

Characteristics of Indium Oxide Rod-Like Structures Synthesized on Sapphire Substrates

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Keywords: Chemical Vapor Deposition, Indium Oxide.

Abstract. In₂O₃ materials consisting of dense arrays of vertically aligned rod-like structures were deposited on sapphire substrates by thermal chemical vapor deposition (CVD) using triethylindium (TEI) and oxygen as precursors at a substrate temperature of 350 °C. The rod-like structure with a triangular cross section had a cubic structure, exhibiting preferred crystallographic orientation in the [111] direction. The photoluminescence spectra of In₂O₃ structures under excitation at 325 nm revealed a visible emission.

Introduction

Indium oxide (In₂O₃) is a technologically important transparent semiconducting oxide material, and has many applications including photovoltaic and electro-optical devices, as well as sensors of oxidizing gases [1-6]. Low-dimensional materials have attracted a great deal of interest on account of their novel physical and chemical properties, which are different from those in the bulk state, and their potential applications in developing new types of electronic, magnetic, optic, photocatalytic, and energy storage devices [7,8]. 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. In₂O₃ one-dimensional (1-D) structures are mainly synthesized by thermal heating or evaporation [9-16], laser ablation [17], electrodeposition [18], and sol-gel deposition [19].

Although vertically aligned 1-D structures can provide an attractive solution for attaining ultra-density advanced nanoscale devices and 3-D nanocircuitry, there are not so many reports, to our knowledge, on the synthesis of aligned In₂O₃ 1-D structures [12]. This study shows synthesized arrays of In₂O₃ rod-like structures on sapphire substrates. Triethylindium (TEI) was used as a precursor in the presence of oxygen. The synthesis of these materials, which is necessary for fundamental research or potential commercialization, would be very interesting to materials scientists.

Experiments

A schematic illustration of the MOCVD reactor used in these experiments was described elsewhere [20]. (0006)-oriented sapphire (α -Al₂O₃), pre-cleaned with acetone and methanol, was used as substrate materials. During the growth process, TEI and O₂ were used as In and O sources with Ar as a carrier gas. The temperature of the TEI bubbler was fixed at 35 °C. The Ar and O₂ gas flow rates were set to 20 standard cubic centimeters per minute (sccm) and 5 sccm, respectively. Two different deposition times were used, 20 and 60 minutes. The substrate temperature was approximately 350 °C. The resulting material was characterized by X-ray diffraction (XRD, X'pert MRD-Philips) using CuK α radiation ($\lambda = 0.154056$ nm), scanning electron microscopy (SEM, Hitachi S-4200), and transmission electron microscopy (TEM, Philips CM-200). The TEM specimens were prepared by sonicating the nanostructured films on sapphire wafers in alcohol, and placing a small drop of the resulting suspension onto a porous carbon film supported on a copper grid. The photoluminescence (PL) measurement was made at room temperature using a He-Cd (325 nm, 55 mW) laser as the excitation light source.

Results and Discussion

Figure 1 shows the XRD patterns, a and b, of the as-synthesized products on sapphire substrates for deposition time of 20 and 60 minutes, respectively. The major peak was observed at $30.58^\circ 2\theta$, corresponding to the (222) diffraction peak of the cubic bixbyite In_2O_3 phase (JCPDS 44-1087). The (222) diffraction peak from the deposits is significantly strong compared with the neighboring diffraction peaks. Therefore, the sample was determined to be cubic In_2O_3 with preferred [111] orientation. No impurity phase was detected within the detection limit of the XRD equipment.

