Spray pyrolysis of organotin compounds for the growth of oriented SnO2 thin films on glass substrates

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The (110) and (200) oriented SnO2 thin films on glass substrates were successfully deposited by spray pyrolysis of organotin compounds with butyl and/or acetate group: $(C_4H_9)_4Sn$ and $(C_4H_9)_2Sn(OOCCH_3)_2$, respectively. The relations between the microstructure and the growth conditions (film thickness, solution concentration, and substrate temperature) were widely investigated. The film formation process has been discussed based on a newly introduced estimation method of the preferred orientation here, which can be more quantitatively related with the microstructure of film.

1. INTRODUCTION

Spray pyrolysis technique, one of the well-known chemical techniques, has the simplicity of its apparatus with good productivity on a large scale SnO2 transparent electrode. Tin oxide is an oxygen-defect type semiconductor with a wide band gap and a large mobility. It is transparent in visible region, and reflective in infrared region. Thus, SnO2 thin films have utilized as sophisticated electronic devices.

We have grown of SnO2 thin films on glass substrate by a spray pyrolysis technique using various organotin compound.[1] We have further reported that SnO2 thin films with oriented (110) and (200) planes have been prepared from $(C_4H_9)_4Sn$ [TBT] and $(C_4H_9)_2Sn(OOCCH_3)_2$ [DBTDA] , respectively.[2,3] Recently, it has been also reported that the gas sensitivity of the (110) oriented SnO2 thin films is high[4] and the electrical conductivity of the (200) oriented SnO2 thin films is large.[5,6] Thus, the preferred orientation is largely expected to improve the physical propaties of SnO2 thin

films. In this study, we have further discussed the effect of the growth conditions on the microstructure and morphology of the oriented SnO2 thin films in detail.

2. EXPERIMENTAL

2.1 Film formation

Ethanol solution including TBT or DBTDA solution was atomized onto a heated Corning 7059 glass substrate by compressed air. Since substrate temperature was lowered by the compressed air, the solution was transported intermittently. The detail of the apparatus used was described in elsewhere.[1]

2.2 Characterization

The structural analysis of film deposited was carried out by an X-ray diffraction (XRD) technique with CuKα radiation using a RIGAKU RINT-1100 diffractometer. The preferred orientation of the (hkl) plane of film was evaluated by a texture coefficient (TC) calculated from equation (1),

$$TC_{hkl}=I_{hkl}/I_{0hkl} \qquad (1)$$

where I and I_0 are the X-ray diffraction intensities of sample and standard non-oriented film measured under the condition of the same thickness. The higher deviation of the texture coefficient from unity indicates the higher preferred orientation of the films. Crystallite size, D_{hkl}, was calculated from the Scherrer's equation. Film thickness was determined by a stylocontact method using a Solan Dectak II A. The association of organotin compound in ethanol was analyzed using a JEOL JNM-EX270 ^{1}H-NMR.

3. RESULTS

Figure 1 shows TC and average crystallite size, D_{av}, of SnO_2 films with various thicknesses deposited from DBTDA solution. In the case of TBT solution, the results showed almost the same tendency as those from DBTDA solution. Both TC and D_{av} increased with an increase in the film thickness and then tended to saturate. In particular, TC gives very small value close to unity in very thin film thickness range, which suggests that the SnO_2 film is initially non-oriented.
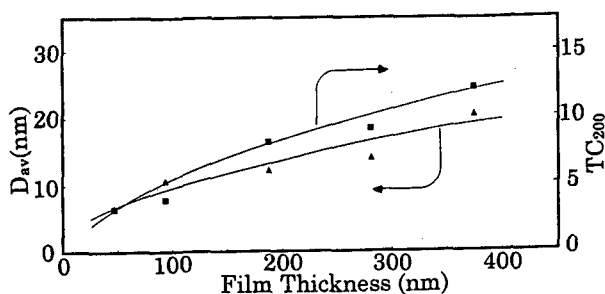

Figure 1. Dependence of TC and D_{av} on film thickness.

