論文の内容の要旨

論文題目

# Crystallization kinetics and microstructures of amorphous $Ti_{1-x}Nb_xO_2$ as a precursor of transparent conducting thin films
# (透明導電膜の前駆体としてのアモルファス $Ti_{1-x}Nb_xO_2$ の結晶化過程と微細構造)

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## Introduction

Transparent conductive oxide (TCO) is an indispensable material in optoelectronic devices, such as flat panel displays and photovoltaics. Currently, indium tin oxide (ITO) is widely used as TCO because of its excellent conductivity and transparency in the visible region. However, the shortage of indium, a major component of ITO, requires the development of TCO alternatives composed of more abundant elements. Recently, it has been reported that Nb-doped anatase $TiO_2$ ($Ti_{1-x}Nb_xO_2$; TNO) thin films in both epitaxial [1] and polycrystalline [2] form exhibit low resistivities ($\rho$) of the order of $10^{-4}$ Ωcm and high transmittances of 60–90% in the visible region, demonstrating the potential of TNO as a next-generation TCO.

There are two main methods for fabricating polycrystalline TNO films: direct deposition of crystallized films on heated substrates [3] and crystallization of amorphous films deposited on unheated substrates by post-deposition annealing [4]. Since it is much easier to obtain TNO films with $\rho < 1 \times 10^{-3}$ Ωcm by the latter method, the crystallization process of amorphous TNO films, including nucleation and crystal growth from the nuclei, has attracted great interest. However, even the basic parameters of crystallization kinetics of amorphous $TiO_2$ have scarcely been examined thus far. In addition, experimental factors that determine grain sizes after crystallization are still unclear.

In this study, the crystallization kinetics of sputter-deposited amorphous TNO films during isothermal annealing was studied by *in situ* X-ray diffraction (XRD). The crystallization of TNO films was found to have two-dimensional saturation growth. This implies that the density of nuclei, which limits the grain size after crystallization, is constant irrespective of annealing condition. To further explore the factors determining the density of nuclei, the microstructures of the amorphous films was investigated. The results show that the microstructures of amorphous films followed Thornton model, in which working pressure has a great influence on microstructure through shadowing effect. The grain size was strongly affected by the working pressure of sputtering,

suggesting that voids formed by shadowing effect behave as the nucleation sites.

## Experimental

Amorphous TNO films were deposited on alkaline-free glass substrates and thermally oxidized $SiO_2$-coated Si substrates without intentional substrate heating by RF magnetron sputtering technique. A 2-inch-diameter ceramic disk with $Ti_{0.963}Nb_{0.037}O_{2-\delta}$ composition was used as a target. For *in situ* XRD measurements, TNO films were deposited at a working pressure $P$ =1 Pa in a mixture of Ar and $O_2$. For structural studies, TNO films were deposited in a mixture of Ar and $H_2$ at the $P$ range of 0.2 to 2 Pa. The as-deposited amorphous films were crystallized by $H_2$ annealing at 600 $^oC$ for 1 h. The crystallization kinetics of the amorphous films during isothermal annealing was monitored by an *in situ* X-ray diffractometer equipped with a heating unit. The *in situ* XRD measurements were continued until the diffraction intensity of anatase (101) no longer changed. *Ex situ* polarized-light optical microscopic (POM) observations were carried out at room temperature to confirm the completion of crystallization and to characterize grain sizes. The surface and cross sectional topography was examined by scanning electron microscope (SEM).

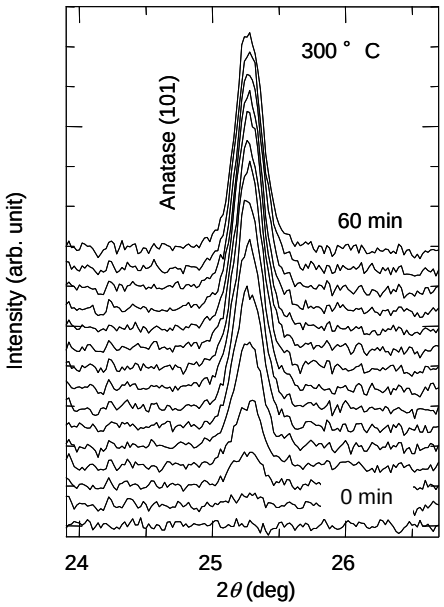


**Fig. 1** *In situ* XR profile of anatase (101) peak of TNO film deposited at $f(O_2)$ = 1%

## Results and discussions

### Crystallization kinetics of amorphous thin films

Fig. 1 shows the evolution of the anatase (101) diffraction peak for the TNO film deposited at $f(O_2) = [O_2/ (Ar+O_2)]$ = 1% ($T_a$ = 300 °C). The amorphous TNO film appears to gradually crystallize into a polycrystalline anatase phase. The volume fraction of the crystallized anatase phase at each

