

## Structural study of $\text{In}_2\text{O}_3$ structures grown by the metalorganic chemical vapor deposition

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**Abstract.** We have synthesized the film-like and rod-like structures of indium oxide ( $\text{In}_2\text{O}_3$ ) by metalorganic chemical vapor deposition (MOCVD) method. The structural morphology of the deposits changed from the film to the arrays of 1-dimensional (1-D) materials with increasing the deposition temperature. The 1-D materials with the serrated surfaces prepared at 350°C possessed a crystalline cubic structure and had preferentially grown along the [111] direction.

### Introduction

Since indium oxide ( $\text{In}_2\text{O}_3$ ) is a technologically important transparent semiconducting oxide material, it has become the choice for many application such as photovoltaic devices, electro-optical devices, and sensor of oxidizing gases [1-6]. Low-dimensional materials have attracted great interest in their novel physical and chemical properties different from those in bulk state and in their potential applications for developing new types of electronic, magnetic, optic, photocatalytic, and energy storage devices. Accordingly, one of the main targets in materials science is to prepare low-dimensional crystals with special morphologies, such as nanorods, nanowires, dendrite crystals, etc. Up to the present, the  $\text{In}_2\text{O}_3$  one-dimensional (1-D) structures have been mainly synthesized by various methods including thermal heating or evaporation [7-11], laser ablation [12], electrodeposition [13], and sol-gel deposition [14].

Although vertically aligned 1-D structures can potentially provide an attractive solution to attain ultra-density advanced nanoscale devices and 3-D nanocircuitries, to our knowledge, there is rare report on the synthesis of aligned  $\text{In}_2\text{O}_3$  1-D structures [8]. In this paper, we have synthesized the arrays of  $\text{In}_2\text{O}_3$  rod-like structures on  $\text{SiO}_2$  substrates. We have used a triethylindium (TEI) as a precursor in the presence of oxygen. The synthesis of these materials, which is necessary for fundamental research or for potential commercialization, would be very interesting to materials scientists.

### Experiments

A schematic representation of the metalorganic chemical vapor deposition system used in this work was previously reported [15]. The vertical reactor was made of stainless steel, and has been cooled by water. We chose the (001)-oriented silicon (Si) as a substrate material. The  $\text{SiO}_2$  layer was thermally grown on the Si(001) with a thickness of 60 nm. In the growth process, we have used TEI and oxygen ( $\text{O}_2$ ), respectively, as the indium and oxygen sources. The Ar carrier gas flowed through the TEI bubbler maintained at 35°C. The  $\text{In}_2\text{O}_3$  film was synthesized by supplying  $\text{O}_2$  and Ar carrier gases, respectively, with the flow rate of 5 standard cubic centimeters per minute (sccm) and 20 sccm. Based on the preliminary experiments, we have used the two different deposition temperature of 300°C and 350°C.

The obtained product was characterized by X-ray powder diffraction (XRD), operating on a Philips X'pert MPD x-ray diffractometer with  $\text{CuK}\alpha$  radiation. The structure of the products has been investigated by scanning electron microscopy (SEM) (JEOL, JSM-6700F), transmission electron microscopy (TEM) (Philips CM-200) and selective area electron diffraction (SAED). TEM

specimens were prepared by ultrasonically dispersing the products in acetone, and then placing a drop of this suspension onto a copper grid coated with amorphous carbon film.

### Results and discussion

Fig. 1 shows the XRD spectra of the products at deposition temperatures in the range of 300–350 °C, revealing that  $\theta$ - $2\theta$  scan data exhibit main peak at 30.58° and smaller peak at 63.67°, respectively, corresponding to (222) and (444) diffraction peaks of cubic bixbyite  $\text{In}_2\text{O}_3$  phase (JCPDS 44-1087). Since (222) and (444) diffraction peaks are significantly strong compared to the neighbouring diffraction peaks representing other crystalline directions, which are invisible in this spectrum, we reveal that the products have a preferred orientation along the [111] direction.