The calculated TC and D_{av} of SnO_2 films deposited from the solutions of various concentrations are shown in Fig. 2. For the films deposited from DBTDA solution, TC_{200} and D_{av} hold large values in the concentration range less than 2 wt% and decrease with an increase in concentration between 2 and 8

wt%. Above the concentration of 8 wt%, these values reaches smallest ones. For the film deposited from TBT sloution, TC_{110} increases with an increase in solution concentration below 4 wt%, and turn to decrease slightly with the concentration above 4 wt%, while D_{av} is almost constant in the whole concentration range.

Furthermore, TC and D_{av} of SnO_2 films with various substrate temperatures were also calculated. For the film prepared from DBTDA solution, TC_{200} and D_{av} increase slightly with an increase in substrate temperature. In particular, TC_{200} is very close to unity below 450°C. At temperatures above 450°C, both TC_{200} and D_{av} increase markedly with increasing substrate temperature. For the film deposited from TBT solution, both TC_{110} and D_{av} show almost no dependence on the substrate temperature under the present experimental conditions.
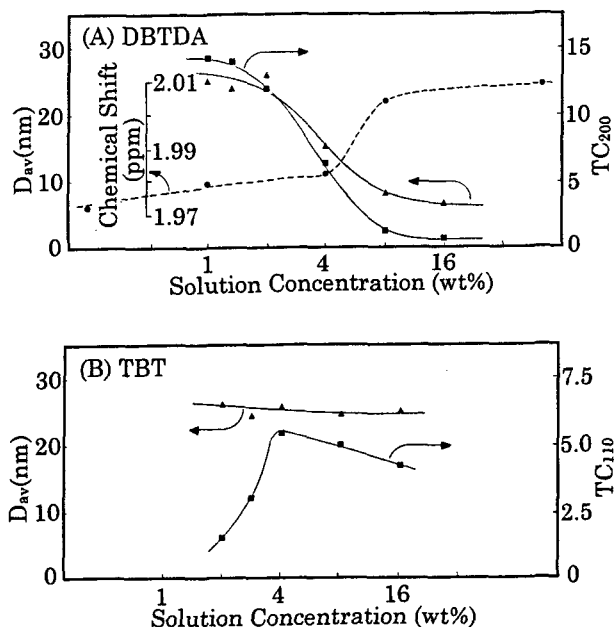

Figure 2. Dependence of TC and D_{av} on solution concentration. ((A) DBTDA, (B) TBT)

4. DISCUSSION

4.1. Film thickness

In order to discuss the microstructure of

the film deposited, we denote an θ_{hkl} as the angle between any (hkl) plane and the oriented plane of the constituent crystallite of the film, i.e., (200) for DBTDA and (110) for TBT in this study. When one (hkl) plane of the crystallite grown is parallel to the substrate, the axis of orientation of this crystallite is inclined by θ_{hkl} from the normal to the substrate. It is proved that TC_{hkl} is equal to ratio of the volume of crystallites whose axis of orientation inclined by θ_{hkl} to the normal of the substrate to the whole volume of the film. Therefore, Fig. 1 is converted to Fig. 3 showing the relation between TC_{hkl} and θ_{hkl}. In small thickness the angle dependence of the volume ratio was weak but in large thickness the volume ratio became high only in the small angle range. The same tendency was also observed for the size of individual crystallite, D_{hkl}, whose (hkl)

plane is parallel to the substrate. The results for TC_{hkl} suggest that the SnO_2 film is non-oriented in the thin thickness range and orient gradually toward the specific direction with increasing thickness. Thus, the cross section of the oriented film is schematically presented in consideration of the result of D_{hkl} (Fig. 4).

