

Initial growth of SnO₂ thin film on the glass substrate deposited by the spray pyrolysis technique

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Abstract

Spray pyrolysis of di-*n*-butyltin(IV) diacetate (DBTDA) has led to the deposition of [200]-oriented SnO₂ film on a glass substrate. In order to clarify growth mechanism of the preferential orientation the sprayed SnO₂ thin film has been investigated by using the atomic force microscopy and the X-ray photoelectron spectroscopy. The results have suggested that the sprayed solution forms the SnO₂ small particles on the glass substrate and they spread overall relatively soon. At the very early stage each particle grows with almost the same rate and only its density increases with no change in a surface roughness.

Keywords: SnO₂ thin film, spray pyrolysis, preferential orientation, film growth, AFM, XPS

1. Introduction

Tin(IV) oxide (SnO₂) is an n-type semiconductor material with wide band gap energy, high donor concentration, and large mobility [1]. The material is transparent in the visible and reflective in the infrared regions. Thus, the SnO₂ thin films have

been utilized as transparent electrodes in sophisticated electronic devices [2-4]. The material also has an advantage in availability of constituent atoms different from ITO (Indium Tin Oxide).

We have reported a deposition of highly oriented SnO₂ thin films on a glass substrate from the organotin compounds by using a spray pyrolysis technique. The results indicated that the (200)- and (110)-oriented thin films were prepared from (C₄H₉)₂Sn(OOCCH₃)₂ (DBTDA) [5] and (C₄H₉)₄Sn (TBT) [6], respectively. Two chemical species, O-Sn-O and Sn, relevant to deposition of the oriented thin films were produced in majority through the pyrolysis of DBTDA and TBT, respectively [7], with which the oriented growth can be attributed to a matching between the atomic configuration and each crystalline plane [8].

Spray pyrolysis, one of the well known chemical techniques applied to form a variety of thin films such as noble metals, metal oxides and chalcogenide compounds, results in good productivity from a simple apparatus. The spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated substrate where the constituents react to form a chemical compound. The chemical reactants are selected so that products except the desired compounds are volatile at the temperature of deposition. We call this technique a SPD (Spray Pyrolysis Deposition) method. One successful application of the technique is in the large-scale formation of CdS thin films for solar cells [9].

In the present study, we have observed initial growth stages of the SnO₂ thin film sprayed on a glass substrate by using the atomic force microscopy (AFM), and measured photoelectron signals from both the film and the substrate by using the X-ray photoelectron spectroscopy (XPS) to clarify the initial growth process of the [200]-oriented SnO₂ thin film.

2. Experimental

2.1 Formation of SnO₂ thin film

Di-*n*-butyltin(IV) diacetate (DBTDA) (>95% purity) was used as a starting compound. It, with no further purification, was dissolved in a dehydrated ethanol. Apparatus used in the present study is illustrated schematically in Fig.1(a). The ethanol solution containing the starting compound was atomized by a pneumatic spraying system. The droplets were transported by the spraying onto a heated Corning 7059 glass substrate measuring 25 mm by 25 mm by 1 mm. Since a substrate temperature was lowered by the spraying air, the solution was atomized not consecutively but intermittently. It thus took several seconds for the next spray until the substrate temperature had recovered, although the period of one spray was 0.1 s. The substrate was mounted on a cordierite ceramic holder (Fig. 1(b)), and a sheath-type thermocouple was inserted between the substrate and the holder to control the substrate temperature. The spray pressure and distance were fixed to be 0.3 MPa and 450 mm, respectively.

2.2 Characterization of SnO₂ thin film

Film thickness was determined by a stylocontact method (Dektak IIA, Sloan). The film thickness, however, of very thin films in a range of several nm was determined by the calculation as follows. In general, the film thickness of deposited film, D [nm] is proportional to a product of concentration, C [wt%] and a total volume, V [ml] of the spraying solution in the SPD method,

$$D = kCV \quad (1)$$

where k is a constant depending on the substrate temperature and determined from a relation between the total volume and the film thickness at the constant substrate temperature. The film thickness determined from eq. (1), D is called as a calculated film thickness hereafter.

In order to investigate the initial film growth process, surface morphologies of the film were observed by using the AFM (JSTM-4200D, JEOL) in a very early deposition stage. Since the AFM technique is very sensitive to a local surface height, the surface roughness (RMS) is calculated from the AFM images to evaluate a surface asperity of the film as follows,

$$RMS = \sqrt{\sum_{i=1}^n (Z_i - B_z)^2 / n} \quad (2)$$

where Z_i is a height at a given position of the film measured by the AFM and n a total number of measured points, and B_z an average height of the film obtained by the following equation,

$$B_z = \sum_{i=1}^n \frac{Z_i}{n} \quad (3)$$

Photoelectrons from Sn3d and Si2p orbitals were measured for the film and the glass substrate, respectively by using the XPS to obtain a relationship between the intensity ratio of Si3d peak to Sn2p peak, Si3d/Sn2p and the film thickness, where the X-ray source line was MgK α (1253.6 eV).

