

Three dimensional nanowire networks and complex nanostructures of indium oxide

Dana A. Magdas, Ana Cremades, and Javier Piqueras

Citation: *J. Appl. Phys.* **100**, 094320 (2006); doi: 10.1063/1.2372435

View online: <http://dx.doi.org/10.1063/1.2372435>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v100/i9>

Published by the [American Institute of Physics](#).

Additional information on J. Appl. Phys.

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>

ADVERTISEMENT

The advertisement banner for AIP Advances features a green and yellow background with wavy lines. The AIP Advances logo is prominently displayed in the center, with a series of orange dots forming a curved path above the word 'Advances'. To the right, a circular seal states 'Now Indexed in Thomson Reuters Databases'. Below the logo, the text 'Explore AIP's open access journal:' is followed by a list of three bullet points: 'Rapid publication', 'Article-level metrics', and 'Post-publication rating and commenting'.

AIPAdvances

Now Indexed in
Thomson Reuters
Databases

Explore AIP's open access journal:

- Rapid publication
- Article-level metrics
- Post-publication rating and commenting

Three dimensional nanowire networks and complex nanostructures of indium oxide

Dana A. Magdas,^{a)} Ana Cremades,^{b)} and Javier Piqueras^{c)}

Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

(Received 30 June 2006; accepted 18 September 2006; published online 13 November 2006)

Elongated In_2O_3 micro- and nanostructures have been grown by two-step thermal treatments of compacted InN powder, at temperatures between 350 and 700 °C. Different thermal treatments have been found to induce the growth of structures with different sizes and morphologies as wires, rods, or arrows. The experimental conditions leading to the different structures, as well as the evolution of the structures during the treatments, have been investigated. Some treatments lead to large scale formation of three dimensional networks of the mentioned structures. The mechanism of network formation is discussed. The structures have been characterized by cathodoluminescence, scanning electron microscopy, and x-ray diffraction. © 2006 American Institute of Physics.

[DOI: [10.1063/1.2372435](https://doi.org/10.1063/1.2372435)]

INTRODUCTION

Indium oxide is a wide band gap semiconductor with applications in different fields such as gas sensing, optical transparency, or optoelectronics. There is an increasing interest in the synthesis and properties of one-dimensional In_2O_3 structures, which have been grown by different thermal methods, involving deposition on a substrate^{1–6} and the use of In or In_2O_3 as starting materials. In the present work, elongated In_2O_3 nanostructures have been grown under argon flow by thermal treatment of compacted InN powder, as reported in Ref. 7. During the annealing, InN decomposes by nitrogen loss, and the oxide is slowly formed by the reaction of indium with the atmosphere. The decomposition of InN takes place at temperatures about 450 °C or higher and the structures grow on the sample surface, without the use of a foreign substrate or a catalyst. This method has been previously applied to grow elongated nanostructures of different semiconductor oxides.^{8–11} As reported in Ref. 7, In_2O_3 structures with different morphologies and sizes are obtained during the thermal treatment of InN. The objective of this work is to determine the experimental conditions to grow specific structures, such as wires, rods, or arrows, and to study the evolution of the structures during extended treatments in order to control the growth process. The resulting structures range from single nanowires to networks of more complex, arrow-shaped, elements. The mechanism of network formation has also been studied.

EXPERIMENTAL METHOD

The starting material was InN powder with 99.9% purity provided by Aldrich Chem. Co. Samples were prepared by compacting the powder under a compressive load of 2 tons to form disks of about 7 mm diameter and 2 mm thickness.

The samples were then annealed at different temperatures, as shown in Table I, under argon or nitrogen flow. The thermal treatments consisted of two steps at different temperatures for 5, 10 or 15 h. The two-step treatments had been found⁷ to favor the growth of elongated structures all over the sample surface. The crystalline structure of the samples was characterized by x-ray diffraction (XRD) with a Philips diffractometer working at 45 kV and 40 mA, using $\text{Cu } K_\alpha$ radiation. Secondary electron (SE) observations were carried out in a Leica 440 scanning electron microscope (SEM). The cathodoluminescence (CL) measurements were carried out at liquid nitrogen temperature with a beam energy of 15–20 keV. CL images in the visible range were recorded with a Hamamatsu R928 photomultiplier, and the CL spectra were recorded with a Hamamatsu PMA-11 CCD camera.

