JOURNAL OF MATERIALS SCIENCE **39** (2004) 675–677

Nanocrystalline rhombohedral In_2O_3 synthesized by hydrothermal and postannealing pathways

M. SORESCU, L. DIAMANDESCU
Duquesne University, Physics Department, Bayer Center, Pittsburgh, PA 15282, USA
E-mail: sorescu@duq.edu

D. TARABASANU-MIHAILA, V. S. TEODORESCU
National Institute of Materials Physics, P.O. Box MG-7, R 76900 Bucharest, Romania

Due to their interesting optical properties as well as to the increasing interest in sensing and microelectronic applications, the synthesis of indium oxides is an important topic. Indium oxide has two crystalline structures: the cubic lattice, known as the bixbyite structure [1, 2] and the rhombohedral or corundum structure [3].

The cubic In_2O_3 phase in powder or thin film forms has been prepared by different methods: calcination [4], laser ablation [5] and spray pyrolysis [6]. The corundum structure In_2O_3 is a high pressure phase [3, 7, 8] and consequently has been rarely produced. This rhombic phase exhibits better physical properties than the cubic one, such as a more stable conductivity. The difference seems to be the result of a better packing of the anion layers in the rhombohedral In_2O_3.

In the present paper we report the synthesis of rhombohedral phase indium oxide nanoparticles by a hydrothermal route, followed by postannealing at moderate temperatures, using indium nitrate, $In(NO_3)_3{\cdot}H_2O$, as raw material.

In the first experiment, the hydrothermal treatments was performed in a 300 ml stainless steel pressure vessel with stirrer (CP-F-12, Pressure Products Industries, USA) using a 0.7 M aqueous solution of $In(NO_3)_3{\cdot}H_2O$ (Alfa Aesar, 99.99% purity). The autoclave was heated for 4 h at 200 °C, then cooled to room temperature. The obtained precipitates were filtered and washed with distilled water several times. The resulting powder was dried at 105 °C for 1.5 h. In a second experiment, the synthesis was performed in a 50 ml Teflon lined autoclave, without stirrer, followed by filtration, washing and drying, similar to the first case. Finally, the samples were annealed in a rapid temperature furnace (CM Furnaces, Bloomfield, NJ) at 500 °C, for 1 h, in normal atmosphere.

X-ray diffraction spectra (XRD) were recorded with a Rigaku D-2013 diffractometer with Cu K_α radiation ($\lambda = 1.540598$ Å). The transmission electron microscopy (TEM) analyses were performed with a Jeol 200 CX electron microscope.

A typical XRD spectrum of the obtained from the stainless steel autoclave hydrothermal sample is presented in Fig. 1a. All peaks correspond to the orthorhombic indium oxyhydroxide (InOOH) phase [9]. The orthorhombic InOOH phase belongs to (Pnnm) space group 58, with the following lattice parameters: $a = 5.260$ Å; $b = 4.560$ Å; $c = 3.270$ Å. For the hydrothermal sample obtained in the first experiment, the Rietveld refinement gives the following parameters: $a = 5.262$ Å; $b = 4.591$ Å; $c = 3.258$ Å. In Fig. 1b a representative XRD spectrum of the hydrothermal sample annealed at 500 °C for 1 h is shown. The displayed peaks can be indexed to the rhombohedral structure In_2O_3[3], ASTM 22-336, space group R-3c (167) with the following lattice parameters: $a = 5.487$ Å and $c = 14.510$ Å. The refined lattice parameters are: $a = 5.469$ Å and $c = 14.491$ Å. The strong peaks indicate a high degree of crystallinity. No peaks corresponding to other indium compounds could be detected in the XRD spectra of the investigated samples. Using the Scherrer equation [10] for the average particle size of the annealed sample (In_2O_3) gives a mean value of 12 nm, with a distribution in the range of 10–18 nm.