3. Results and discussion

3.1 AFM observation of SnO₂ thin film

Firstly, behaviors of a SnO₂ grain formation on the glass substrate were observed as a function of the deposition amount by using the AFM. The deposition conditions were 2.0 wt% in a concentration of the spraying solution and 475°C in the substrate temperature, which are the same as those for the highest [200]-oriented SnO₂ thin film. Number of spraying was varied from 1 to 100 corresponding to the calculated film thickness from 0.5 to 50 nm. Prior to the film deposition, surface asperity of the glass substrate was also observed by using the AFM. The result indicates that the glass surface is relatively flat with 1.23 nm in height difference and 0.16 nm in RMS.

Figs. 2(a) - (d) show the AFM images of SnO₂ thin films with 0.5, 2.0, 5.0 and 50 nm in the calculated film thickness, respectively, where the scanning area is 0.5 μm x 0.5 μm. In the AFM images a larger film thickness is displayed by a whiter pixel, and the vertical scales are different among the images. Glass surface is covered entirely by the small particles with ca. 20 nm in a diameter and 1 nm in a height through only one spraying as shown in Fig. 2(a), and the particle size and its height does not change up to 4 times of the spraying (Fig. 2(b)). With 10 times of the spraying, however, a grain growth is found such that the particle size and its height become ca. 30 nm and 2 - 4 nm, respectively as shown in Fig. 2(c). Large surface asperity is also recognized due to the different grain heights. The grain grows up to ca. 80 nm in a diameter with 100 times of spraying but its height does not increase very much which is still ca. 5 nm (Fig. 2(d)).

RMS values determined from eq. (2) are depicted as a function of the calculated film thickness in Fig. 3. From first to 6 times of the spraying, 0.5 nm to 30 nm in the thickness, the RMS is almost constant around 0.5 nm because the SnO₂ grains grow with a same growth rate. The RMS shows, however, a rapid increase between 6 times and 50 times of the spraying, which suggests that the grains grow with different growth rates resulting in an existence of very large grains. After 50 times of the spraying the increase in RMS tends to saturate because the neighboring grains coalesce into larger ones.

Secondly, in order to investigate a very early stage of the SnO₂ nucleation, concentration of the spraying material was decreased to 0.04 wt% from 2.0 wt%. According to eq. (1), the reduced concentration can give a very thin film thickness. Figs. 4(a) – (c) show the AFM images of SnO₂ thin films with 1, 3 and 50 times of the spraying corresponding to 0.01, 0.03 and 0.50 nm in the calculated thickness, respectively, where the scanning area is 2.0 μm x 2.0 μm. Isolated grain formation is revealed by the first spraying as shown in Fig. 4(a). The grain size, however,

reaches ca. 400 nm in a diameter and its height becomes 6 nm which are much larger than those in Fig. 2(a). It is seemed that in the case of the spraying material with the concentration of 2.0 wt% a number of critical nucleus for the SnO₂ nucleation increases due to a higher degree of supersaturation of the material than that for the material with 0.04 wt% in the concentration resulting in a reduction of each nucleus size. The grains spread over the glass surface with an increase in the number of spraying (Fig. 4(b)) and covers entirely with 50 times of the spraying as shown in Fig. 4(c). The calculated film thickness for Fig. 4(c), 0.50 nm is the same as that for Fig. 2(a) but the grain size is significantly different between two images. For the concentration of 0.04 wt%, the growth rate seems to be different among grains and overlapping grains are also observed. The behavior is strongly reflected in the dependence of RMS values on the film thickness as shown in Fig. 5. The surface roughness increases drastically up to 1.74 nm with the first spraying and decreases down to 0.78 nm with an increase in the number of spraying, namely the number of grains, but the RMS increases again to 1.48 nm with 50 times of the spraying.

3.2 XPS measurement of SnO₂ thin film

Fig. 6 shows ratios of the XPS signal intensity between Sn3d and Si2p spectra as a function of the calculated film thickness. The spectra are calibrated by using that of C1s(284.6 eV), where the thickness is determined under the conditions of 2.0 wt% in the solution concentration and 1 to 10 times of the spraying. The ratio of Si/Sn decreases with an increase in the film thickness corresponding to a homogeneous covering with the SnO₂ thin film over the glass surface.