RESULTS AND DISCUSSION

XRD shows that after the treatments, the samples consist of In_2O_3 . The treatments listed in Table I produce elongated structures on the sample surface, whose morphology depends on the treatment. Also, in some samples the morphology depends on the position of the region considered, relative to the gas inlet. In the region opposite to the gas inlet, the structures are more developed due to the transport of evaporated material towards this part of the sample. This effect was observed in sample 1, where nanowires are formed near the gas inlet, while more and complex structures are observed in the opposite side. Figure 1 shows wires in different regions of the sample, showing different stages of growth. The wires have

TABLE I. Samples and treatments.

Sample	Treatment
1	700 °C(5 h)+350 °C(10 h)-Argon
2	700 °C(5 h)+350 °C(15 h)-Argon
3	350 °C(10 h)+650 °C(10 h)-Argon
4	350 °C(10 h)+650 °C(10 h)-Nitrogen

^{a)}Permanent address: Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania.

^{b)}Electronic mail: cremades@fis.ucm.es

^{c)}Electronic mail: piqueras@fis.ucm.es

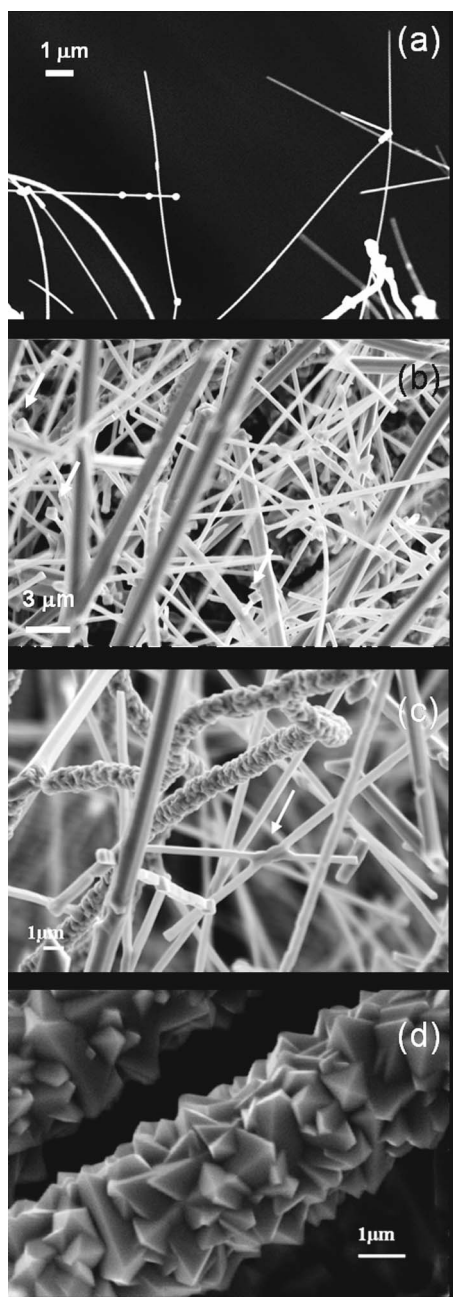


FIG. 1. (a) Nanowires in a region of sample 1 close to the gas inlet. (b) Wires in other region of sample 1 close to the gas inlet. Some nanowires, marked with arrows, terminate in a small crystal with incipient pyramidal shape. (c) Wires at a larger distance from the gas inlet. A sintered junction of two wires is marked with an arrow. (d) Nanopyramids covering the surface of some of the wires are shown in (c).

transversal dimensions from hundred or few hundreds of nanometers, to the micron range, and lengths of up to hundreds of microns. Figure 1(a) shows a region, at the sample edge, with a small number of nanowires and Fig. 1(b) shows a region of the sample with a high density of wires forming a network whose junctions appear, as observed in the SEM images, to be sintered points rather than points of physical contact between the wires.