The samples obtained from the Teflon lined autoclave without stirrer are characterized by similar XRD

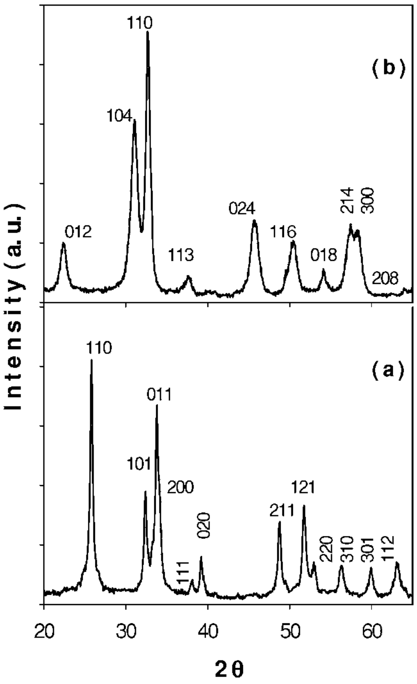

Figure 1 Room temperature X-ray of diffractograms of (a) the as-obtained (stainless steel autoclave) hydrothermal sample and (b) after annealing at 500 °C.

0022–2461 © *2004 Kluwer Academic Publishers*

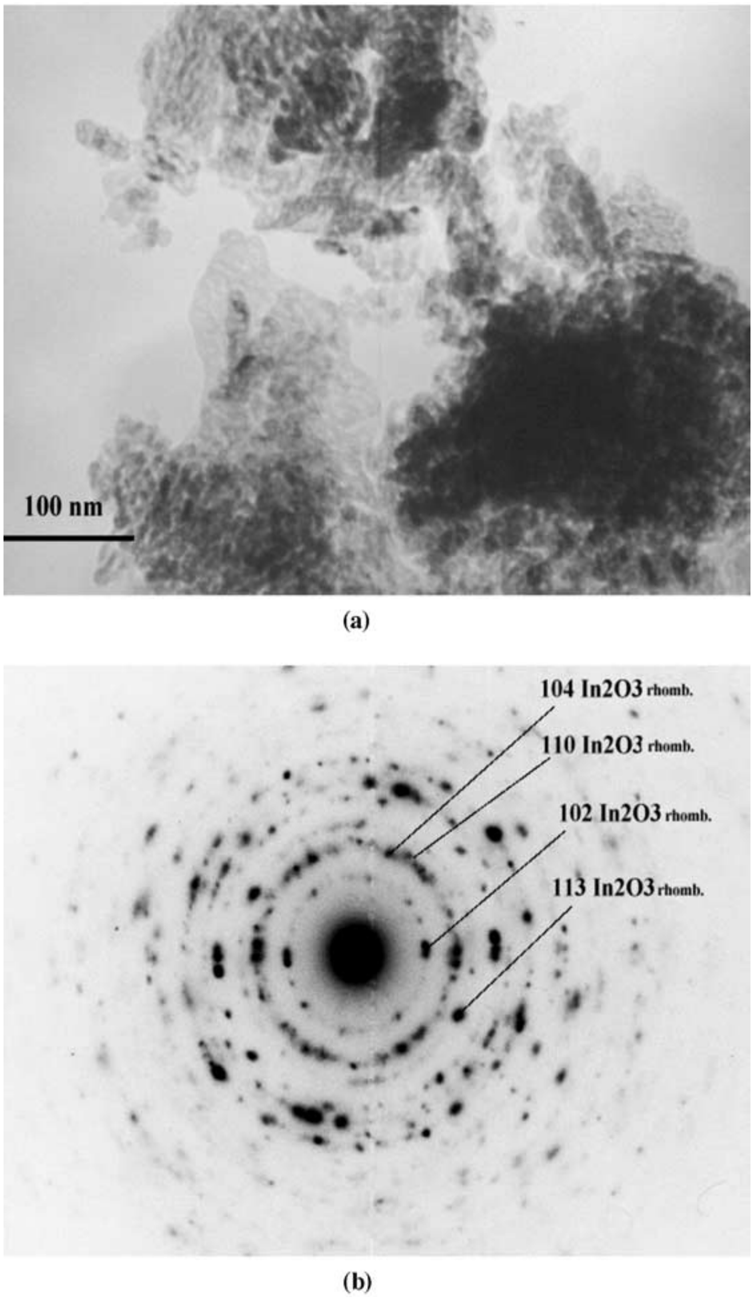

Figure 2 TEM image (a) and the diffraction pattern (b) of the hydrothermal sample (stainless steel autoclave) annealed at 500 °C for one hour, showing the nanometer particles and the characteristic diffraction pattern of the rhombohedral phase In_2O_3.

spectra, representing the orthorhombic InOOH structure. After annealing at 500 °C, for 1 h, these transform into rhombohedral In_2O_3. The only difference that can be inferred with respect to the samples synthesized in the two different autoclaves is the particle dimensions. A mean value of 22 nm, and a distribution in the range of 19–26 nm characterize the annealed samples synthesized in Teflon lined autoclave. The difference in the particle mean dimensions in these two experiments can be ascribed to stirring effects in the hydrothermal system.

Transmission electron microscopy images (Fig. 2) confirm the nanometric distribution of indium oxide synthesized via a hydrothermal and postannealing route. The electron diffraction rings belong to the rhombohedral indium oxide, in agreement with XRD analyses, indicating also a good crystallization of the final products.

