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Microtubes decorated with nanowires

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We report a hierarchically ZnO micro/nanostructured material where ZnO microtubes are covered with ZnO nanowires. The synthesis process is partially driven by electrical current and accompanied in situ by electrical resistivity measurements. The thermal activated energy of the obtained semiconducting microtubes was estimated to be 0.5 eV. Microtubes topped with nanowires may have multifunctional nature and tailored properties for technological applications.

In the past few years, a considerable effort has been devoted in order to grow one-dimensional (1D) nanostructured materials.1–5 Besides being of great importance to fundamental science, micro-nanostructured materials are very attractive for electronic industry. As far as this point is concerned, transition metal oxides such as ZnO, CuO, and TiO are important materials with remarkable applications. Tailoring 1D micro-nanostructure for functional devices of these materials has been the key for technological applications such as electromechanics, optoelectronics, solar cells, and sensors.6–9 In particular, tubular structures are of exceptional interest due to their many multifunctional properties such as confinement effect, and applications like fluid path, fuel cells, and hydrogen storage.10–12 Functionalization may occur on the surface, inner part, and extremities of the tubes. These multifunctional properties from hierarchical morphol- ogy may attract considerable scientific interest given their potential for addressing important technological challenges. Some methods have been developed to synthesize simple microtubular structures including wet chemical method, hydrothermal, template-assisted, and vapor phase deposition.13–16 On the other hand, there are several routes to grow nanostructured transition metal oxide materials such as nanowires, nanotubes, nanobelts, and nanoleaves.17–19 Among them, the thermal oxidation process by using pure metal may be the simplest one.20–22 In this context, it is accepted that the growth of an oxide layer is necessary prior to nanostructure formation. For example, in the case of ZnO, a layer is formed first, followed by the formation of nanowires (NWs) on the top of it. In this work, we have, to some extent, used this process to grow nanostructured ZnO layer on the surface of a microwire in the liquid phase. On the phase of this layer, nanowires grow homogeneously and well aligned as a result of lattice diffusion of Zn ions across the ZnO layer. Afterwards, this process is followed by the evaporation of the remaining liquid Zn core leaving a tubular structure. The thermally driven microtube formation with nanowires on its surface occurs simultaneously with the passage of an electric current.

Scanning electron microscopy (SEM) images were obtained using a JEOL FEG-SEM JSM 6701F. X-ray powder diffraction (XRD) data were collected at room temperature on a STADI-P diffractometer Store. Simultaneous to sample growth process, electrical resistivity was measured in situ with a four-probe method by using a custom-built dedicated apparatus. In this method, separation of current (two outer points) and voltage (two inner points) electrodes eliminates the lead and contact resistance from the measurement. The four-probe station is composed of alumina, and the wiring is made from platinum. The silver epoxy, used to attach the platinum wire to Zn microwire, is cured at 160 °C. The metallic silver at the four point contacts covers Zn and protect this interface from oxidation during the process. It is worth noticing that the microwire is suspended on top of the four probes, not resting in any kind of surface. Data were collected in both air and O2 flow by warming to the high temperature set point and followed by a cooling stage in a tubular furnace. As-received pure zinc metal microwire is used in the oxidation process as a starting material.

The fabrication method of a microtube covered with nanowires presented in this study is simple and fast, and the final products are free of external catalyst agent. Simply stated, a Zn microwire is submitted to a thermal cycle in an atmosphere controlled chamber (O2 and air) while in situ electrical resistivity measurements are carried out. Fig. 1 shows representative curves of the temperature dependence of the electrical resistivity. As the temperature increases, the electrical resistivity also increases as expected for metals. At T ~ 420 °C, the electrical resistivity jumps revealing the Zn solid/liquid first order phase transition. Even in the liquid phase, the ρ(T) measurement persists. A thin ZnO layer is formed already in the initial temperature rise prior to the melting point. Moreover, the formation of ZnO can influence the wettability and adhesion/cohesive force of the Zn liquid.23 The combined effects of the structural aid provided by the solid ZnO layer and the wettability of the liquid Zn provide the necessary conditions for the processing of hierarchically micro-nanostructured samples.

In Fig. 1, curve I depicts the process performed in the presence of O2 flow. The temperature was raised up to 515 °C and maintained constant for 30 min, in order to oxidize the metal, and then lowered back to room temperature. At 515 °C, during the waiting time, an electrical resistivity increase of approximately 1.2 × 10−5 Ω-cm was detected. Note that, as the system is cooled down, the sample

