



## Microtubes decorated with nanowires

C. M. Rivaldo-Gómez, A. Zúñiga, D. Criado, J. Schoenmaker, and J. A. Souza

Citation: Applied Physics Letters **106**, 213104 (2015); doi: 10.1063/1.4921795 View online: http://dx.doi.org/10.1063/1.4921795 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/106/21?ver=pdfcov Published by the AIP Publishing

## Articles you may be interested in

A ZnO nanowire resistive switch Appl. Phys. Lett. **103**, 123114 (2013); 10.1063/1.4821994

Graphene shell on silica nanowires toward a nanostructured electrode with controlled morphology Appl. Phys. Lett. **103**, 013101 (2013); 10.1063/1.4811781

Controlled growth of vertical ZnO nanowires on copper substrate Appl. Phys. Lett. **102**, 083105 (2013); 10.1063/1.4793758

All solution processed, nanowire enhanced ultraviolet photodetectors Appl. Phys. Lett. **102**, 043503 (2013); 10.1063/1.4789757

Mismatched alloy nanowires for electronic structure tuning Appl. Phys. Lett. **99**, 233111 (2011); 10.1063/1.3666223



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.200.93.147 On: Tue, 26 May 2015 16:57:17



## Microtubes decorated with nanowires

C. M. Rivaldo-Gómez, A. Zúñiga, D. Criado, J. Schoenmaker, and J. A. Souza<sup>a)</sup> Universidade Federal do ABC-Santo André, São Paulo 09210-580, Brazil

(Received 30 March 2015; accepted 18 May 2015; published online 26 May 2015)

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. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4921795]

In the past few years, a considerable effort has been devoted in order to grow one-dimensional (1D) nanostructured materials.<sup>1–5</sup> 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.<sup>6–9</sup> 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.<sup>10–12</sup> Functionalization may occur on the surface, inner part, and extremities of the tubes. These multifunctional properties from hierarchical morphology 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.<sup>17–19</sup> Among them, the thermal oxidation process by using pure metal may be the simplest one.<sup>20-22</sup> 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 top 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  $O_2$  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 (O<sub>2</sub> 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  $T \sim 420$  °C, the electrical resistivity jumps revealing the Zn solid/liquid first order phase transition. Even in the liquid phase, the  $\rho(T)$  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.<sup>23</sup> 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  $O_2$  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  $1.2 \times 10^{-5} \Omega$  cm was detected. Note that, as the system is cooled down, the sample

<sup>&</sup>lt;sup>a)</sup>Author to whom any correspondence should be addressed. Electronic mail: joseantonio.souza@ufabc.edu.br.



FIG. 1. The temperature dependence of electrical resistivity for Zn metal wire measured up to 515 °C with two different waiting times—30 (curve I) and 60 (curve II) minutes. Other two runs measured up to 810 °C in O<sub>2</sub> flow (curve III) and in air (curve IV). T<sub>m</sub> is the Zn melting point. (b) The electrical resistivity measurement in the high temperature range (curve III) and (c) its linear behavior when plotted as  $\ln \rho / \rho_0$  versus 1/T revealing thermally activated behavior.

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,  $\rho$  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 O<sub>2</sub> 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  $O_2$ presents a higher resistivity slope when compared to the process in the presence of air flow. At  $T_{BDP} = 680 \degree C$  (for  $O_2$ 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,  $\rho(T) = \rho_0 \exp(-E_A/kT)$ , where  $\rho_0$  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  $(E_g)$ .<sup>24</sup> From the temperature dependence of the electrical resistivity  $(\ln \rho / \rho_0 \text{ versus 1/T})$ , the activation energy is found to be  $E_A = 0.5 \text{ eV}$ , which is much lower than the optical energy gap of the bulk  $E_g = 3.3 \text{ eV}$ .<sup>25</sup> 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.<sup>26</sup> 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



FIG. 2. X-ray diffraction of the (a) pure Zn microwire, (b) the microwire heated up to  $700 \,^{\circ}$ C in air, and (c) microtube after the complete Zn evaporation. The tick marks below each pattern indicate the expected Bragg reflection positions for Zn (*P63/mmc*) metal, printed in black, and ZnO (*P63mc*) crystal phase, in red. SEM images represent each stage of the process.

