Synthesis, structure and optical properties of single-crystalline In_2O_3 nanowires

N.M.A. Hadia [a,*], H.A. Mohamed [a,b]

[a] Physics Department, Faculty of Science, Sohag University, 82524 Sohag, Egypt
[b] King Saud University, Teachers College, Science Department (Physics), 11148 Riyadh, Saudi Arabia

ABSTRACT

Indium oxide In_2O_3 nanowires have been recently synthesized revealing interesting properties and used in various applications. In order to reduce as much as possible the influence of undesired dopants and/or impurities on the observed properties, In_2O_3 nanowires have been grown without the use of catalysts, directly from metallic indium by a vapor transport technique and a controlled oxidation with oxygen–argon mixtures. Depending on the growth conditions (temperature, vapor pressure, oxygen concentration, etc.) different results have been achieved and it has been observed that a 'proper' In condensation on the substrates may enhance the nanowires growth. Detailed structural analysis showed that the In_2O_3 nanostructures are single crystalline with a cubic crystal structure. The grown In_2O_3 nanowires were optically characterized in order to evaluate the absorption coefficient, optical band gap, refractive index and extinction coefficient. Room temperature Photoluminescence (PL) spectrum showed broad and intense blue emission at 375 nm.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Today the interest in the 'nanowire-like' structures is growing up exponentially for many different materials. The peculiar properties showed by one-dimensional (1D) nanostructures stimulated several discussions about their potential applications in various fields and research on the synthesis of these nano-materials.

In the last few years several functional oxides have been successfully synthesized [1,2] by vapor transport/deposition techniques (SnO_2 [3–7], ZnO [3,8–10], In_2O_3 [3,11], Ga_2O_3 [12–14], SiO_2 [15–17], MgO [18,19], PbO_2 [20], etc. – see references for some detailed examples) in a quasi-1D form, where 'quasi' means that their smaller dimension is in the nano-scale range but it is generally too large to give rise to quantum confinement effects (e.g. the critical Bohr radius is reported to be 2.15–2.4 nm in In_2O_3 [11,21]). Nevertheless the 'reduced' dimension of these nanowires, together with the frequent natural non-stoichiometry of these oxides, gives rise to peculiar properties which are different from those of bulk material.

The number of successful reports in literature about the synthesis of In_2O_3 nanowires is much smaller than those for zinc oxide or tin oxide nanowires. This can testify that the growth of these nanostructures by a simple physical method is not trivial. The reason for such a difficulty may rise from the intrinsic high symmetry of the cubic crystal cell of In_2O_3.

To overcome this problem, metal catalysts, such as Au, Ag, or Ni [22–29], have been often used to force the In_2O_3 crystals to follow a highly oriented growth through a VLS (vapour–liquid–solid) mechanism. On the other hand, some authors [30,31] reported that In_2O_3 nanowires and branched nanostructures can also be obtained without catalysts by a carbothermal reaction with an In_2O_3 or In source.

Unfortunately the use of catalysts or other reagents (like carbon, nitrates, other reducing/oxidizing compounds, In precursors, etc.) may introduce undesired dopants inside the nanowires or leave alloys particles on the growth tip that may affect the nanowires properties.

Here we present the results of a simple process in which vapor transport, condensation and oxidation are employed, involving only metallic indium and oxygen in the reaction. Especially the role of the liquid indium phase is discussed. The optical constants are determined by Jasco 570 double beam spectrophotometer for optoelectronic applications and the results are compared with results obtained using other preparation methods, the PL properties of the In_2O_3 nanowires have been studied at room temperature.

2. Experimental

The preparation of In_2O_3 nanowires was carried out in a conventional horizontal tube furnace. The high purity (99.999%) of metal indium granulated was placed in an alumina boat as the source, and several wafer and *quartz* substrates were placed downstream along the tube, where a strong temperature gradient is expected. The furnace was then heated up to a maximum temperature of 1200 °C, while a small amount of inert gas (argon) flew along the tube. After two minutes oxygen was introduced into the reaction system by mixing it with the argon flow and 40 min later the furnace was cooled down to room temperature. The substrates, on which

* Corresponding author. Tel.: +20 1129264358; fax: +20 93 4601159.
E-mail address: nomery_abass@yahoo.com (N.M.A. Hadia).

In_2O_3 was deposited within a 500–1050 °C temperature range, were easily removed from the furnace and directly characterized by several techniques. The general structure was determined by by X-ray diffraction using a Schimadzu 7000 diffractometer. The diffraction patterns were obtained using Cu-Kα radiation (λ = 0.15406 nm), images obtained with a (JEOL JSM 6360LA, Japan) scanning electron microscope (SEM). The optical transmittance (T) of the In_2O_3 film was studied using a Jasco 570 double beam spectrophotometer in the wavelength (λ) range of 200–2500 nm at normal incidence. For further considerations, Photoluminescence (PL) measurements were performed using a 337 nm ILGI 503 N_2 laser.

3. Results and discussion

3.1. Structural and morphological of In_2O_3 nanostructures

The substrates were put along the furnace tube to collect samples with In_2O_3 crystals grown in different conditions. Indeed, the high temperature gradient in the growth/collection region generated a variety of local conditions, in which both vapor and liquid In phases may be present in various concentrations. This circumstance gave rise to different growth mechanisms that can be observed in the numerous collected In_2O_3 samples.