annealing time $t$ was evaluated as $x(t) = I(t)/I(\infty)$, where $I(t)$ and $I(\infty)$ are the integrated intensities of the (101) diffraction peak at time $t$ and at the end of the measurement, respectively. The obtained $x$ vs $t$ curve is shown in Fig. 2(a).

According to the JMA formula [5], the crystallization kinetics is given by

$$x(t) = 1 - \exp(-kt^n), \qquad (1)$$

where $k$ is a time constant depending on both the nucleation rate and growth rate, $n$ is the Avrami exponent, which reflects the dimensionality of crystal growth and the nucleation rate relative to the growth rate. For isothermal crystallization, the Avrami plot of $\ln(-\ln(1-x))$ vs $\ln(t)$ yields a straight line with a slope of $n$. Fig. 2(b) shows $\ln(-\ln(1-x))$ vs $\ln(t)$ curves for the three TNO films. From Fig. 2(b), The value of $n$ equal to 2.7, 2.0, and 2.2 were obtained for the TNO films deposited at $f(O_2)$ = 0, 1, and 5 %, respectively. In a conventional three-dimensional crystal growth process, $n$ is known to be in the range of 3–4, while a two-dimensional growth process is characterized by $n$ in the range of 2–3. Thus, it can be concluded that the crystallization of the present sputter-deposited TNO films proceeds mostly in a two-dimensional manner. The range of $n$ values also gives information about the nucleation process. When nucleation occurs continuously with a constant rate, $n$ should be 3. In a process with saturated nucleation sites, where the total number of nucleation sites is limited, $n$ takes a value of 2. The $n$ values of the TNO films deposited at $f(O_2)$ = 1 and 5 % are very close to 2, indicating that the nucleation sites are consumed in the early stage of growth and that crystal growth propagates in lateral directions from the nuclei. On the other hand, the $n$ value of the TNO film deposited at $f(O_2)$ = 0 % is rather close to 3, implying continuous nucleation during the crystal growth.

The two-dimensional growth of fully crystallized TNO films was also confirmed by POM observations. As shown in Fig. 3(a)–3(c), the grains have lateral sizes exceeding several μm. Therefore the crystal growth of TNO films is two-dimensional as the grain size in the lateral direction was much larger than the film thickness (300 nm). This result is consistent with the *in situ* XRD measurements described in the paragraph above.

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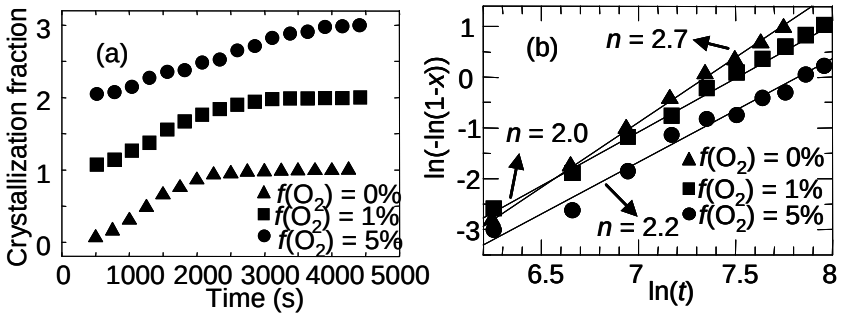


**Fig. 2** (a) Crystalline fraction $x$ as a function of time $t$ for TNO films deposited at $f(O_2)$ = 0%, 1% (vertically shifted by 1 for clarity), and 5% ( vertically shifted by 2 for clarity), (b) Avrami plots for TNO films derived from (a).