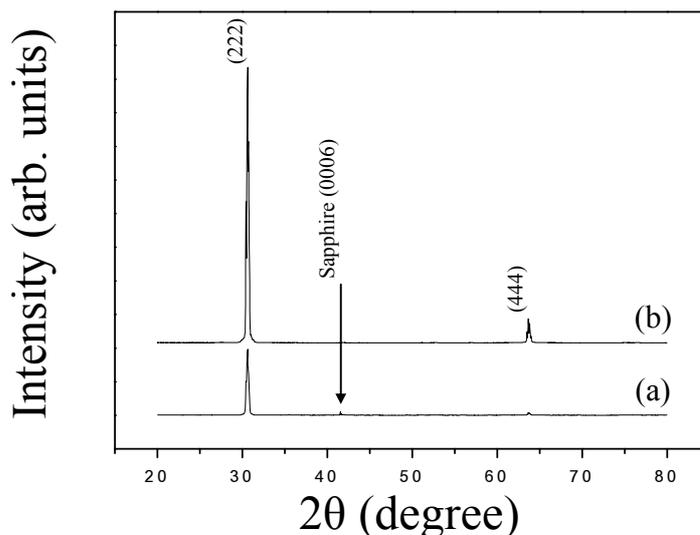


Fig. 1 XRD patterns of as-synthesized products on sapphire substrates for deposition time of (a) 20 and (b) 60 minutes.

Figures 2a and 2b show the cross-sectional SEM images of products for deposition time of 20 and 60 minutes, respectively. The total heights of the structures were measured to be approximately 2.3 and 12.6 μm for deposition time of 20 and 60 minutes, respectively. The lower left inset in Fig. 2b shows a closer view of a side-view SEM image of In_2O_3 products deposited for 60 minutes, indicating that the vertically aligned rod-like structures were isolated from each other. The upper right inset in Fig. 2b shows the top-view SEM image of a typical rod-like structure, showing that the rod-like structures have a triangular cross section.

TEM analysis of the product deposited for 60 minutes was carried out in order to obtain more details about the individual rod-like structure. Figure 3a shows a TEM image of two rod-like structures. It should be noted that the two independent rod-like structures were broken and separated during the sample preparation process. Although it is unclear why the rod-like structures have a rough or serrated surface, the rod-like structure is crystalline (not shown here). Therefore, it is possible that the structures resemble dendrites with serrated surfaces and the serrated surfaces may represent secondary arms [21]. Further investigation of this phenomenon is currently underway. Figures 3b and 3c show selected area electron diffraction (SAED) patterns corresponding to the locations indicated by white arrows 1 and 2, respectively. Since two SAED patterns were taken from different regions without further tilting during the TEM operation, it is believed that the rod-like structure is a single crystal. The SAED pattern, which was recorded perpendicular to the rod long axis, can be indexed for the $[0\bar{1}1]$ zone axis of crystalline In_2O_3 . The length direction of the rods is along the $[111]$ direction. Figures 3d and 3e show the SAED pattern and high resolution TEM (HRTEM) image corresponding to the location indicated by white arrow 3, respectively. The SAED pattern was indexed to be the

$[1\bar{2}1]$ zone axis of crystalline In_2O_3 , as labeled in Fig. 3d. The lattice resolved HRTEM image indicates that the interplanar spacings are approximately 0.72 nm and 0.29 nm, respectively, which correspond to the $(10\bar{1})$ and (222) planes of cubic In_2O_3 . The $[10\bar{1}]$ direction was perpendicular to the length direction of the rod.

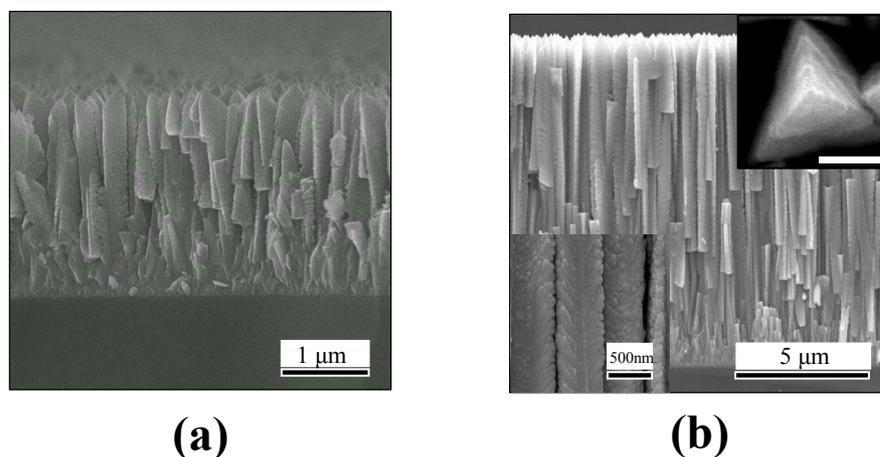


Fig. 2 SEM images of the products for deposition time of (a) 20 and (b) 60 minutes. The lower left inset and upper right inset represent the side-view and top-view image, respectively. The scale bar in the upper right inset corresponds to 250 nm.