In general, a two-dimensional film growth gives a following equation for the intensity of XPS spectra from both the film and the substrate [10],

$$I_d/I_0 = \exp(-d/\lambda) \quad (4)$$

where I_0 is a photoelectron intensity from the substrate, I_d the intensity of those which penetrate the overlayer film with a thickness of d , and λ an average escape

depth in the film. Thus, when Fig. 6(a) is replotted in a semi-logarithmic scale, the two-dimensional film growth should give a linear relation. Indeed, as shown in Fig. 6(b) clearly, the linear relation is obtained until the calculated film thickness reaches 2 nm. The thicker film, however, tends to deviate from the linear relation, which suggests that a three-dimensional growth becomes prominent for the film with the thickness thicker than 3 nm in the present study. Similar behavior has been observed by G.H. Lee et. al. [10] for the LiNbO₃ film on the Al₂O₃ substrate. They have found the intensity ratio of the XPS spectrum from the formed film to that from the substrate is linear up to the film thickness of 1.5 nm and deviates for the thicker films than 2 nm. Finally, it has been concluded also based on the observations with the RHEED and the AFM that the formed film grows with layer by layer (two-dimensionally) until the thickness reaches 1.5 nm and turns to an island growth (three-dimensionally) later.

3.3 Initial growth process of SnO₂ thin film

Although the AFM observations reveal the formation of SnO₂ grains from the very early stage of the film growth (Fig. 4), the XPS measurements suggest the two-dimensional growth in the same stage. It is seemed that in the very early stage, each grain keeps its size and only a density of the grains increases with an increase in the film thickness. The XPS spectrum intensity ratio, therefore, shows the two-dimensional behavior similar to eq. (4).

After the calculated film thickness exceeds 2 or 3 nm, the growth of grains themselves becomes prominent with the different growth rates and the surface roughness increases rapidly with a deviation from the linear relation in eq. (4). The different grain growth rates originate from a difference in the crystal phase of a growth front of the grain. The three-dimensional growth brings an increase in both the grain size and the film thickness, but the surface roughness tends to saturate at the calculated thickness of 25 nm as shown in Fig. 3. The saturation indicates a

coalescence among the neighboring grains. It is, therefore, suggested that only a growth of the specified crystal plane at growth front of the grain is promoted in the three-dimensional film growth stage resulting in a sharpening of the grains, but the sharpened grains become unstable than the neighboring grains with a slower grain growth due to a less number of bonded atoms at the top of grain. The sharpened grains, therefore, coalesce one another to reduce their surface energy with a less surface area. The phenomenon is called as “Ostwald ripening” [11]. Furthermore, when the grains with different crystal orientations coalesce one another, the resultant orientation keeps that of the larger grain. For a formation of the oriented thin film, therefore, it is very important to promote a growth of the oriented grains and increase their density at the initial growth stage.

It is concluded from the above results that the initial growth process of the SnO₂ thin film formed by the SPD method is described as follows and illustrated in Fig. 7:

- (1) Isolated grains are formed on the glass substrate,
 - (2) Only the density of grains increases,
 - (3) Each grain grows with a same rate and the surface roughness keeps almost constant,
 - (4) The growth rate of grains becomes different and the surface roughness increases,
- and
- (5) The film grows through a coalescence among the neighboring grains.

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Figure Captions

Figure 1. Schematic drawings of (a) SPD apparatus, and (b) substrate and holder.

Figure 2. AFM images of SnO₂ thin films. The calculated film thicknesses are (a) 0.5 nm, (b) 2.0 nm, (c) 5.0 nm and (d) 50 nm. The scan area is 500 nm x 500 nm. The substrate temperature is 475°C and the DBTDA concentration is 2.0 wt%.

Figure 3. RMS roughness for SnO₂ thin films as a function of the calculated film thickness. The DBTDA concentration is 2.0 wt% and the substrate temperature is 475°C.

Figure 4. AFM images of SnO₂ thin films. The calculated film thicknesses are (a) 0.01 nm, (b) 0.03 nm, (c) 0.50 nm. The scan area is 2 μm x 2 μm. The substrate temperature is 475°C and the DBTDA concentration is 0.04 wt%.

Figure 5. RMS roughness for SnO₂ thin films as a function of the calculated film thickness. The DBTDA concentration is 0.04 wt% and the substrate temperature is 475°C.

Figure 6. (a) Atomic ratios of the photoelectron intensities, Si2p and Sn3d and (b) the logarithmic ratio for Si2p, as a function of the calculated film thickness.

