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# A study of atypical grain growth properties for $SnO_2$ thin films

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ABSTRACT

$SnO_2$ thin films were grown on Si substrate using the chemical vapor deposition(CVD) method. The surface of the thin film was examined using a transmission electron microscope (TEM) and a scanning electron microscope (SEM). Atypical shaped grains and atypical columnar structures were observed on the $SnO_2$ thin films that were exposed to air after first deposition and during re-deposition in anaerobic conditions in the CVD. The electrical properties of $SnO_2$ thin films feature a lower range of resistance in single mode, but after the atypical particles appear, the electrical resistance decreased.



## 1. Introduction

There have been many studies of $SnO_2$ thin films, which have many uses in transparent electrodes, solar cells, and gas sensors [1]. It is important to be aware of any deficiencies in thin films, and to understand the structural properties in order to use them for electric devices or sensors [2]. The studies of such structural properties and deficiencies of the layer have frequently been conducted [3]. Commonly, $SnO_2$ thin films show several kinds of forms that depend on the method of manufacture. There have been many studies on the particle forms and growth of thin films for several different conditions [4–9]. Few studies have been systemically done on the particle growth of atypical particles [10]. The appearance of atypical grains of thin films increases its ratio of surface to volume and influences to electronic properties [11,12]. The emergence of atypical particles influences the application of transparent electrodes, sensors, and electric devices. This paper presents that the achievement of atypical growth was exposed to air after first deposition and during re-deposition in anaerobic conditions in the CVD. We used SEM and TEM to demonstrate the structural forms of growth, and to measure the electrical resistance of thin films to study the mutual relationship of atypical particles and the intra-electrical resistance of thin films.

## 2. Experiment

Dibutyl tin diacetate (DBT, Aldrich, purity > 99.99%) was used as a starting material, and was transported by argon (Ar) gas, then evaporated onto the films by oxygen ($O_2$) flowing into the chamber. Si substrate has been washed initially for 30 s in acetone solution followed by pure water and exposed in spilled nitrogen gas in the vacuum state. All films were fabricated with the following procedure after the introduction of the substrate in the vacuum system, the chamber was pumped below $10^{-7}$ Torr. Afterward, the substrate was heated to ~200 °C by infrared radiation for 30 min. This is pre-heating was done to release the molecules of the water trapped in the system, it also enabled the substrate to keep a better pressure and cleaner atmosphere during the deposition. The amount of transporting gas, deposition temperature, and vacuum state in the chamber are the main factors of forming thin films. The deposition was conducted at 550 °C for 10–30 min, flow 100-sccm oxygen partial pressure, 10-sccm argon gas pressure, and a 0.001-torr vacuum state of the bubbler. After deposition, the thin

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**Table 1**
Condition of sample for $SnO_2$ thin films.

| Sample | 1st deposition time (min) | 2nd deposition Time (min) | Deposition temperature (°C) |
|---|---|---|---|
| S500-30 | 30 | 0 | 500 |
| S500-10-30 | 10 | 30 | 500 |

films were exposed to air and subjected an additional 30 min of deposition. The surface of the deposited $SnO_2$ thin films could be observed using scanning electron microscopy (SEM; Hitachi, S-4700,Japan), and transmission electron microscopy (TEM, Technai, F20, Phillips, Netherland) was needed to observe the thin film, by the electron density penetrating through the layer with an electron beam emitted with 200 kV. An image analyzer was used to measure the sizes of particles and the thickness of the cross section. The surface resistance was measured by inflowing nitrogen gas ($N_2$) in a closed circuit (HP34401A, Multi meter). Table 1 shows the sample conditions used in this experiment.

## 3. Results and discussion

Fig. 1 shows SEM pictures of the thin film surfaces of the S500-30 and S500-10-30 samples. The S500-30 $SnO_2$ thin film was grown at 500 °C with 30 min deposition. The grains show typical form. The average size of the particles is 0.1 μm. The S500-10-30 thin film was grown with 10 min of deposition and air exposure, followed by an additional 30 min of deposition at 500 °C. The grain shape differed from the S500-30 and showed atypical form, with an upsized average particle size increased to 0.5 μm, and cocoon-shaped particles. The average size of the particles drastically increased, and it is expected that the secondary deposition results in plane growth.