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undergoes the phase transition from liquid to solid in a reverse process, however on a slightly higher electrical resistivity level and slightly shifted to a lower temperature. At the end of the process, the sample is consisted of a metallic core covered with a nanostructured ZnO shell topped by nanowire array on the surface. Curve II depicts a measurement similar to the previously described, except for the 60 min waiting time. Due to the longer waiting time, the electrical resistivity jumps suddenly three orders of magnitude. Afterwards, as the system is cooled down, ρ increases rather modestly showing another significant jump around 300 °C. At this point of the process, the electrical contacts break and the measurement stops. Other two runs are shown in Fig. 1 and refer to processes in the presence of O2 flow (curve III) and in air (curve IV) where the temperature was raised up to 810 °C, followed by cooling the system back to room temperature. The process undertaken in the presence of O2 presents a higher resistivity slope when compared to the process in the presence of air flow. At Tm = 680 °C (for O2 flow) and 740 °C (in air), the electrical resistivity increases sharply suggesting that the metallic percolation path in the liquid phase brakes down (break down of percolation (BDP)). In other words, at this temperature, the Zn liquid medium loses continuity turning into liquid islands throughout the wire breaking down the path of electrical current. As time and temperature increase, the metallic islands separated by ZnO regions become smaller, increasing the electrical resistivity as revealed by the stair-like behavior of the curves. The electrical resistivity of ZnO is much higher than the Zn metal. For the sake of reproducibility, we have repeated these measurements several times, and the results are consistent except that the percolation breakdown temperature is different for each run, however, taking place in the range from 650 °C to 750 °C. On cooling down from 810 °C, the electrical resistivity increases exponentially indicating a thermally activated behavior which corroborates the semiconducting behavior of the produced material (see Figure 2(b)) (around 600 °C for curve III, the electrical contacts break and the measurement stops). The electrical conductivity in semiconductors is described by Arrhenius equation, ρ(T) = ρ0exp(−EA/kT), where ρ0 is a constant, E_A the activation energy, k is the Boltzmann constant, and T is the absolute temperature. In general, at high temperatures this activation energy is equal to half of the band gap energy (Eg).24 From the temperature dependence of the electrical resistivity (ln(ρ/ρ0) versus 1/T), the activation energy is found to be E_A = 0.5 eV, which is much lower than the optical energy gap of the bulk E_g = 3.3 eV.25 We suggest that this result, obtained at very high temperature, is influenced by both the presence of interstitial Zn species in ZnO lattice and oxygen vacancies as structural defects.26 As we shall see, in this process, one starts with a metal microwire and end up with a semiconducting microtube decorated with nanowires with activation energy of 0.5 eV.

We have carried out x-ray diffraction and scanning electron microscopy experiments as shown in Figs. 2 and 3, respectively. In Fig. 2, we show the evolution from the Zn metallic crystal phase to the formation of the ZnO. Fig. 2(a), the pattern of Zn microwire before the oxidation process start: the Zn metal has hexagonal structure with P63/mmc.
space group symmetry. In Fig. 2(b), the x-ray diffraction of a microwire, heat treated up to 700 °C, in the intermediate process is displayed revealing the coexistence of the Zn metallic and ZnO. In Fig. 3(c), the x-ray diffraction reveals only the ZnO phase. The ZnO has also a hexagonal structure with \( P6_3mc \) space group symmetry which is in agreement with literature. Besides the x-ray diffraction patterns, images showing the morphology of the microwires are accordingly illustrated.

Figure 3 shows representative images of ZnO microtubes obtained with the process indicated by the curve IV in Fig. 1. In a first stage, the oxygen present in air reacts with Zn forming a thin solid layer of ZnO. Note that ZnO melting point is significantly higher, being \( T_m = 1970 \) °C. In a second stage, nanowires are formed as a result of lattice, grain and surface diffusion of Zn ions from the liquid inner part across the ZnO layer. During the oxidation process, the ZnO solid shell covered with nanowires encloses the Zn metallic liquid. As suggested by the electrical resistivity measurements, around \( T = 750 \) °C, the Zn liquid evaporates forming tubular structures. When the process is carried out in O\(_2\) flow atmosphere (see curve III in Fig. 1), the oxidation evolution is different. The nanowires grown on the top of ZnO shell have slightly different morphology—larger diameter and shorter length. In some cases, the microwire was cut in several segments after the thermal process with applied electrical current. Some sections were tubular and others still presented the metallic core. In large diameter microwires and depending on the warming rate, the solid layer does not preserve the tubular shape of the wire. Instead, the ZnO wall distorts in a peculiar form with a cross section resembling an 8-shape, resulting in two attached microtubes. Usually, this problem can be solved by decreasing the warming temperature rate. Fig. 3(a) shows an impressive image of the biggest microtube decorated with nanowires, \(~120 \) \( \mu \)m in diameter, that we have obtained, indicating that the metallic Zn core has completely evaporated even at a temperature much lower that the Zn boiling point. In this large microtube, the nanowires have length from 3 \( \mu \)m to 8 \( \mu \)m and diameter from 200 nm up to 250 nm. Other processes performed in such wider microwires with higher electrical currents and higher temperature rates also rendered hollowed structures. In order to confirm the hollow structure in larger and long microwires, we have broken some of them in a few sections. We found out that hollowed tubes as long as \(~300 \) \( \mu \)m in length can be processed. Furthermore, one can see in Figs. 3(b) and 3(c) a circular ZnO shell and nanowires growing homogeneously up to 10 \( \mu \)m in length and 50 nm in diameter on the top of it which is in agreement with previous works based on transmission electron microscopy characterization.\(^{27}\) The thickness of the oxide layer is around \(~3 \) \( \mu \)m.

Figure 4 sketches different morphologies assumed by the microwire as a function of temperature during the process. Three main stages may be identified. In the initial stage (Fig. 4(a)), while the temperature is still below the melting point, a thin ZnO layer is formed on the surface of the microwire. As the temperature rises the ZnO layer thickens and ZnO nanowires are grown due to lattice diffusion of Zn ions from the liquid inner part across the layer (Fig. 4(b)). The formation of the tubular structure is due to the thermal evaporation of liquid Zn in high temperature region, however, below the Zn boiling point. Even though the vapor pressure of Zn is high,\(^{28}\) we believe that the electric current used to measure the electrical resistivity plays a role increasing the evaporation rate of the metallic Zn. The passage of electrical current may increase the temperature in the inner part of the microwire (Joule effect) becoming close to the boiling point of metallic Zn (\( 911 \) °C) and/or somehow increasing the vapor pressure of Zn liquid.

We have also observed that the nanowire dimensions and morphology on the shell can be controlled by the maximum set point temperature and heating rate—it can be changed from nanowires to nanobats and nanoclapboards. A systematic evolution from nanowires to nanobats and to big
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