Figure 7. Schematic drawing of the initial growth model of SnO₂ thin film formed by the SPD method.

Fig.1 Murakami et al.

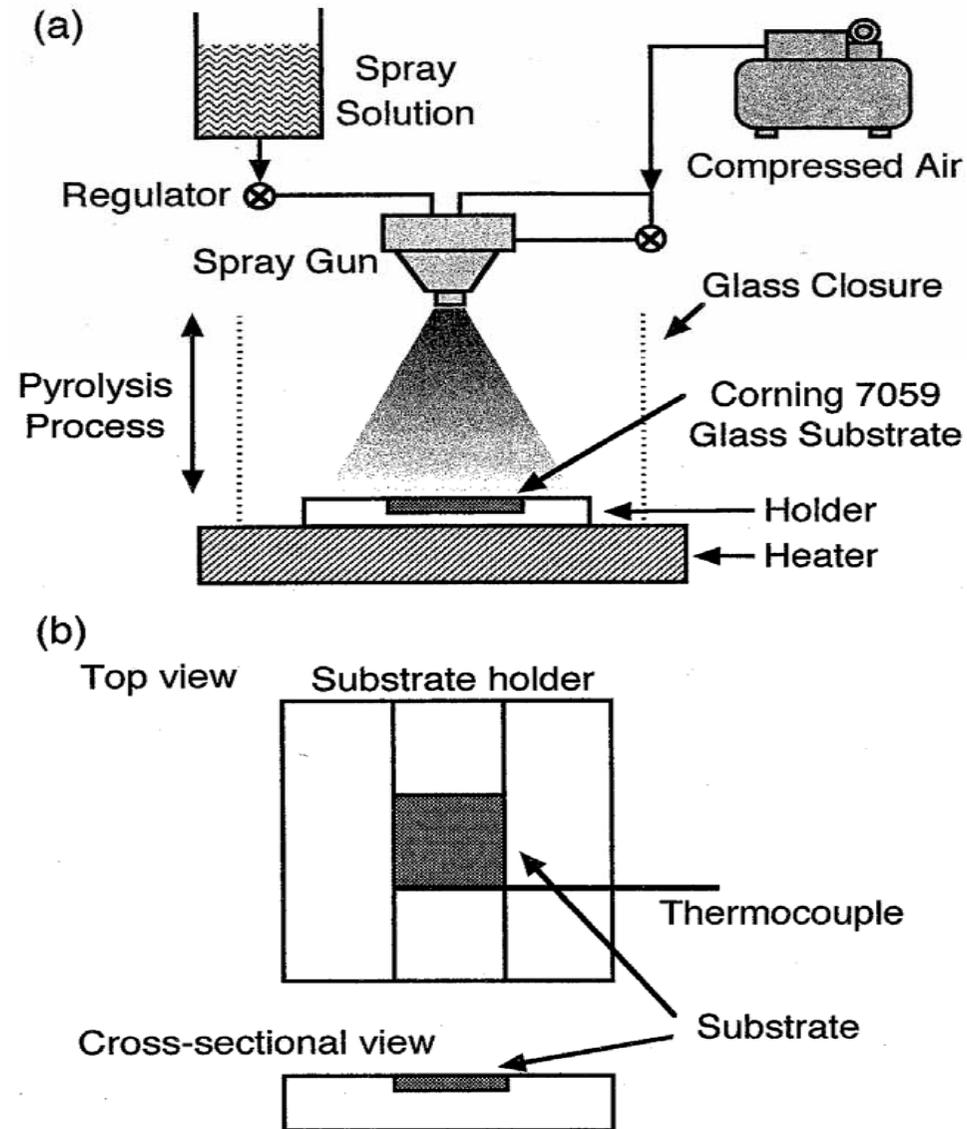


Fig. 2 Murakami et al.