Since Fig. 2a indicates predeposited films between the sapphire substrates and the rod-like structures with a thickness of $< 1\text{-}2\ \mu\text{m}$, it is possible that the layer was formed before the formation of rods. During the growth, the crystallographic effects have an influence and the rod-like structure growth towards preferred $\langle 111 \rangle$ direction with a cross section of the structure being of energetically favorable crystallographic geometry. It was assumed that the lowest surface energy of the $\{110\}$ planes, compared with the $\{111\}$ planes of body-centered cubic In_2O_3 , promotes rod elongation in the $[111]$ direction with its body enclosed by three $\{110\}$ planes. This assumption agrees with the findings presented here, i.e. the SEM image showed a triangular cross-section of the rod-like structure (upper right inset of Fig. 2b) and TEM analysis revealed that $[10\bar{1}]$ and $[0\bar{1}1]$ planes were perpendicular to the length direction of the rods (Fig. 3). These results are comparable to the work reported by Nguyen et al. [12], who reported the growth of In_2O_3 nanowires with a square cross-section along the $[100]$ direction with its body enclosed by four $\{110\}$ planes.

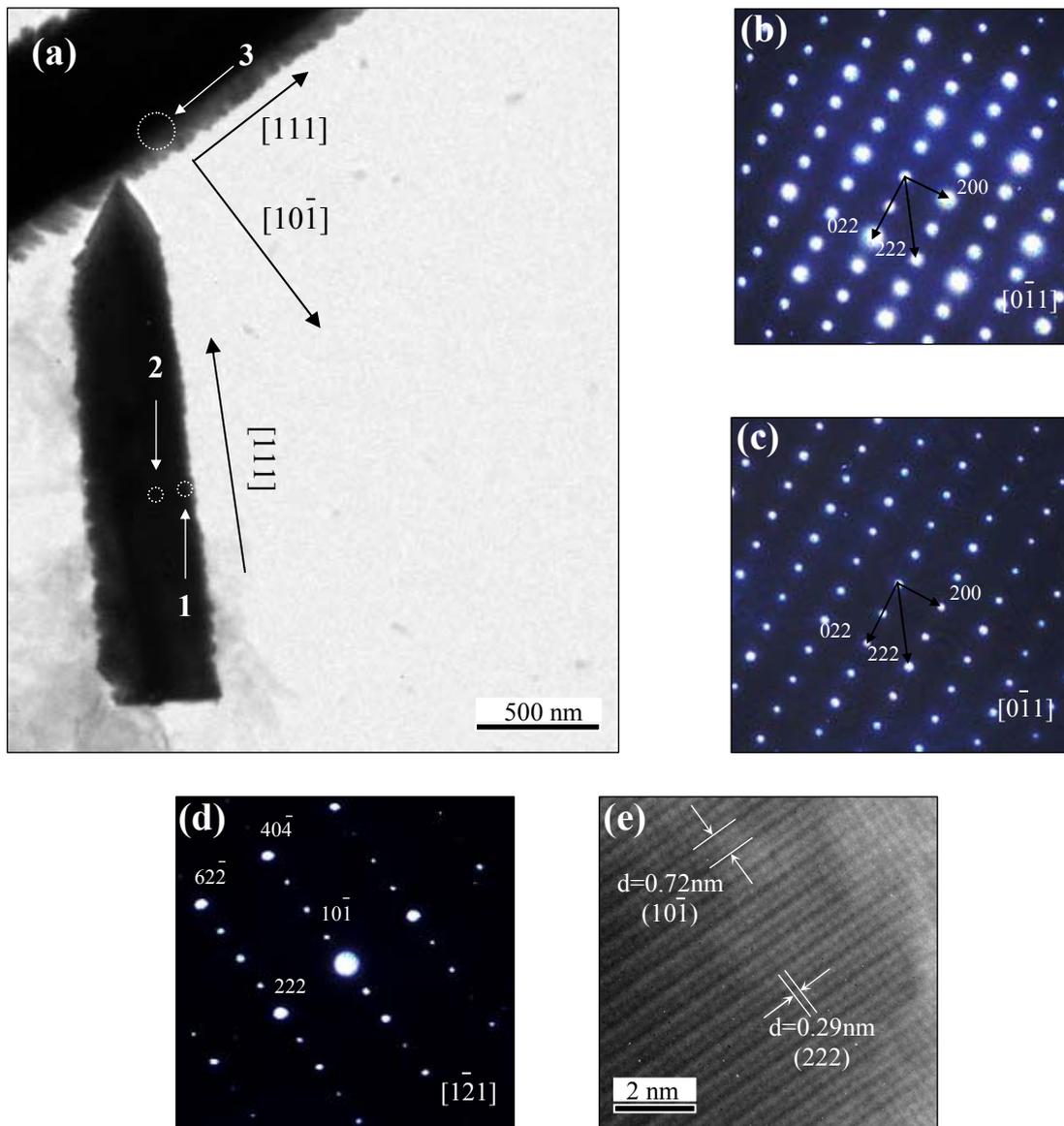


Fig. 3 (a) TEM image of the two rod-like structures. The SAED patterns were taken perpendicular to the stem of the rod, corresponding to the locations indicated by (b) white arrow 1, (c) white arrow 2, and (d) white arrow 3 in Fig. 3a. (e) A lattice-resolved HRTEM image corresponding to the location indicated by white arrow 3 in Fig. 3a.