It is to be noticed that many nanowires, as those marked with arrows in the image of Fig. 1(b), terminate in a small crystal with incipient pyramidal shape. In Fig. 1(c), which would correspond to a more advanced stage of growth, the

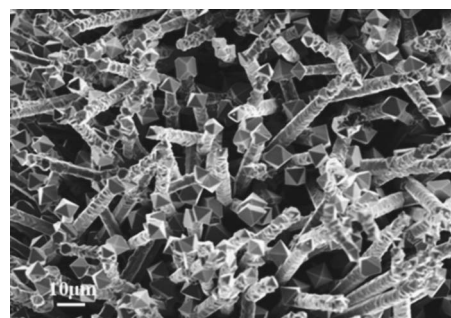


FIG. 2. Arrow structures in an intermediate stage of formation in a region of sample 1 opposite to the gas inlet.

wires have larger transversal dimensions. In addition some of the larger wires show a rough surface which is due to a dense distribution of nanopyramids [Fig. 1(d)]. In regions at increasing distance from the gas inlet, a higher number of wires with the surface covered by nanopyramids are observed. In_2O_3 nanopyramids have been previously reported in other configurations, as isolated pyramids on a substrate,^{12,13} chains¹⁴ or arrows.⁷ Since In_2O_3 pyramids have efficient field emission properties¹² the formation of rough nanowires should improve the field emission of the structures.

At the sample region opposite to the gas inlet, arrow structures formed by rods with rough lateral surfaces, and with pyramids on the top, similar to the pyramids of some wires in Fig. 1(b), are observed (Fig. 2).

The structures shown in Figs. 1 and 2 appear to correspond to different stages of growth, with the more complex structures in the region opposite to the gas inlet. A similar effect has been observed in ZnO samples¹⁰ which showed longer elongated structures at the side of the disk opposite to the gas inlet. The differences observed at both sides of the disk are not related to temperature gradient, which is negligible across the small disk diameter. Since the disk acts as a source and a substrate of a vapor-solid process, the formation of more complex, or well formed, structures in the side opposite to the inlet would be due to a higher, gas assisted deposition in that region.

Increasing the time of the second annealing, as in sample 2, caused the growth of well ordered elongated structures in some regions. Figure 3(a) shows such network consisting of rods with some preferential orientations and with pyramids, in different stages of growth on the top. Figure 3(b) shows details of a set of pyramids, all with the same orientation. The growth of a number of well oriented arrow structures would be of interest regarding the above mentioned field emission applications. Images, as those in Fig. 3(c), show that the formation of the networks takes place by the growth of lateral branches with incipient pyramids at the top.

Sample 3, which was treated with a first step annealing at lower temperature, contains large regions with well faceted arrow structures, as those shown in Fig. 4, not observed in sample 1. This suggests that the formation of such structures is favored when the first step of the treatment is a low temperature annealing at 350 °C which causes InN grain growth, but not material decomposition, which takes place during the second step at 650 °C.

