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Appearance of Indium Oxide Nanorods in MOCVD growth

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Abstract. We report on the first synthesis of nanosized In_2O_3 rods using the TEI as a precursor in the presence of oxygen. The samples were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy. XRD analysis revealed that the products are In_2O_3 phase with a tetragonal cubic structure. SEM analysis indicated that the obtained nanorods have a circular cross section and a diameter in the range of 50-150 nm.

Introduction

One-dimensional (1D) nanostructured systems have recently attracted much attention for their novel properties and potential applications in numerous areas such as nanoscale electronics and photonics. Also, indium oxide (In_2O_3), which is a wide bandgap transparent semiconducting material, has been widely used in the microelectronic applications [1,2]. Up to the present, In_2O_3 1D nanomaterials, including nanowires, nanobelts, nanofibers, and nanotubes, have been synthesized mostly by the thermal heating or evaporation of In_2O_3 powders [3,4], In [5,6], a mixture of In and In_2O_3 [7], and InP substrates [1]. For these purposes, various techniques, such as laser ablation [8], electrodeposition [9], sol-gel deposition [10], and nanocasting [11] have been successfully employed to produce In_2O_3 1D materials. Although the metalorganic CVD (MOCVD) method is a good candidate for the growth of nanostructures, to the best of our knowledge, the production of In_2O_3 1D nanomaterials by the MOCVD technique has not previously been reported.

In this paper, we investigate the possibility of growing In_2O_3 nanorods using a triethylindium (TEI) as a precursor in the presence of oxygen.

Experiments

A schematic diagram of the MOCVD reactor used in our experiments was previously described elsewhere [12]. First, p-type (100) oriented Si wafers were selected as substrates. After they were cleaned by a standard Shiraki procedure, the Cr film with 30 nm thickness was deposited onto Si (100) substrate before depositing the gold (Au) film with 150 nm thickness by the r.f. magnetron sputtering. High-purity Ar (99.999% purity) passed through the TEI bubbler and delivered TEI vapor to the reactor. The bubbler was maintained at a temperature of 35°C. The In_2O_3 was synthesized by supplying O_2, Ar, and N_2 gases with the O_2 gas flow ratio of 4 %, at a substrate temperature of 500°C for 20 min. The flow rates of O_2, Ar, and N_2 gases were set to 5 standard cm^3/min (sccm), 20 sccm, and 100 sccm, respectively.

The samples were characterized and analyzed by grazing angle X-ray powder diffraction (XRD) using CuKα radiation (Philips, X'pert MPD), scanning electron microscopy (SEM) (Hitachi S-4200), and energy-dispersive X-ray (EDX) spectroscopy (attached to the Hitachi S-4200).