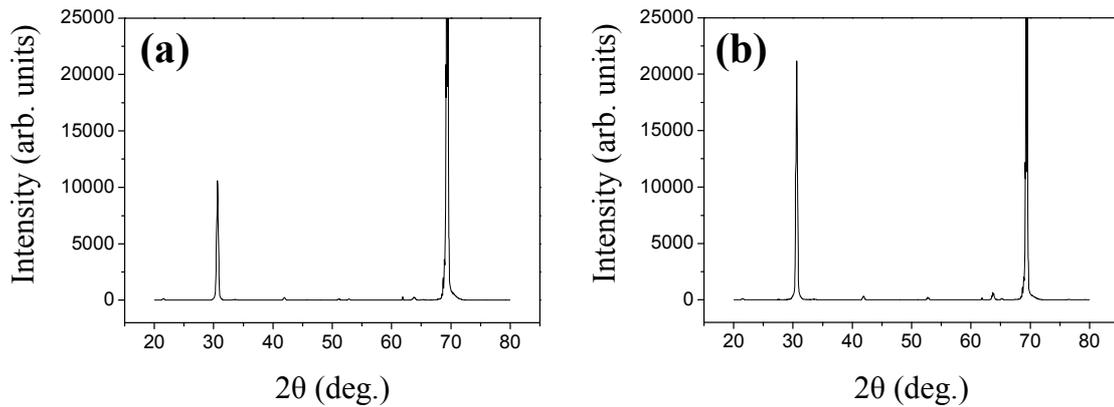


Fig. 1. XRD patterns of products at a deposition temperature of (a) 300 °C and (b) 350 °C.

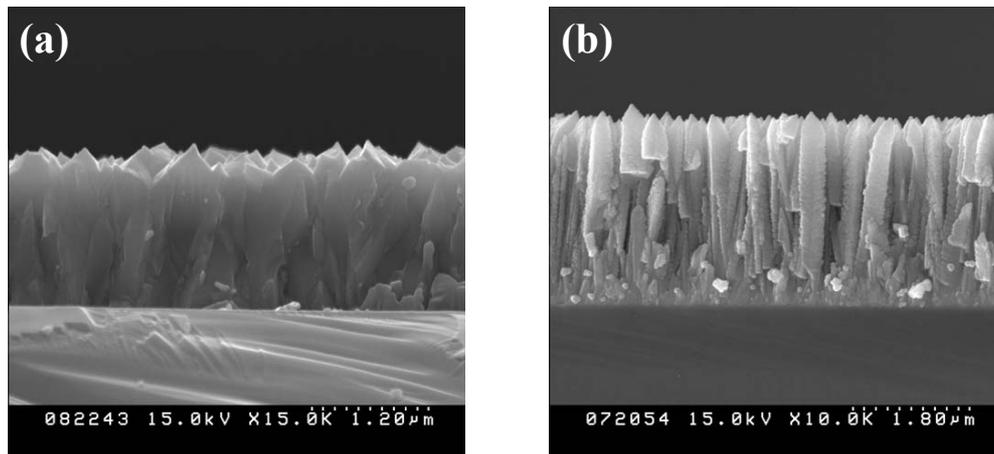


Fig. 2. Cross-sectional SEM images of products at a deposition temperature of (a) 300 °C and (b) 350 °C.

Fig. 2 shows the cross-sectional SEM images, indicating that the product at 350 °C consists of the arrays of 1-D structures, while the product at 300 °C is a film consisting of columnar-like grain structures. Close examination of Fig. 2b reveals that the products at 350 °C consist of rod-like structure vertically aligned on the substrate. Fig. 3a shows the plan-view SEM image of products at 300 °C, revealing that the grain structures with smooth facets and a sharp tip are shown on the surface

of the films. From their geometrical shapes and the XRD analysis, we surmise that the tip direction is along the  $[111]$  direction. Fig. 3b reveals that the 1-D materials have triangular cross sections with acute angles. From the top view, we reveal that the side length of the triangular cross section ranges from 200 to 800 nm. The growth has changed from 2-D to 1-D mode by increasing the deposition temperature in the range of 300-350°C.