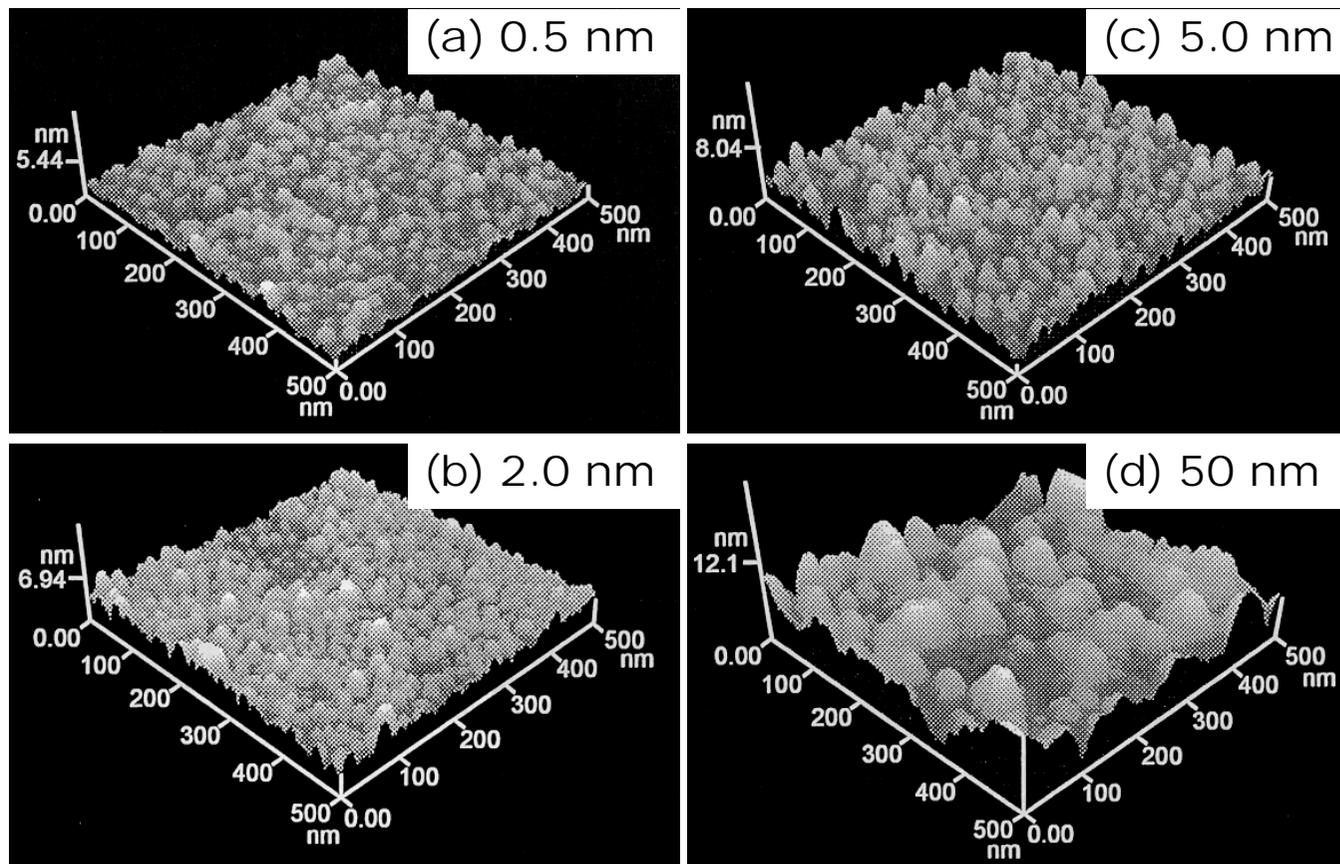


Fig. 3 Murakami et al.