Fig. 2 shows SEM images of the thin film cross sections of the S500-30 and S500-10-30 samples. The S500-30 $SnO_2$ thin film cross section has typical columnar structure. The average size of the cross section was 0.5 μm. At a fixed temperature of 500 °C, the thin film was grown with 10 min of deposition, air exposure, and 30 min further deposition. The size of the cross section was 0.6 μm, which is similar to that of the S500-30 thin film. There is rare possibility that the thin films deposited for 30 min in 500 °C and high vacuum state have contamination such as molecules of water trapped or carbon species. Merely, first deposited grains could play a role as a seed for secondary growth of thin films and it affects morphology and the interface of $SnO_2$ thin films.

This result could mean that the primary 10-min deposition results in mono-layer columnar structure, but after the air exposure and additional 30 min of deposition, it causes bi-layer atypical grains to form. The overall size of the cross sections are similar, as shown in Fig. 1 (plane growth), and the plane growth does not really influence the size of the cross section. This result shows that the cross section growth of the S500-10-30 sample has more difficulties than the one in conditions that started with smooth Si substrate mono-layer columnar structure.

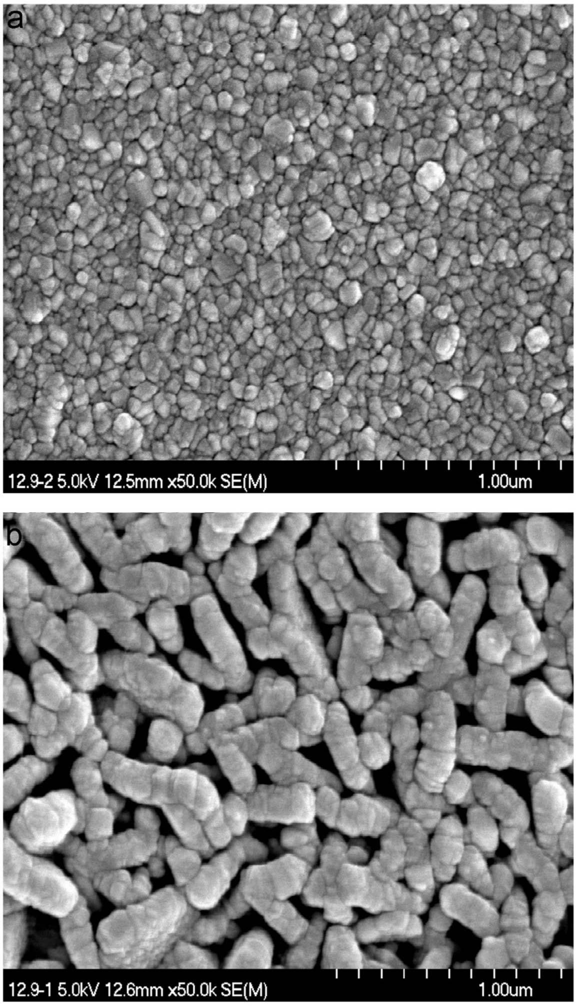


**Fig. 1.** Scanning electron microscopy images of $SnO_2$ thin films (a) S500-30 and (b) S500-10-30.

Table 2 shows the EDAX of S500-30 and S500-10-30. The ratio of oxygen of S500-10-30 thin films was bigger than that of S500-30 and increases the ratio of oxygen atomic percent of S500-10-30 thin films was exposed to air after first deposition and during re-deposition in anaerobic conditions. The deficiency of the inner thin films and the surface to volume ratio are crucial to the application of sensor of the thin films. Hence, the atypical grain shape can be highly effective to the sensor of the thin films.

Fig. 3 shows a high-magnification TEM picture of the S500-10-30 thin film. By observing the sample with the penetrating microscope, it was found that the thin film has wrinkled shape. At the initial phase, oxygen deposition on the Si substrate leads to an $SiO_2$ layer. Then, Sn flows onto the surface of the Si substrate [13]. At this time, because of the high pressure making the mean free path of particles short, many collisions between atoms and molecules occur. This is due to the influence of the diffusion constant and the mass transfer coefficient induced by the speed of delivery in the growth of thin