**Fig. 3** POM images of the isothermally crystallized TNO films for $f(O_2)$ = (a) 0, (b) 1, and (c) 5% at $P$ = 1 Pa

**Impact of microstructure due to shadowing effect**

As described above, amorphous TNO films crystallize with a site saturation mode in a two-dimensional manner. The site saturation growth means that the density of nuclei, which reflects grain size after crystallization, is constant irrespective of annealing condition. Therefore, the difference in the density of nuclei should be attributed by the structure of amorphous films.

According to Thornton model, films deposited at higher $P$ tend to show porous structures and rough surfaces due to the shadowing effect [6]. Because of collisions with Ar atoms, the mean free path of sputtered particles decreases with increasing $P$, which enhances the shadow effect and thus affects the microstructures of the films. Figs. 3(a), 3(b), 3(c) show cross sectional SEM micrographs of amorphous films deposited at $P$ = 0.2, 1, and 2 Pa, respectively. The microstructure becomes more porous with increasing $P$, being consistent with Thornton model. Figs. 4(a), 4(b) show POM images of crystallized TNO films fabricated under $P$ = 0.2 and 1, respectively. The microstructure of the TNO films fabricated at $P$ = 2 Pa was observed by SEM, instead of POM, due to small grain, as shown in Fig. 4(c). It is evident that the TNO films deposited at lower $P$, where the influence of shadow effect is weak, exhibit larger grain sizes. It is suggested that the shadowing effect becomes less significant at lower $P$, resulting in the decrease of the density of nuclei and thus the enhancement of grain sizes. That is reasonable because the surface of void, a kind of interface, could work as nucleation centers. The existence of shadowing effect was further confirmed by the following experiment shown in Fig. 5. Three holes with diameters of 1, 1.5, and 2 mm were made on a 1-mm-thick metal mask. As the diameter decreases, slant particles, which are responsible for the shadowing effect, are expected to be filtered. Fig. 5 shows POM images of the films crystallized from amorphous ones prepared by this mask at $P$ = 1 Pa. Notably, the grain size increases with decreasing the diameter of the holes, supporting the conclusion that shadowing effect determines the density of nucleation centers and thus the size of TNO grains.

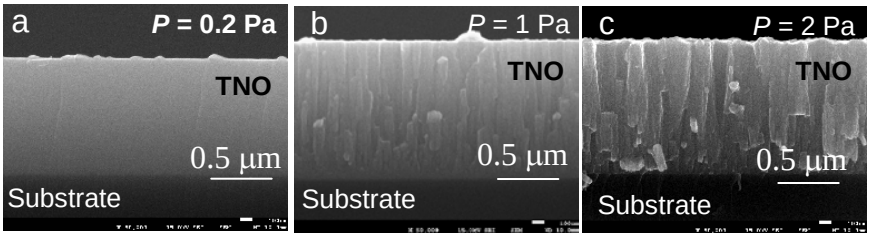


**Fig. 4** Cross sectional SEM micrographs of amorphous TNO films deposited under different conditions: (a) $P$ = 0. Pa, (b) $P$ = 1 Pa, and (c) $P$ = 2 Pa.

**Fig. 5** (a)-(b) POM images of TNO films crystallized from amorphous films deposited under conditions: (a) $P$ = 0.2 Pa, (b) $P$ = 1 Pa, and (c) Surface SEM micrograph of film crystallized from amorphous film deposited at $P$ = 2 Pa

**Fig. 6** (a) Schematic illustration of metal mask. (b)-(d) POM images of TNO films crystallized from amorphous films deposited at $P$ = 1 Pa with metal mask.

**Summary**

The crystallization kinetics of amorphous sputtered TNO thin film during isothermal annealing was studied using *in situ* XRD measurements. The obtained Avrami exponents were in the range of 2.0 to 2.7, suggesting that the crystallization of amorphous TNO films is two-dimensional with dominant site saturation. This result is consistent with the results of *ex situ* POM . The microstructures of amorphous films were well explained by Thornton model. That is, the microstructure became more porous with increasing *P.* On the other hand, the grain size of crystallized films increased with decreasing *P*. These results suggest that voids act as nucleation sites. By using a mask to prevent the arrival of slant particles on substrates, the grain size was drastically improved even at high *P.*

**References**

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