Appl. Phys. Lett. 106, 213104 (2015)



FIG. 3. Representative images of SEM showing the formation of nanowires on the top of microtubes. (a) The biggest obtained microtube decorated with nanowires with  $\sim 120 \,\mu\text{m}$  in diameter. (b) and (c) Other long microtube with  $50 \,\mu\text{m}$  in diameter.

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 *P63mc* 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  $T_m = 1970 \,^{\circ}$ 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  $T = 750 \,^{\circ}$ C, the Zn liquid evaporates forming tubular structures. When the process is carried out in O<sub>2</sub> 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,  $\sim 120 \,\mu m$  in diameter, that we have obtained, indicating that the metallic Zn core has completely evaporated even at a temperature much lower

FIG. 4. Sketch of the process. (a) Microwire just below the melting point of Zn ( $T_m \sim 420$  °C). (b) Core/shell (Zn/ZnO) structure with ZnO nanowires covering the surface in the liquid phase range. (c) Formation of microtube after the evaporation of the Zn liquid in the inner part of the wire around  $T_{BDP} = 700$  °C.

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  $\sim 300 \,\mu m$  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.<sup>27</sup> The thickness of the oxide layer is around  $\sim 3 \,\mu m$ .

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 bellow 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,<sup>28</sup> 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 nanoclapboards due to different warming temperature rate (decreased from 8°C/min down to 5°C/min.) until the complete coalescence into grains of a sample heated up to 930 °C has been done.<sup>29</sup> We suggest that both diffusion and vaporsolid processes play a role to form, increase the size, and transform nanowires into lager nanostructures. After the formation of nanostructure, larger nanowires are formed by the coalescence of two neighboring nanowires. As the temperature rate is low, some ZnO nucleation sites (grains) on the surface may melt before the growing of the nanowire becoming thicker and as a consequence larger nanobats grow from the root of these large individual grains. At higher temperature, the vapor pressure of Zn increases, and, with the presence of electrical current, a significant amount of Zn would be evaporated into atmosphere leaving a hollow microtube. At this temperature range, vapor-solid process may contribute for the growing of nanostructures, rather than solely lattice/grain/surface diffusion. ZnO gas would condense on the nucleation sites such as nanowire tips and on adjacent sites between two nanowires. A detailed study involving the relevant parameters to grow nanostructures by using oxidation process such as set point temperature, warming temperature rate, electrical current, annealing time, and atmosphere will be published elsewhere.

We believe that promising breakthrough may be revealed when combining the different applications of microtubes and nanowires. For instance, taking advantage of the different scale and volume-to-surface ratio presented by microtubes and nanowires, one can associate sensor capabilities of nanowires with fluid properties of liquids in microtube, in one single device. As another example, one can use properties of the nanowires (field emission and sensor devices, for example) while fluid is passing inside the microtube. Furthermore, it is known that ZnO is n-type semiconductor. Thus, one can fill the microtube with a p-type organic semiconductor creating, for example, a diode-like device which may indicate different routes to microelectronic field. It can be filled with any other materials with exotic properties as well building devices with multifunctional applications. We hope that the discussion presented here will attract attention from the scientific community and other insights may come out along this line.

Summarizing, this work presents a processing synthesis method to obtain hierarchically structured materials. A fast, simple, and reproducible synthesis method to produce microtubes topped with nanowires is described. Our study contributes to both fundamental material science and material design with potential smart multifunctionalities. It put forward possibilities of integration of the two hierarchical morphologies into one device that could rationally combine the advantages of different applications of microtubes and nanowires. The processing technique, going beyond the melting point of Zn and the breakdown of the metallic percolation threshold, was accompanied *in situ* by electrical resistivity measurements. One can tune in the morphology of ZnO nanowires on ZnO layer by choosing the set point temperature, temperature rate, and probably electric current magnitude. We believe that the present fabrication approach may be applied to grow hierarchical structures of other metals with low melting point. Hierarchical morphologies such as presented in this work may have multifunctional properties in technological applications.

This material is based upon work supported by the Brazilian agency CNPq under Grant Nos. 471863/2008-4, 485405/2011-3, 305772/2011-2, and 455092/2014-1 and Fapesp under Grants No. 2009/18618-5 and 2013/16172-5.