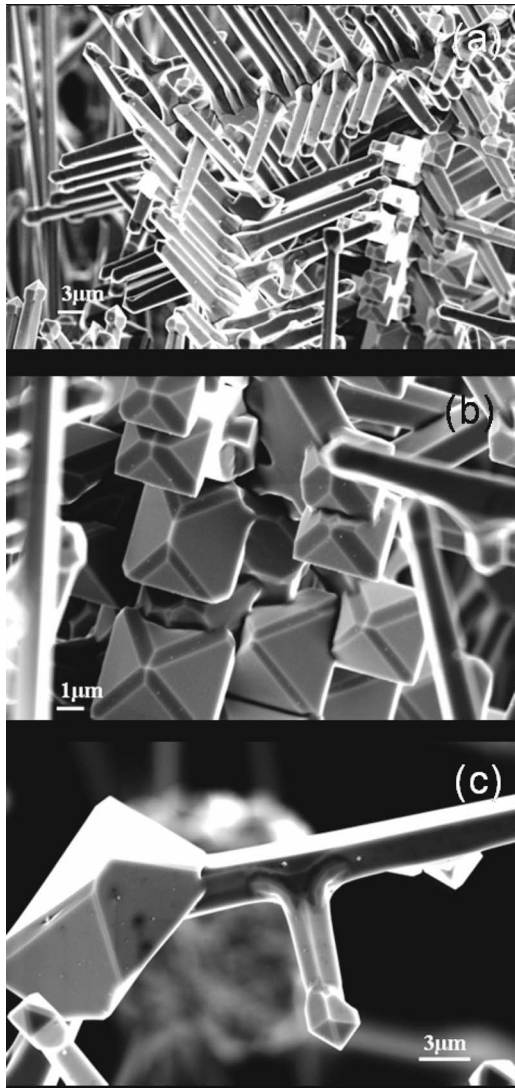


FIG. 3. (a) Ordered structures in sample 2. (b) Details of a set of oriented pyramids in the structure shown in (a). (c) Growth of a secondary rod at the side of a main rod.

No significant differences were observed between samples 3 and 4 which were annealed with the same treatments but in argon and nitrogen atmospheres, respectively. In both cases elongated In_2O_3 structures are formed but appear to be more developed, with the presence of a higher density of arrows, in the case of argon atmosphere.

The growth of three-dimensional nanowire or nanorod networks by a high temperature deposition process has been previously reported for several oxides as ZnO (Ref. 15) or WO_3 .¹⁶ The degree of the networking, by sintering in the intersection of the nanowires, and the thickness of the network were found to increase with the duration of the deposition.¹⁵ Nanowire networks with thicknesses in the range of tens of microns have potential applications related to their high surface area. In the present work, the duration of the deposition influences the degree of the networking as well as the nature of the structures, wires, or arrows. The mechanism of network formation appears to depend on the structure. In the case of wires, the junction are formed mainly by sintered wires, as shown in Fig. 1. The existence

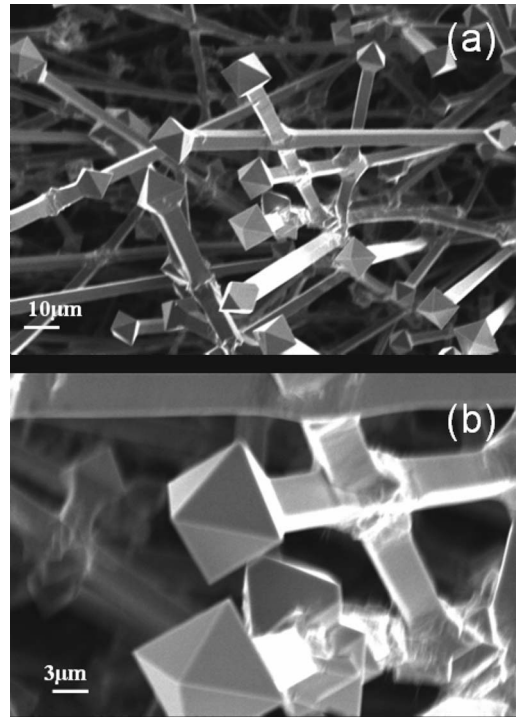


FIG. 4. (a) Well faceted arrow structures in sample 3. (b) Network of arrows.

of networks with the nanowires sintered at the junctions, as observed here, has been reported by Gao *et al.*¹⁵ for ZnO where the two nanowires of the junctions are joined together with a clear grain boundary, as revealed by transmission electron microscopy. In the case of the large arrows, the images, as those of Fig. 4, indicate that interpenetration could take place during growth. Yang and Wang¹⁷ have studied the interpenetrative growth of ZnO nanorods and proposed a model in which longitudinal and transverse growth leads to the joining of the nanorods. The arrows expand at the interpenetration site, as in some intersection of Fig. 4, which is the effect observed in Ref. 17 for the nanorods and is explained by transverse growth. When an arrow meets another one during its longitudinal growth the pyramid at the front has to pass the existing arrow. The model of Ref. 17, mainly based on SEM observations, considers that when the growth forefront meets the second rod, the unblocked part of the front continues its longitudinal growth and, after passing the obstacle, regains the original shape through transversal growth. This mechanism could possibly apply to the case of the In_2O_3 arrows, but this could not be confirmed because no front pyramids were clearly observed in the transversal growth phase during the interpenetration. In any case, the observations clearly show that one mechanism for the network formation appears to be the growth of secondary rods, as the one shown in Fig. 3(c). Lao *et al.*¹⁸ reported the growth of nanowire networks, with very low density of wires, by thermal evaporation of In_2O_3 powder on SiO_2/Si substrate with gold as catalyst. Their wires contain nanocrystals forming chain structures, and the nanocrystals are often the junctions of the networks. This was not found in our case, in which the junctions appear to be not related to the presence of nanocrystals but to the soldering of wires in in-