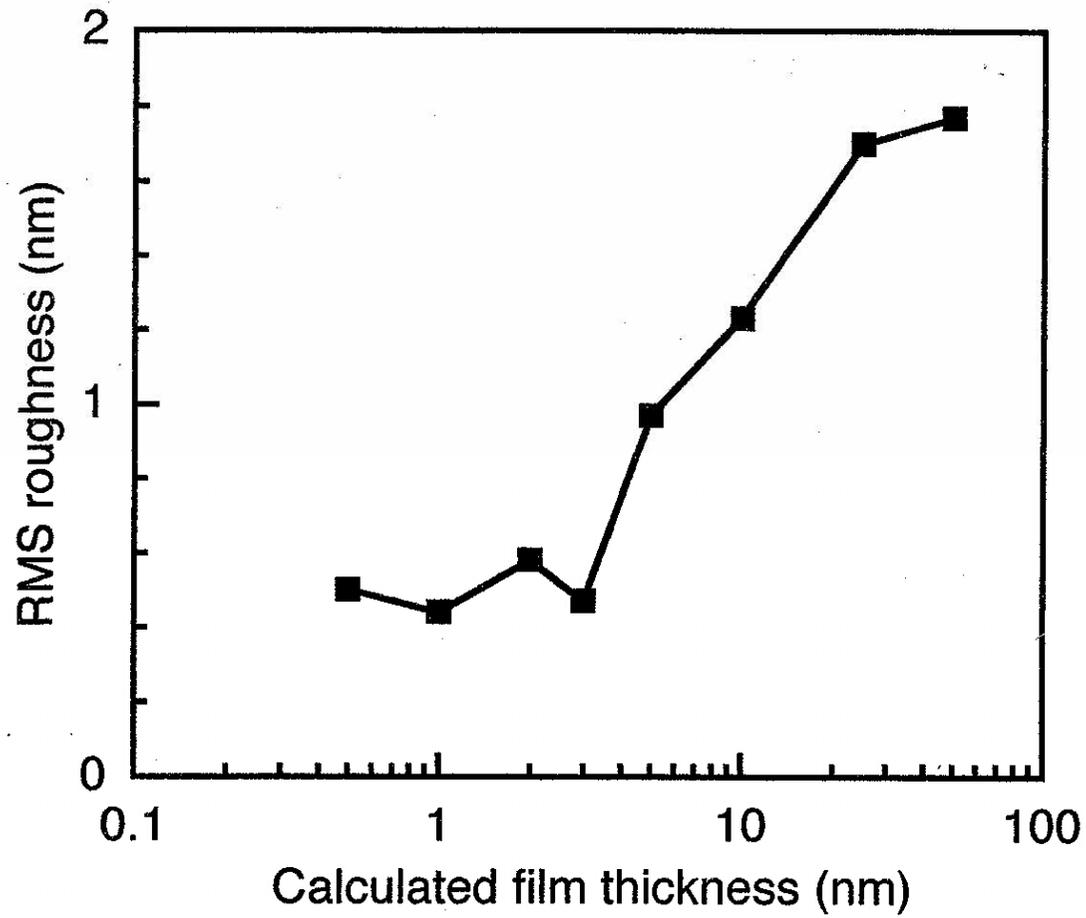


Fig. 4 Murakami et al.