Results and discussion

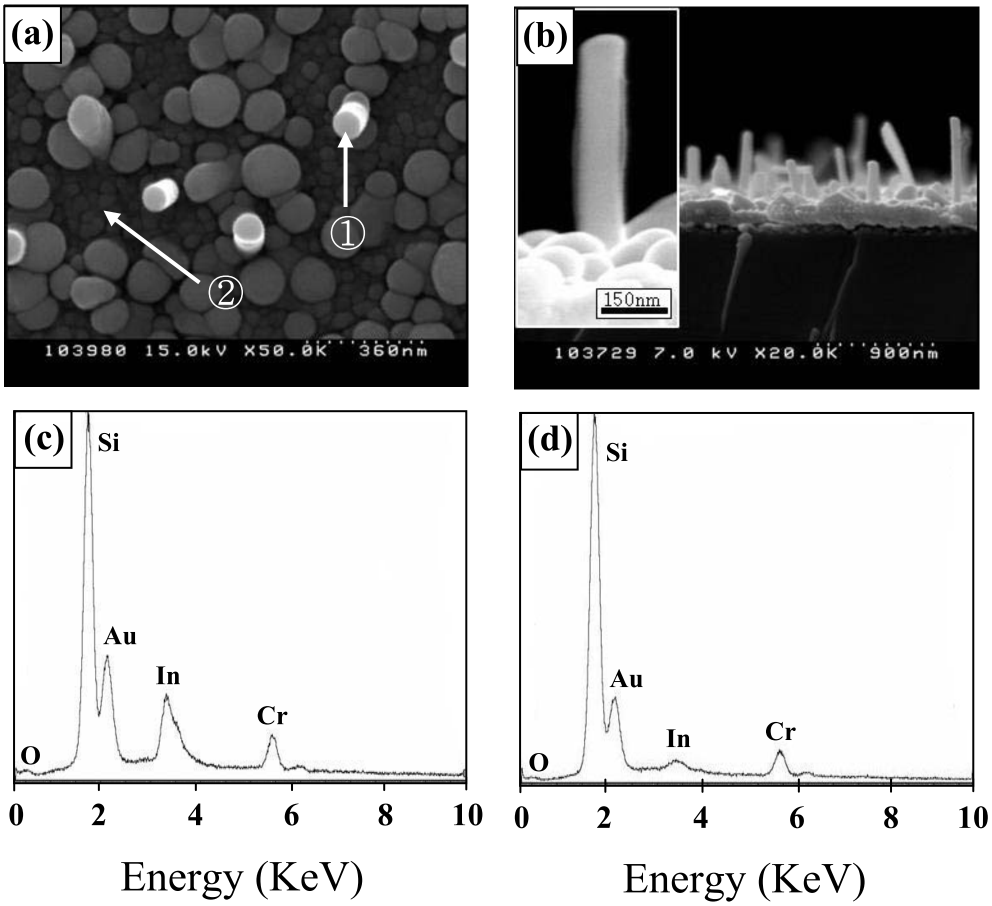

Fig. 1 (a) Top-view and (b) side-view SEM images (Inset: A SEM image enlarging a nanorod). (c,d) EDX spectra from the regions indicated by (c) arrow 1 and (d) arrow 2 in Fig. 1a.

Fig. 1a shows the top-view SEM image of the products, revealing that 1D nanomaterials with a circular cross-section can be found on the surface. A cross-sectional SEM image given in Fig. 1b indicates that the as-prepared product consists of 1D nanorods with various dimensions. Statistical observation of many SEM images indicated that the diameter of nanorods ranged from 50 to 150 nm. The length of the nanorods was up to one micrometer. The left inset in Fig. 1b gives an enlarged SEM image of a single nanorod, showing an almost straight-line morphology. From the SEM observation, we could find no evidence of metal particle at the ends of the nanorods.

EDX measurements are carried out to determine the chemical composition of the as-prepared products. Fig. 1c and 1d, respectively, show the EDX spectrum corresponding to the regions indicated by arrow 1 and arrow 2 in Fig. 1a. EDX analysis made on the rod (Fig. 1c) demonstrates that the elements in this region are composed of Si, Au, Cr, In, and O. By comparing Fig. 1c with Fig. 1d, in which the Si peak has the almost same intensity, we reveal that the elements in the rod-containing region (see arrow 1) consist of more amount of In, O, and Au than those in the region where the rod does not exist (see arrow 2). Since we do not observe the metal particle at the tips of the nanorods, we assume that the nanorod itself does not contain the Au elements. Although we do not know the exact chemical composition of the nanorod, we deduce that the nanorod at least comprises In and O elements. We surmise that the Si-, Cr-, and Au-related peaks in Fig. 1c are raised from the substrates underneath or in the vicinity of the nanorod.

A typical XRD spectrum is shown in Fig. 2. The several sharp peaks can be indexed to the (211), (222), (400), (440), and (622) crystal planes of a cubic bixbyite structure of In_2O_3 (JCPDS File No. 06-0416). In addition, four peaks from the Au layer can also be identified. However, no obvious reflection peaks from the impurities, such as unreacted In or other indium oxides, were detected. Since the angle of the incident beam to the substrate surface was approximately 0.5° and the detector was rotated to scan the samples in our XRD measurements, we surmise that the XRD peaks are mainly from the products and the Au layer on the substrate. XRD results indicate that the as-prepared products were of a cubic In_2O_3 phase. Combining the results of XRD, SEM, and EDX, we recognize that the prepared nanorods have a cubic In_2O_3 phase.