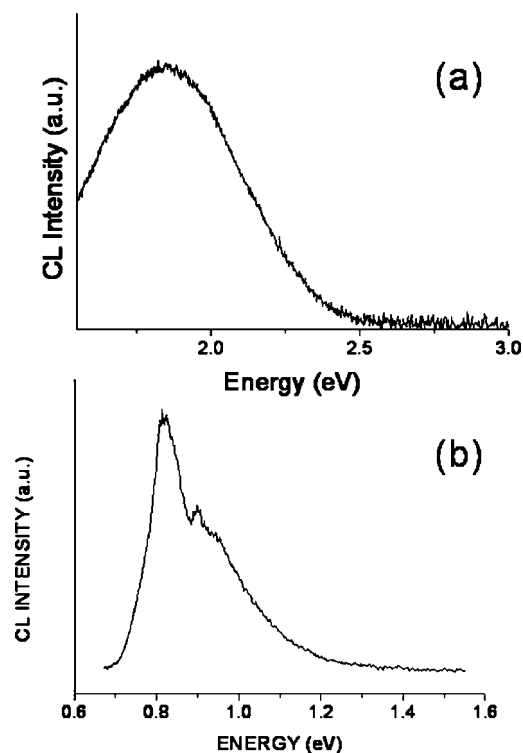


FIG. 5. (a) CL spectrum in the visible range recorded on sample 3 and (b) CL spectrum in the near infrared range recorded on the structures of sample 1.

tersection points. Also, in Ref. 18 gold was found necessary for the growth of the networks, while in this work the growth takes place by a vapor-solid mechanism without a catalyst.

The elongated structures in different steps of formation were previously found⁷ to have different cathodoluminescent behavior. In particular, well formed structures have the main emission band at 1.9 eV while the presence of structures in the first stage of formation, as chains of nanopillars connected by nanowires, favors the blue-green emission at 2.5–2.6 eV. Since the treatments of this work lead to different structures in advanced stages of formation, the main emission band appeared in all cases at 1.9 eV, while weaker components were present at higher energies. Figure 5(a) shows the visible CL spectrum of sample 3. The 1.9 eV luminescence band is observed in untreated commercial In_2O_3 powder and has been previously reported in photoluminescence studies of polycrystalline In_2O_3 .¹⁹

Also the emission at 2.5–2.6 eV, observed in the samples of this work along with the 1.9 eV, has been reported for different In_2O_3 nanostructures, e.g., Ref. 13. These CL results confirm the XRD data showing that In_2O_3 structures are formed during thermal treatment of InN powder. However, since energy dispersive x-ray spectroscopy (EDX) measurements⁷ show the presence of nitrogen in amounts of up to a few at. % in the In_2O_3 structures, CL measurements in the near infrared range have been performed in order to detect the possible presence of InN. The luminescence of InN is a subject of interest related to a controversy on the band gap value of this material, which has been for a long time believed to be 1.9 eV (Ref. 20) but which more recently has been proposed to be about 0.9 eV (Ref. 21) or in the

range of 0.7–0.8 eV.²² Luminescence emission of InN at about 0.8 eV has been reported for films^{21–23} and nanowires.²³ Figure 5(b) shows the near infrared spectrum of sample 1, showing a main band at about 0.8 eV and a less intense emission at 0.9 eV. The shape of the spectrum was found similar to that of pure InN powder. This result suggests that the In_2O_3 micro- and nanostructures could contain small amounts of InN nanoclusters not detectable by XRD.