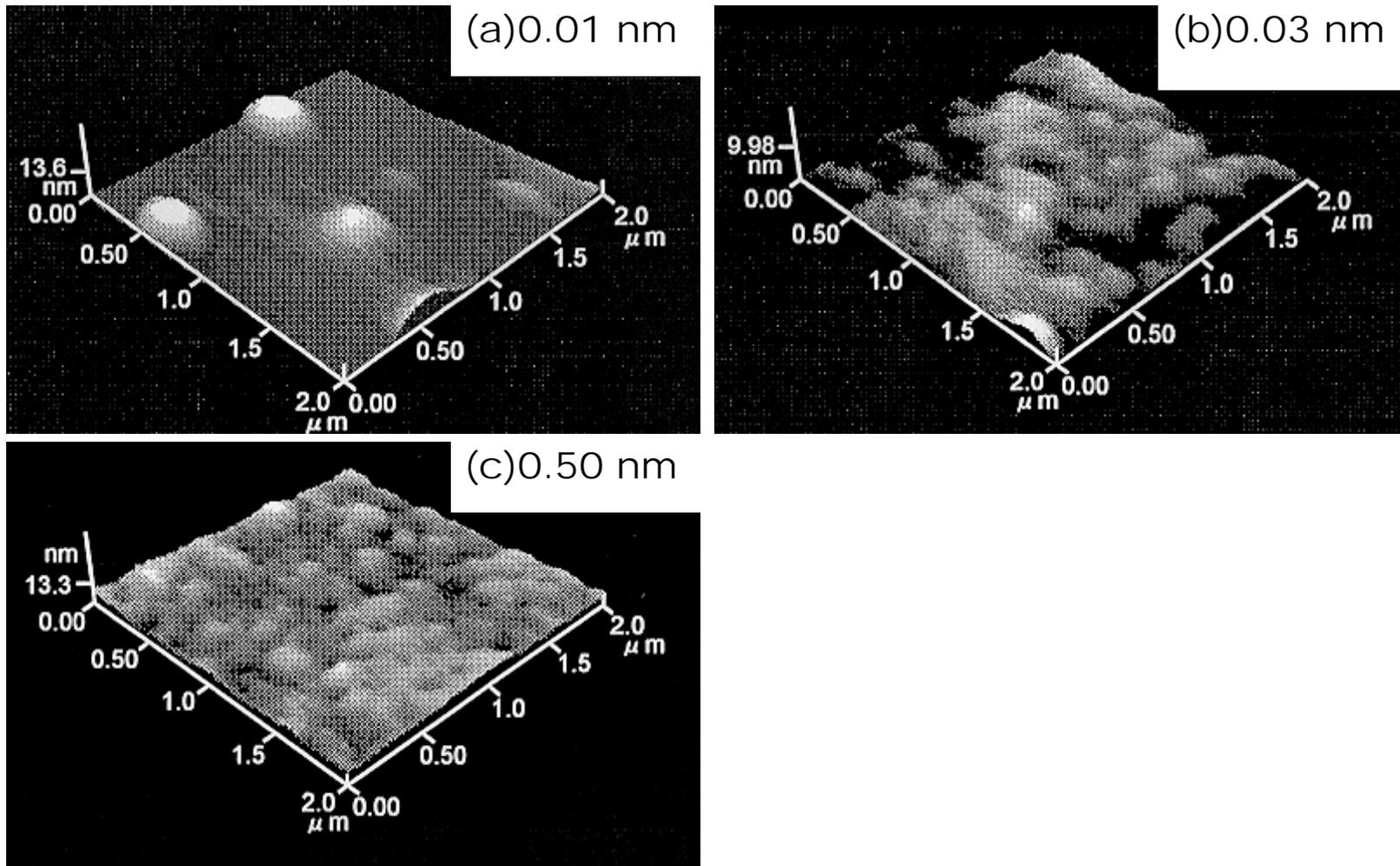


Fig. 5 Murakami et al.

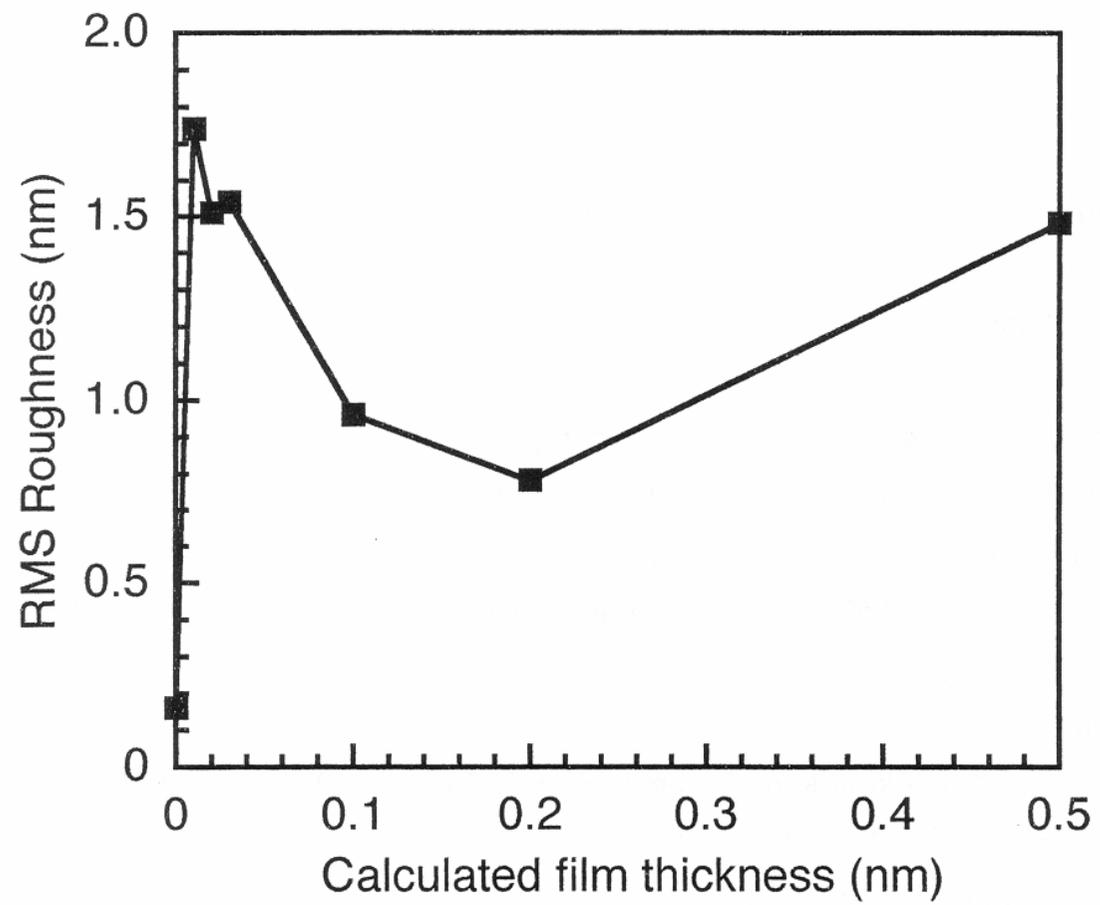


Fig. 6(a) Murakami et al.