- <sup>1</sup>S. Xu and Z. L. Wang, Nano Res. 4, 1013–1098 (2011).
- <sup>2</sup>M. Nath, A. Govindaraj, and C. N. R. Rao, Adv. Mater. **13**, 283–286 (2001).
- <sup>3</sup>Y. Li, G. W. Meng, L. D. Zhang, and F. Phillipp, Appl. Phys. Lett. 76, 2011 (2000).
- <sup>4</sup>W. Lu and C. M. Lieber, J. Phys. D: Appl. Phys. 39, R387 (2006).
- <sup>5</sup>B. M. Wen, J. E. Sader, and J. J. Boland, Phys. Rev. Lett. **101**, 175502 (2008).
- <sup>6</sup>M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. Yang, Nat. Mater. 4, 455 (2005).
- <sup>7</sup>Z. L. Wang and J. Song, Science **312**, 242–246 (2006).
- <sup>8</sup>Y. Xi, J. H. Song, S. Xu, R. S. Yang, Z. Y. Gao, C. G. Hu, and Z. L. Wang, J. Mater. Chem. **19**, 9260–9264 (2009).
- <sup>9</sup>Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, and C. L. Lin, Appl. Phys. Lett. **84**, 3654 (2004).
- <sup>10</sup>K. Ajima, M. Yudasaka, K. Suenaga, D. Kasuya, T. Azami, and S. Iijima, Adv. Mater. 16, 397–401 (2004).
- <sup>11</sup>W. Li, C. Liang, J. Qiu, W. Zhou, H. Han, Z. Wei, G. Sun, and Q. Xin, Carbon 40, 791–794 (2002).
- <sup>12</sup>C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, and M. S. Dresselhaus, Science **286**, 1127–1129 (1999).
- <sup>13</sup>C. Yan, J. Liu, F. Liu, J. Wu, K. Gao, and D. Xue, Nanoscale Res. Lett. 3, 473–480 (2008).
- <sup>14</sup>Y. Kashiwaba, T. Abe, A. Nakagawa, I. Niikura, Y. Kashiwaba, M. Daibo, T. Fujiwara, and H. Osada, J. Appl. Phys. **113**, 113501 (2013).
- <sup>15</sup>C. L. Yan and D. F. Xue, Electrochem. Commun. 9, 1247–1251 (2007).
- <sup>16</sup>Z. Y. Yao, X. Zhu, C. Z. Wu, X. J. Zhang, and Y. Xie, Cryst. Growth Des. 7, 1256–1261 (2007).
- <sup>17</sup>J. Ham, W. Shim, D. H. Kim, K. H. Oh, P. W. Voorhees, and W. Lee, Appl. Phys. Lett. **98**, 043102 (2011).
- <sup>18</sup>E. Przeździecka, E. Kamińska, I. Pasternak, A. Piotrowska, and J. Kossut, Phys. Rev. B 76, 193303 (2007).
- <sup>19</sup>Z. Wang, X. Qian, J. Yin, and Z. Zhu, Langmuir. **20**, 3441–3448 (2004).
- <sup>20</sup>X. Jiang, T. Herricks, and Y. Xia, Nano Lett. **2**(12), 1333–1338 (2002).
- <sup>21</sup>S. Rackauskas, A. G. Nasibulin., H. Jiang, Y. Tian, V. I. Kleshch, J. Sainio, E. D. Obraztsova, S. N. Bokova, A. N. Obraztsov, and E. I. Kauppinen, Nanotechnology **20**, 165603 (2009).
- <sup>22</sup>M. Chen, Y. Yue, and Y. Ju, J. Appl. Phys. **111**, 104305 (2012).
- <sup>23</sup>E. Ricci, E. Arato, A. Passerone, and P. Costa, Adv. Colloid Interface Sci. 117, 15–32 (2005).
- <sup>24</sup>C. Kittel, *Introduction to Solid State Physics* (Wiley and Sons, Inc., New York, 1973).
- <sup>25</sup>A. Janotti, D. Segev, and C. G. Van de Walle, Phys. Rev. B **74**, 045202 (2006).
- <sup>26</sup>A. Janotti and C. G. Van de Walle, Rep. Prog. Phys. **72**, 126501 (2009).
- <sup>27</sup>W. Yu and C. Pan, Mater. Chem. Phys. **115**, 74–79 (2009).
- <sup>28</sup>D. R. Lide, Handbook of Chemistry and Physics (CRC Press, LLC, 2001/ 2002).
- <sup>29</sup>See supplementary material at http://dx.doi.org/10.1063/1.4921795. One can see a systematic evolution from nanowires to nanobats and until the complete coalescence into grains covering the microtube.