Consequently, a simple route to synthesize the rhombohedral phase of indium oxide has been presented. The corundum structure In_2O_3 has been synthesized starting with $In(NO_3)_3{\cdot}H_2O$ using coupled hydrothermal and postannealing methods at moderate temperatures. The obtained particles are nanometric with a mean dimension of ∼12 nm. To our knowledge, this is the first report of the synthesis of rhombohedral In_2O_3 in mild conditions of temperature and pressure. This result should be helpful for the future investigations and sensing applications of indium oxide based compounds.

Acknowledgments

This paper was prepared with the support of the U.S. Department of Energy, under Award No. DE-FC26-02NT41595. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE. The work in Bucharest, Romania, was sponsored by MEC under the CERES program No. 10/2002.

References

1. N. NADUAD, N. LEQUEUX, M. NANOT, J. JOVE and T. ROISNEL, *J. Solid. State Chem.* **135** (1998) 140.
2. M. MAREZIO, *Acta Cryst.* **20** (1966) 723.
3. C. T. PREWITT, R. D. SHANNON, D. B. ROGERS and A. W. SLEIGHT, *Inorg. Chem.* **8** (1969) 1985.
4. C. P. UDAWATTE and K. YANASIGAWA, *J. Amer. Ceram. Soc.* **84** (2001) 251.
5. C. CALI, M. MOSA and G. TARAGIA, *Solid State Electron.* **42** (1998) 877.
6. G. KOROTCENKOV, V. BRINZARI, A. CERNEAVSKI, A. CORNET, J. MORANTE, A. CABOT and J. ARBIOL, *Sensors & Actuators* B **84** (2002) 37.
7. T. ATOU, K. KUSABA, K. FUKUOKA, M. KIKUCHI and Y. SYONO, *J. Solid State Chem.* **89** (1990) 378.
8. A. N. CHRISTENSEN, N. C. BROCH, O. HEIDENSTAM and A. NILSON, *Acta Chem. Scand.* **21** (1967) 1046.
9. A. N. CHRISTENSEN, R. GRONBEK and S. E. RASMUSSEN, *ibid.* **18** (1964) 1261.
10. H. P. KLUG and L. E. ALEXANDER, “X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials” (J. Wiley and Sons, New York, 1974) p. 966.

Received 21 May
and accepted 14 August 2003