Knuyt et al. have successfully explained the oriented growth of TiN film using a PVD method with the following principle; a growing film shows a tendency for having the lowest possible surface energy.[7] Their model could be applied to the present film growth after two modifications. Firstly, the surface energy of crystal is replaced by electrostatic energy attributed to the interaction between thermally decomposed chemical species and surface atoms of the growing film, since the preferred orientation depends on the source
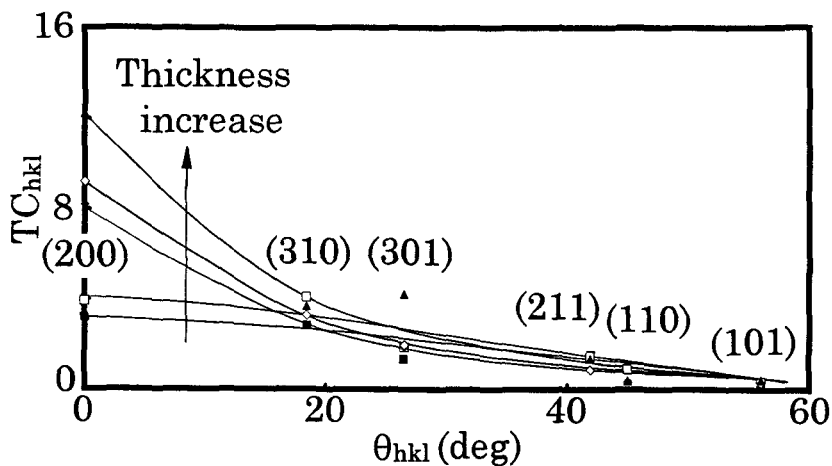

Figure 3. Texture coefficient of (hkl) plane, TC_{hkl}, as a function of angle between oriented (200) plane and (hkl) plane, θ_{hkl}.
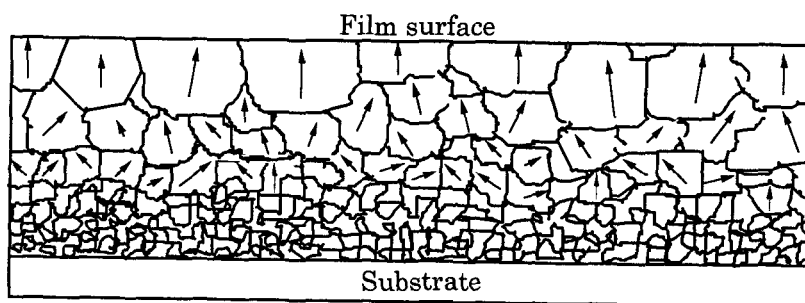

Figure 4. The scheme of film section. The arrow indicates the axis of orientation.

compound. Yagi et al. have suggested that two chemical species, O-Sn-O and Sn, were produced in majority by the pyrolysis of DBTDA and TBT, respectively.[8] Murakami et al. have presented that the chemical species, O-Sn-O, was easy to approach to the (200) plane, and then the growth rate of this plane was higher for DBTDA.[9] On the other hand, Sn was easy to   move on any growing surface, and then the growth rate of the most densely packed (110) plane was higher for TBT. In this case the Knuyt model can be applied without the above   modification. Secondly, it is needed to introduce a consideration on the nucleation in the growing film in addition to on the substrate, because TC tends to saturate with increasing film thickness, as shown in Fig. 1. If the nucleation occur only at the substrate surface according to the Knuyt's model, TC should increase infinitely with the film thickness.

4.2. Solution concentration

An alternative plane, TC_{101}, increased, however TC_{110} decreased drastically in the solution concentration range less than 4 wt% (Fig. 2). Namely, only the axis of orientation changed rather than low oriented growth in this range. This finding is also supported by the constant D_{av} in the range. Similar results on the shift of direction have been obtained with the different source compound, $SnCl_4$, reported by Goyal et al..[10]

To investigate the molecular association of source compound in ethanol, ^{1}H-NMR measurement was performed for the solutions with various concentrations. The NMR spectra from TBT solution does not change regardless of the solution concentration, while the chemical shift of a peak around 2 ppm does not change in those from DBTDA solution. This peak corresponds to protons in the acetate group. The chemical shift increases with an increase in solution concentration, as shown in Fig. 2(A). It is considered that this change is caused by the molecular association of DBTDA. This association prevents the continuous growth of the crystallites and introduces further nucleation in the film.

4.3. Substrate temperature

The difference between DBTDA and TBT on the temperature dependence of both TC and D_{av} arise presumably from a difference in the the activation energy of two species, O-Sn-O and Sn, to move on the crystal surface. The activation energy of O-Sn-O produced by the decomposition of DBTDA is considered to be higher than that of Sn from TBT because of the difference in the shape and the size of species. Consequently, the species from TBT solution move around on the film surface without a temperature dependence but that from DBTDA solution does only at high temperatures.

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