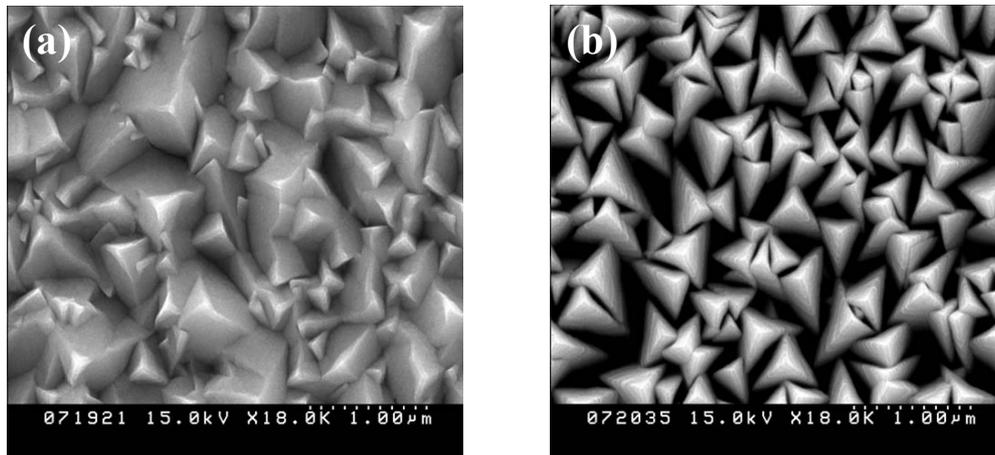


Fig. 3. Plan-view SEM images of products at a deposition temperature of (a) 300°C and (b) 350°C.

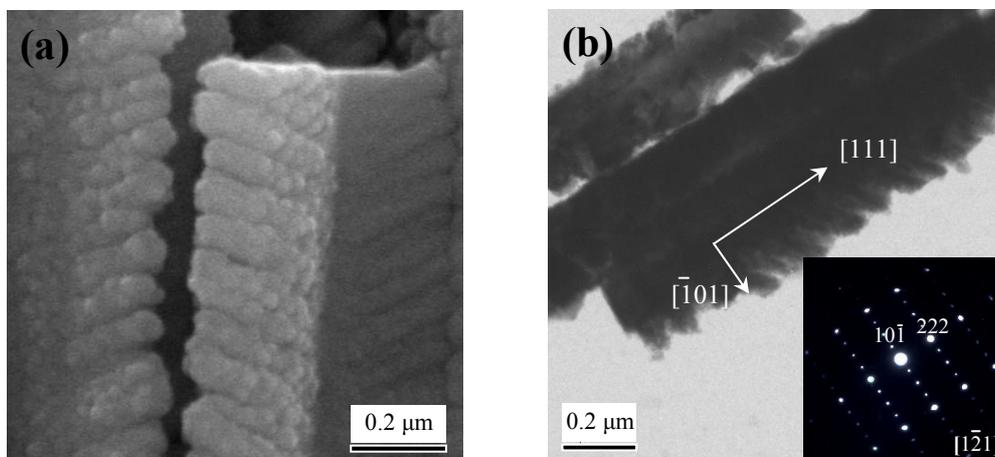


Fig. 4. (a) High magnification SEM image and (b) TEM image of the 1-D material at a deposition temperature of 350°C (Inset: Corresponding SAED pattern).

Fig. 4a shows the high magnification SEM image of the products at 350°C, indicating that the products consist of 1-D materials with serrated surfaces. Although some of 1-D materials were broken during the cross-sectional SEM sample preparation, we observe that the serrated surface of the 1-D material stems corresponds to the arrays of “nanobumps”. The rod-like structures may resemble the dendrites with serrated surfaces and the serrated surfaces may represent the secondary arms just discernible [16]. Fig. 4b shows the TEM image of the 1-D material, with the length direction indexed to be  $[111]$ . The reflections in the SAED pattern, shown in the inset of Fig. 4b, indicate that the 1-D materials are single crystalline.

From Fig. 1, we observed that the products have a preferred orientation along the [111] direction regardless of deposition temperature in the range of 300-350°C. During the growth at 350°C, the crystallographic effects exert an influence and the rod-like structure still grow toward the preferred [111] direction with its body enclosed by the crystallographically preferred planes with the lower surface energy. We surmise that the main driving force for the crystallographic effects is the thermal energy related to the deposition temperature. Further investigation is underway in order to obtain more crystallographic information, which will contribute to deriving the exact mechanism for the formation of the rod-like In<sub>2</sub>O<sub>3</sub> structures.

### Summary

In this paper, we have demonstrated the deposition of highly-oriented In<sub>2</sub>O<sub>3</sub> thin films and 1-D structure arrays on SiO<sub>2</sub> substrates using the TEI as a precursor in the presence of oxygen. The structural morphology is found to be dependent on the substrate temperature. We reveal that both film and 1-D structures are cubic structures with the predominant (111) orientation.

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