional bright field TEM micrographs.

1. Introduction
Tin oxide (SnO₂) films are widely used for a variety of applications because of their high conductivity, high transparency in the visible region, and mechanical and chemical stabilities [1-3]. Chemical solution methods, such as metal organic deposition (MOD), are candidate methods for preparing oxide films because of their simplicity and low cost investment. However, heat treatments at temperatures higher than 500°C are required for the formation of the polycrystalline SnO₂ films [4-5]. In addition, to prepare oriented SnO₂ films, it is necessary to heat the films at higher temperatures with longer annealing times [6]. To overcome these problems, an excimer laser would be considered to be a powerful tool because an excimer laser has the characteristics of a high photon energy and short pulse, thus decreasing the thermal effects of the non-irradiated part of the substrate. We have already investigated the preparation of the SnO₂ films [6] using this technique. In a previous study [6], we investigated the effect of various substrates on the formation of the SnO₂ films using a KrF laser, and obtained epitaxial SnO₂ films on the (100) TiO₂ substrates at low temperature. However, the formation of the epitaxial or polycrystalline SnO₂ film was not clarified. To clarify the formation mechanism of the SnO₂ or other oxide films using an excimer laser – assisted metal organic deposition (ELAMOD), it would be necessary to investigate the microstructure of the product films on various substrates using transmission electron microscopy. In this study, to clarify the formation of the SnO₂ film, we investigated the microstructure of the SnO₂ films on TiO₂ and MgO substrates prepared by ELAMOD, and discuss the formation mechanism of the SnO₂ films.
2. Experimental
A homogeneous starting solution was prepared by mixing di-n-butylbis (2, 4-pentanedionate) tin (Sn-acac) solution and n-butyl alcohol to the appropriate concentration and viscosity for spin coating. This solution was spin-coated onto a single-crystal (001) TiO$_2$ substrate at 4000 rpm. The Sn-acac coated films were dried at 100 °C in air to eliminate the solvent. The films were then heated at 300 °C in air for 10 min to decompose the organic components of the film. Finally, the films were irradiated by the KrF laser at 25°C and 10 Hz for 3000 shots in air. The irradiated area was 8mm×8mm. To increase the film thickness, the spin-coating, the preheating and laser irradiation procedures were repeated five times. The film thickness was 200 nm. The crystallinity or epitaxy of the films was examined by x-ray diffraction (XRD; MAC Science, MXP3A) θ-2θ scans and φ scanning analysis. The cross-section transmission electron microscopy (XTEM) observations were performed using a high resolution electron Hitachi H-9000 microscope operated at 300 kV. The XTEM specimens were prepared following the conventional method, i.e., mechanical cutting, face-to-face gluing, mechanical grinding, polishing and dimpling, followed by Ar-ion milling at 4 KV.

3. Results
3.1 SnO$_2$/TiO$_2$ films
At first, to identify the phase of the product films, we performed XRD measurement for the product films. Figure 1 shows the XRD patterns of the SnO$_2$ films prepared by the KrF laser irradiation at 150 and 200mJ/cm$^2$ at 10 Hz at the 3000 shots. At 150 mJ/cm$^2$, the SnO$_2$ (110), (101) and (211) peaks appeared. Compared with the standard XRD spectrum (JCPDS: 41-1445), the intensity of the SnO$_2$ (002) peak increased whereas SnO$_2$ (110), (101) and SnO$_2$ (211) are observed. At 200 mJ/cm$^2$, highly (002) oriented SnO$_2$ films was formed on the TiO$_2$ substrate as shown in Fig 1 (b). To examine the in-plane alignment of the (002) oriented SnO$_2$ films on the TiO$_2$ substrate, we performed an XRD φ scanning.

![Fig.1 the typical line profiles of the XRD Θ-2Θ scans of a (002) oriented SnO$_2$ on the (001) TiO$_2$ substrate prepared by ELAMOD.](image1)

![Fig.2 the typical line profiles of the XRD φ scans of (a) a (002) oriented SnO$_2$ on the (001) TiO$_2$ substrate prepared by ELAMOD and (b) the (001) TiO$_2$ substrate.](image2)
Fig. 2 shows the typical line profiles of the XRD $\phi$ scans of a (002) oriented SnO$_2$ on the (001) TiO$_2$ substrate prepared by this technique. As shown in Fig. 2(a), eight sharp peaks were recognized for the films, and each peak was located at the same $\phi$ angle as that for the (211) reflection of the substrates. To confirm whether the $\phi$ scan peaks of Fig. 2(a) were due to the SnO$_2$ films or (001) TiO$_2$ substrate, we measured the XRD $\phi$ scans of the (001) TiO$_2$ substrate under the same analysis conditions for the SnO$_2$ film. As a result, the peaks due to the (001) TiO$_2$ substrate were much smaller than that of the SnO$_2$ films on the (001) TiO$_2$ substrate as shown in Fig. 2(b). Therefore, the epitaxial SnO$_2$ film on the (001) TiO$_2$ substrates was successfully obtained by the excimer laser annealing process. The relationship for the epitaxial SnO$_2$ film on TiO$_2$(001) is [010] (001) SnO$_2$ // [010] (001) TiO$_2$.