At high temperature (1050–900 °C) and high vapor pressure values the growth generally results in large In_2O_3 crystals (Fig. 1a). But in some special conditions, when the oxygen–argon ratio was not too high, some VLS match-like wires can grow (Fig. 1b). Differently from a common catalyzed VLS growth, in which the metal drop on the growth tip is made of Au or other metals that act as interface solutions, here the drop is made of In (see also [30,31]). Being In an active reagent in the In_2O_3 nanowire growth, it 'consumes' during the growth of the nanowire. So, this kind of growth was possible only when the vapor-to-liquid (vapor-to-drop) condensation rate is higher, or at least comparable, with the oxidation and growth rate, i.e. only at very high In vapor pressure values. At low temperature (<600 °C) In_2O_3 was present on the substrates in the shape of octahedral nanocrystals (Fig. 1c). These nanocrystals seem to generate directly in the vapour phase and then precipitate onto the substrates. Indeed they are not 'attached' to the substrate and they can be easily removed by any gentle blow.

Between these two temperature regions the used growth setup and conditions favor liquid In condensation during the first step of the growth (vapor transport). Inside this intermediate region, where the temperature is about 900 °C large metal droplets can be found even at the end of the growth, i.e. after the oxidation step. Condensation of In homogeneously decreases along the furnace and temperature gradient and, at about 600 °C, it is practically reduced to zero. Between 700 and 800 °C, where In condensation was not 'too strong' or 'too weak', a dense entanglement of In_2O_3 nanowires generally grows (Fig. 2a). Depending on the growth parameters, samples with different dimensions can be collected. The largest nanowires usually have a 'belt-like' or 'tape-like' rectangular section (Fig. 2b). Their thickness is in the 30–190 nm range, the width is about 5–10 times larger and they can be few hundreds of micrometers long. The smallest nanowires, instead, have a 10–30 nm round section.

Fig. 3 shows the XRD patterns of the obtained In_2O_3 nanowires. All the peaks in the XRD pattern could be indexed to cubic In_2O_3 with a lattice constant of a = 10.11 Å (JCPDS card No. 06-0416). Moreover, no other impurity phases were detected.

The size distribution was generally larger in the collected samples than in those reported in literature for VLS growths catalyzed with metals. TEM images revealed that there was no In metal particle at the end of the nanowires (on the growth tip) and so this means that, in the used growth process, the nanowire size could not be directly controlled by the size of metal droplets.

No In metal droplet is found on the growth tip, but in this growth the mechanism does not seem to be simply a 'direct VS (vapour–solid)' one, as those reported and discussed for other growths in literatures (e.g. see Refs. [30,31]). In this growth it
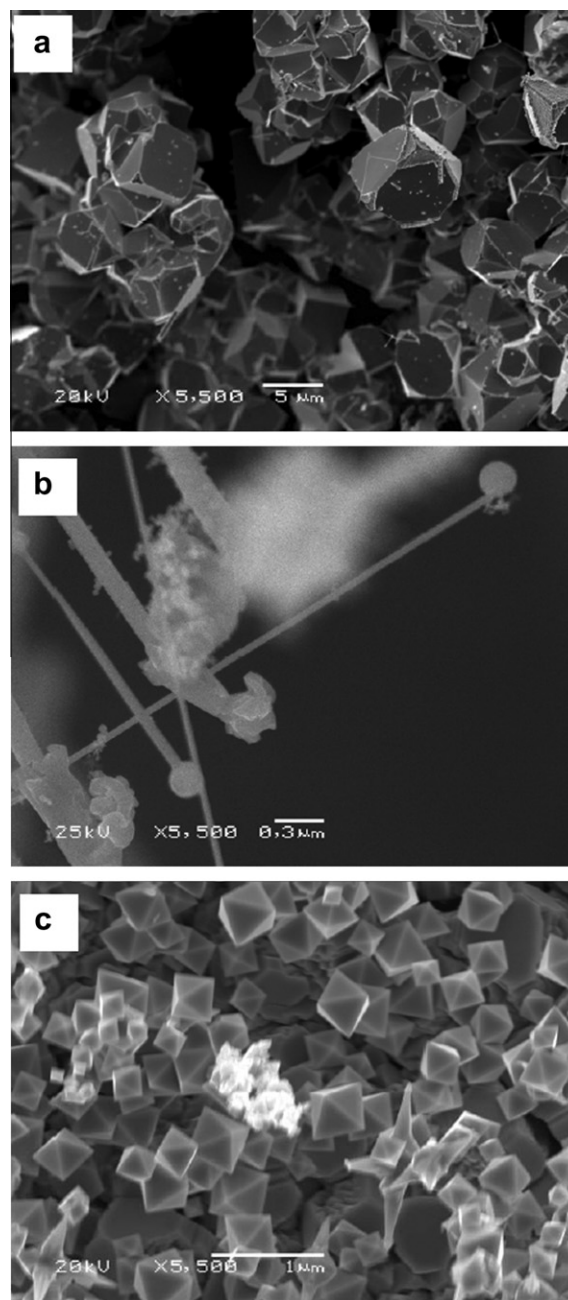
Fig. 1. SEM images of In_2O_3 crystals growth in different zones of the reactor: (a) large In_2O_3 crystals grown at high temperature; (b) In_2O_3 whiskers-like nanowires with a In metal drop at the top (also grown at high temperature); (c) In_2O_3 octahedral nanocrystals grown from the vapor phase and collected downstream at low temperature.

has been observed, indeed, that In_2O_3 nanowires grow only in the region where some condensation of indium occurs. Hence the liquid phase is involved also in this growth, even if not in the usual vapor–liquid–solid mechanism reported in the literature. Studying the samples with a lower density of nanowires, it has been observed that the In_2O_3 nanowires generally grow starting from the edges of micron-size faceted In_2O_3 crystals (Fig. 4), while no nanowire has been found to elongate directly from the surface of the substrates. Even if the definition of the whole growth mechanism require further investigations, it is clear that liquid In condensation acts as a catalyst for the growth of In_2O_3 nanowires, in a 'self-catalytic' process. On the opposite, it has been observed that when the transport flow is slightly increased and In vapour does