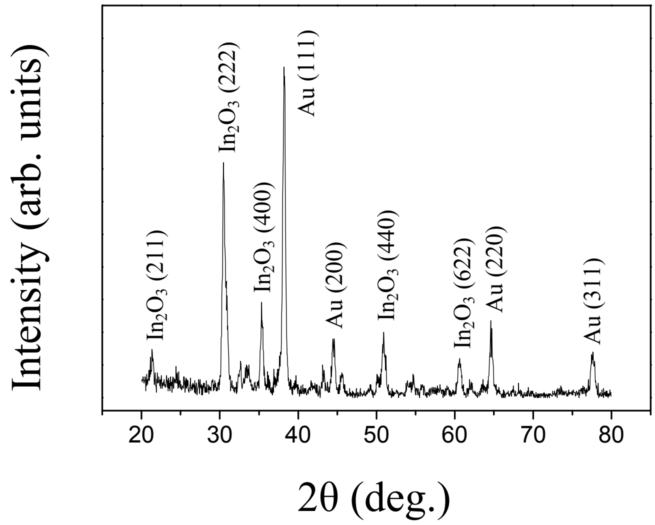

Fig. 2 XRD patterns of the products.

Our previous experiments using the same synthesizing conditions but with bare Si substrates without Au layers indicated that the prepared samples consisted of In_2O_3 film-like structures without any 1D structure (Fig. 3a). Accordingly, we found that the formation of In_2O_3 nanorods is affected by the Au layer. However, since the nanorod tips are free of Au-related particles, we surmise that the growth of InO_2 nanorods in the present route is not dominated by a conventional tip-growth vapor-liquid-solid mechanism, in which the morphology feature is a catalyst particle located at the end of the rod. Instead, Au may remain on the substrate surface during the synthesis process.

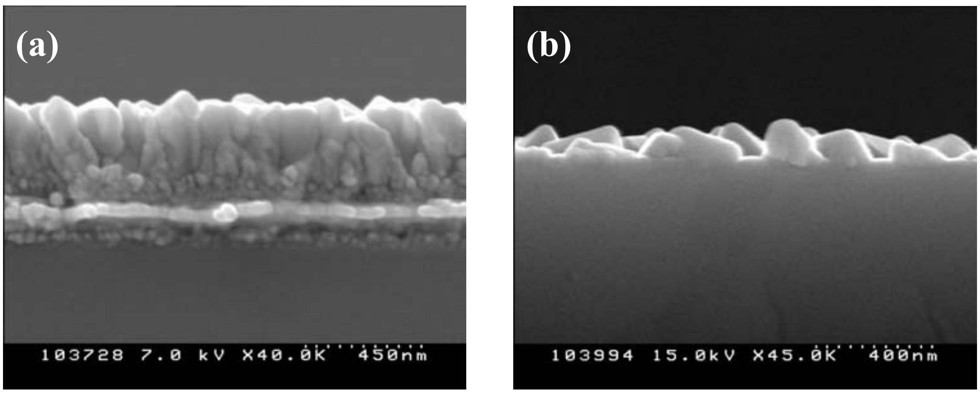

Fig. 3 Side-view SEM images when the experiments were peformed (a) with a bare Si substrate and (b) with a higher oxygen gas flow ratio of 20 %.

When the synthesis was performed on Au-coated substrate in the experiment under the same condition but with a higher oxygen content (in terms of O_2 gas flow ratio), we obtained the thick rod- or cluster-like structures without any thin 1D structure, as shown in Fig. 3b. The variation of structural morphology with O_2 content indicates that O_2 gas plays an important role in controlling nucleation and growth of InO_2. The higher oxygen content provides additional oxygen, which may facilitate a large supersaturation of O_2 gas, subsequently resulting in a fast condensation of solid InO_2 on the substrate. Therefore, a large supersaturation may activate a secondary growth sites and heterogeneous nucleation on the side of the 1D structures, tending to produce thicker structures. Under low supersaturation, however, narrow 1D structures are easy to grow. Further study is necessary to reveal the formation mechanisms.

Summary

We have demonstrated the synthesis of nanosized In_2O_3 rods using a mixture of TEI and oxygen. SEM images show that nanorod has a circular cross section and a diameter in the range of 50-150 nm. By EDX analysis, we deduce that the nanorod-like structures comprise In and O elements. XRD analysis revealed that the products are In_2O_3 phase with a tetragonal cubic structure, without unreacted In or other indium oxides. We found that the MOCVD method provides a possible way to fabricate In_2O_3 nanorods.

Acknowledgements

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