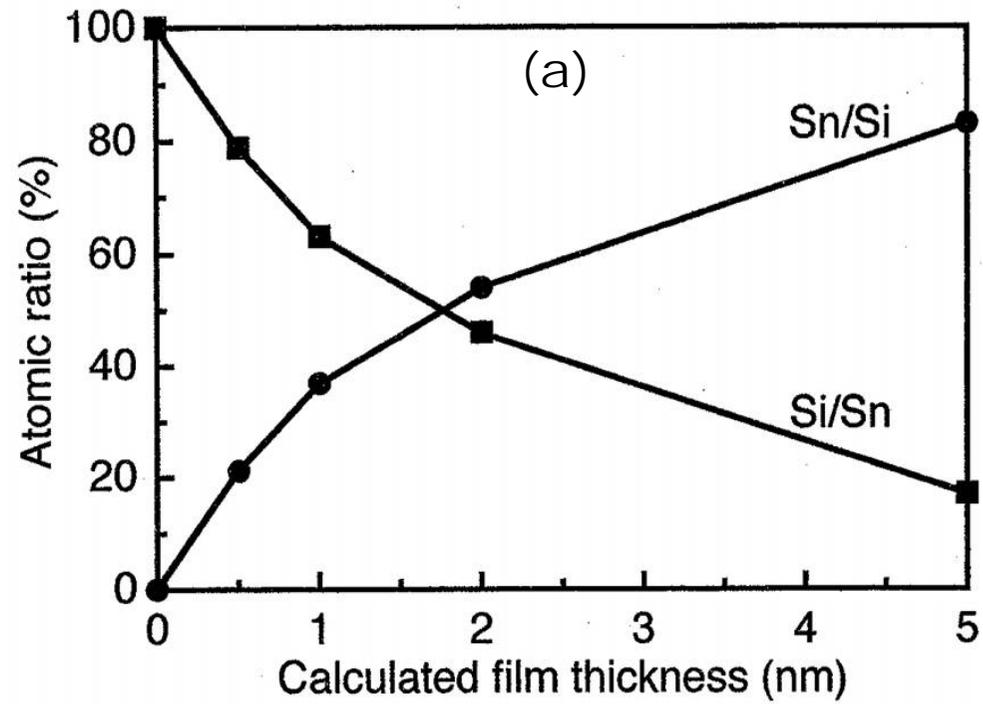


Fig. 6(b) Murakami et al.

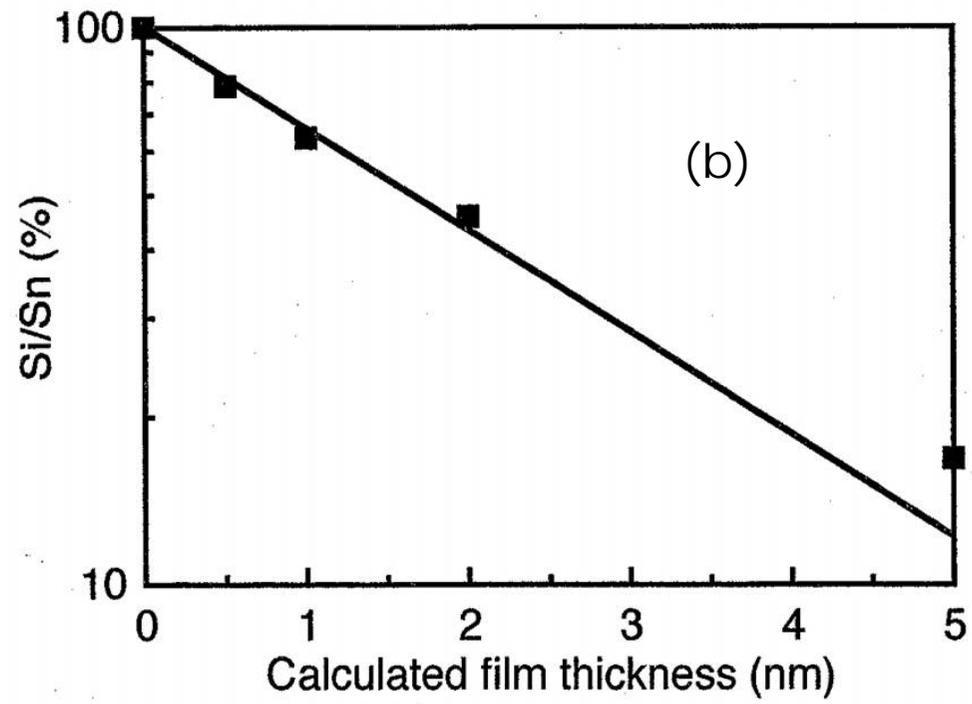


Fig. 7 Murakami et al.