CONCLUSIONS

Different thermal treatments of InN compacted powder, at two temperatures, lead to the growth of In_2O_3 one-dimensional structures on the sample surface in the shape of nanowires, rods, or arrows in different stages of formation. In one of these stages, microwires with the surface covered by nanopillars are obtained; they are structures of potential interest as field emitters. The shape and dimensions of the resulting structures depend on the temperature and duration of the treatment. In samples with high density of structures, three dimensional networks are formed. In the junctions of the nanowire networks the wires appear sintered. Growth of arrows, such as branches of main arrows, also takes place during network formation. The growth of the structures takes place by a vapor-solid process, without catalyst. Cathodoluminescence measurements indicate that a small fraction of InN could remain as nanoclusters in the In_2O_3 structures.

ACKNOWLEDGMENTS

This work has been supported by EU Marie Curie program (HPMT-CT-2001-00215) by MEC (Project MAT-2003-00455), and by CAM (Project GR/MAT 630-04). One of the authors (D.A.M.) acknowledges the Marie Curie fellowship in the frame of the HPMT-CT-2001-00215 project.

¹Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science* **291**, 1947 (2001).

²X. Y. Kong and Z. L. Wang, *Solid State Commun.* **128**, 1 (2003).

³C. Liang, G. Meng, Y. Lei, F. Phillipp, and L. Zhang, *Adv. Mater. (Weinheim, Ger.)* **13**, 1330 (2001).

⁴L. Dai, X. L. Chen, J. K. Jian, M. He, T. Zhou, and B. Q. Hu, *Appl. Phys. A: Mater. Sci. Process.* **A75**, 687 (2002).

⁵X. S. Peng, Y. W. Wang, J. Zhang, X. F. Wang, L. X. Zhao, G. W. Meng, and L. D. Zhang, *Appl. Phys. A: Mater. Sci. Process.* **74**, 437 (2002).

⁶F. Zeng, X. Zhang, J. Wang, L. Wang, and L. Zhang, *Nanotechnology* **15**, 596 (2004).

⁷D. A. Magdas, A. Cremades, and J. Piqueras, *Appl. Phys. Lett.* **88**, 113107 (2006).

⁸D. Maestre, A. Cremades, and J. Piqueras, *J. Appl. Phys.* **97**, 44316 (2005).

⁹E. Nogales, B. Méndez, and J. Piqueras, *Appl. Phys. Lett.* **86**, 113112 (2005).

¹⁰J. Grym, P. Fernández, and J. Piqueras, *Nanotechnology* **16**, 931 (2005).

¹¹P. Hidalgo, B. Méndez, and J. Piqueras, *Nanotechnology* **16**, 2521 (2005).

¹²H. Jia, Y. Zhang, X. Chen, J. Shu, X. Luo, Z. Zhang, and D. Yu, *Appl. Phys. Lett.* **82**, 4146 (2003).

¹³P. Guha, S. Kar, and S. Chaudhuri, *Appl. Phys. Lett.* **85**, 3851 (2004).

¹⁴C. L. Hsin, J. H. He, and L. J. Chen, *Appl. Surf. Sci.* **244**, 101 (2005).

¹⁵P. X. Gao, C. S. Lao, W. L. Hughes, and Z. L. Wang, *Chem. Phys. Lett.* **408**, 174 (2005).

¹⁶J. Zhou, Y. Ding, S. Z. Deng, L. Gong, N. S. Xu, and Z. L. Wang, *Adv. Mater. (Weinheim, Ger.)* **17**, 2107 (2005).

- ¹⁷R. Yang and Z. L. Wang, Solid State Commun. **134**, 741 (2005).
- ¹⁸J. Lao, J. Huang, D. Wang, and Z. Ren, Adv. Mater. (Weinheim, Ger.) **16**, 65 (2004).
- ¹⁹M. S. Lee, W. C. Choi, E. K. Kim, C. K. Kim, and S. K. Min, Thin Solid Films **279**, 1 (1996).
- ²⁰T. L. Tansley and C. P. Foley, J. Appl. Phys. **59**, 3241 (1986).
- ²¹V. Yu. Davidov *et al.*, Phys. Status Solidi B **229**, R1 (2002).
- ²²J. Wu *et al.*, Appl. Phys. Lett. **80**, 3967 (2002).
- ²³T. Matsuoka, H. Okamoto, M. Nakao, H. Harima, and E. Kurimoto, Appl. Phys. Lett. **81**, 1246 (2002).