Figure 4 shows the typical PL spectrum of In_2O_3 structures recorded at room temperature (300K). The dominant emission is a broad band located at a peak wavelength of 596 nm, corresponding to energy of 2.086 eV. A similar spectrum has been reported for In_2O_3 nanobelts [22] and In_2O_3 nanotubes [23], due to defects in In_2O_3 [22,23]. Since the In_2O_3 structures with a high aspect ratio were produced at sufficiently high temperatures, it is believed that the defects such as oxygen vacancies could be easily generated. The In_2O_3 structures in this study may have potential applications in optoelectronic nanodevices due to their strong emission.

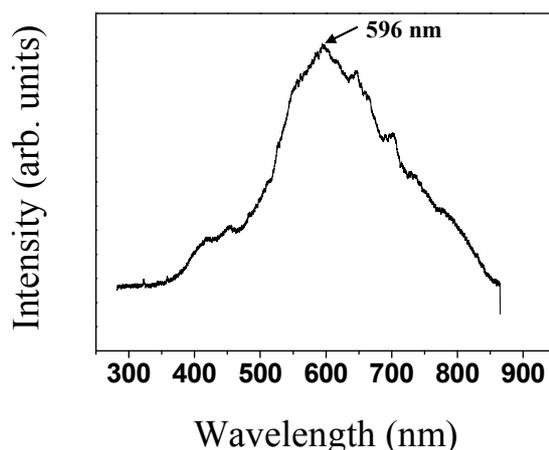


Fig. 4 PL spectrum of the In_2O_3 rod-like structures with an excitation wavelength at 325 nm.

Summary

Indium oxide (In_2O_3) rod-like structures were deposited on sapphire substrates using triethylindium (TEI) as a precursor in the presence of oxygen. The SEM images revealed the rod-like structures with a triangular cross section to be aligned perpendicular to the substrate. HRTEM and XRD demonstrate that the synthesized rods have a single-crystal cubic structure with an axis direction in the [111] direction. The PL spectra under excitation at 325 nm showed a broad emission peaked at approximately 596 nm.

Acknowledgements

This work was supported by grant No. R05-2004-000-10762-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

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