Figure 3 shows an XTEM image and the corresponding selected area electron diffraction (SAED) pattern of the SnO$_2$ film grown on a TiO$_2$ substrate obtained by the ELAMOD process using KrF irradiation at room temperature. The laser fluence was set in at the constant fluence of 200 mJ/cm$^2$. The film shown in Fig. 3 is obtained by 5 superimposed layers; each layer is preheated at 300˚C and irradiated for 5 min (3000 pulses, pulse duration 20 ns, 10 Hz). The total film thickness is approximately 150 nm, thus each layer is approximately 30 nm. The SAED pattern (Fig. 3 b) was evidence for the single-crystalline structure of the obtained film. The SAED pattern also shows the diffraction spot of the TiO$_2$ substrate. The high quality epitaxy of the SnO$_2$ film was also confirmed by the HRTEM image (Fig. 4) taken in the region close to the SnO$_2$/TiO$_2$ interface.

![Fig. 3: XTEM image and the corresponding SAED pattern of the SnO$_2$ film grown on TiO$_2$ substrate [preheated at 300˚C, 3000 pulses, and 200 mJ/cm$^2$].](image)

![Fig. 4: HRTEM image showing details of the SnO$_2$ film grown on TiO$_2$ substrate [preheated at 300˚C, 3000 pulses, and 200 mJ/cm$^2$].](image)
3.2. SnO$_2$ / MgO film

Fig. 5 shows the XRD pattern of the SnO$_2$ film on MgO substrate prepared by the KrF laser irradiation at 200mJ/cm$^2$ and 10 Hz at the 3000 shots. The SnO$_2$ (110), (101) and (211) peaks appeared, and no epitaxial SnO$_2$ film was formed.

Fig. 5 the XRD pattern of the SnO$_2$ film on MgO substrate prepared by the KrF laser irradiation at 200mJ/cm$^2$ at 10 Hz for 3000 shots.

Figure 6 (a) shows an XTEM image of the SnO$_2$ films grown on the MgO substrate. The gradient perpendicular to the surface is clearly revealed on the XTEM image. In Fig. 7, the HRTEM images taken from different regions [I and II indicated in Fig. 6] of the SnO$_2$ film grown on MgO substrate are shown. In the region (I) close to the substrate and middle part, the SnO$_2$ film is composed of small grains. The thickness of this part of the film (I) is approximately 50 nm and the grains sizes are in the interval of 5 to 10 nm (Fig. 6(a)).

The selected area electron diffraction (SAED) patterns of the SnO$_2$ film on MgO substrate are shown in Fig. 6(b). The SAED patterns show the typical 110, 101 and 211 rings that correspond to the polycrystalline cassiterite structure, in accordance with the XRD results. Moreover, the continuity of the rings in the SAED patterns of films indicates the presence of randomly oriented SnO$_2$ crystallite of small dimension.
4. Discussion
We considered that the formation mechanism of the SnO$_2$ films prepared by the ELAMOD process. In a previous study, we have successfully obtained epitaxial Pb(ZrTi)O$_3$(PZT)[7, 8] and La$_x$Sr$_{1-x}$MnO$_3$(LSMO) films [9, 10] using this technique, and found that the epitaxial growth of the PZT film depends on the optical properties of the substrate materials[7]. That is to say, when the metalorganic (MO) films were irradiated by an excimer laser, the MO films were converted to amorphous oxide films by the photolysis during the first irradiation step, and then the crystallization or orientation of the oxide films were considered to occur through a photothermal reaction due to the light absorption of both the amorphous films and substrates during the second irradiation step. Similarly, the epitaxial SnO$_2$ film on TiO$_2$ substrate was easily formed by the KrF laser irradiation at the lower laser fluence of 150mJ/cm$^2$ because TiO$_2$ substrate has an optical absorbance in the UV region. In contrast, according to the TEM data, the gradient perpendicular to the surface is clearly

Figure 6: (a) XTEM image and (b) SAED pattern of SnO$_2$ film grown on MgO substrate (preheated at 300°C, 3000 pulses, and 200 mJ/cm$^2$).

Figure 7: HRTEM images showing details in (a) top part (region I) and (b) middle part (region II) of the SnO$_2$ film grown on MgO substrate.
revealed on the XTEM image of the SnO₂ film on the MgO substrate. The gradient perpendicular to the surface would be considered to be related to the crystallization mechanism of the SnO₂ film on the MgO substrate using KrF laser. The MgO material is transparent in the UV region [7], and then there is no photothermal effect due to the MgO substrate, when the first SnO₂ layer was irradiated by the KrF laser (248 nm). When the film thickness (i.e., the number of layers) increases to 60 ~ 150 nm, the KrF laser is absorbed in the SnO₂ film (region II) and then, the photothermal reaction of the SnO₂ layer would take place. Therefore, the crystallization of the SnO₂ film would be accelerated by the under SnO₂ layer and the grains size was changed to 80 nm in the upper part of the film (region I). Based on these results, it was found that the crystallization of the SnO₂ film would be strongly affected by not only the optical absorbance of the preheated amorphous SnO₂ film but also the optical absorption of the substrate materials.

5. Conclusions

Epitaxial SnO₂ thin films were prepared on (001) TiO₂ substrates by the excimer laser annealing using KrF laser. When the amorphous SnO₂ film on the TiO₂ substrate was irradiated by the KrF laser at a fluence of 200 mJ/cm² and 25 °C, epitaxial SnO₂ film was obtained. The relationship for the epitaxial SnO₂ film on TiO₂ (001) is [010] (001) SnO₂// [010] (001) TiO₂. The high quality epitaxy of the SnO₂ film was also confirmed by the HRTEM image. On the other hand, when using the MgO substrate at a fluence of 200 mJ/cm², polycrystalline SnO₂ film was formed. It was found that the formation of the epitaxial and polycrystalline SnO₂ would be affected by the photothermal effect of the substrate or the first SnO₂ layer which undergoes an absorption.

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