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Growth of ZnO micro and nanowires using the template method

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The electrochemical deposition in ion track nanoporous membranes was employed for ZnO micro and nanowires preparation. A $ZnNO_3$ bath was employed for the deposition, performed at -800 mV (vs. SCE) and at temperatures around 90 °C. Scanning and transmission electron microscopy were used to characterize the wires from a morphological point of view. Electron and X-ray diffraction were employed for the characterization of materials from the point of view of structure. The technique allowed the fabrication of nanowire arrays with good morphological and structural quality.

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1. Introduction

The development of new miniaturized electronic and optoelectronic devices for special applications as, e.g. data storage or antibodies detectors, requires the development of a new generation of building blocks such as semiconductor nanowires or nanodots [1]. For such applications the template technique opens the possibility for the preparation of highly ordered semiconductor nanowire arrays in a straightforward manner, by non classical methods of preparation such as electrochemical deposition [2]. Metal chalcogenide semiconductor nanowires were reported in a previous paper [3].

Zinc oxide is one of the most promising materials from the class of oxide semiconductors due to its optical, electrical and piezoelectrical properties. The material presents a wurtzite structure, with a band gap of 3.3 -3.6 eV. Recent reports in literature focused on light emission properties of ZnO nanowires, these presenting a narrow emission peak at 385 nm due to near band to band transitions and another broad one in the range 450 – 650 nm attributed to defects [4,5].

Several methods were employed for fabricating ZnO nanowires, the most used being vapor phase methods [6]. In this approach species in vapor phase condense on the substrate surface. By controlling the over saturation factor one can obtain quasi one dimensional structures over large areas. In some of the studies a catalyst patterned surface was used [7] while in others an intrinsic growth mechanism was exploited in order to achieve the growth of zinc oxide nanowires [8]. The template method was also applied to obtain ZnO nanowires, e.g. in anodic alumina nanoporous membranes, the pores were filled with metallic zinc (in one experiment by metal evaporation [9] while in another by electrochemical deposition [10]), subsequently the metal being oxidized at high temperature. In another report the nanowires were prepared in the pores of alumina by cathodic electrodeposition from a zinc chloride solution in the presence of molecular oxygen and in a dimethyl sulfoxide solution [11].

In this paper we used the template method for preparing micro and nanowires of zinc oxide, using as template polycarbonate ion track nanoporous membranes.

2. Experimental

Polycarbonate foils (Makrofol N, Bayer) with 30 micrometer thickness were irradiated with swift heavy ions (e.g. U with specific energy 11.4 MeV/nucleon). The fluences used for irradiation were in the range $10^6 – 10^8$ ions/cm^2. Taking into account that for each ion which passed through the polymer foil a track is formed, thus, a pore is obtained, the number of pores in the membrane is equal with the number of ions which were counted by the three foil detector during irradiation.

The etching of ion tracks was performed using an aqueous NaOH solution with addition of methanol (5M NaOH with 10% methanol) at 50 °C. In this high selectivity etching conditions cylindrical pores are obtained (pore diameter increases linearly with time with a rate of 2 micrometer/hour).

The working electrode was obtained by sputtering a thin film of gold (a few tens of nanometers thick) on one side of the membrane. The film was thickened by a subsequent electrodeposition of a copper layer. This has two major roles, to completely close the pores and to increase the mechanical stability of the working electrode.

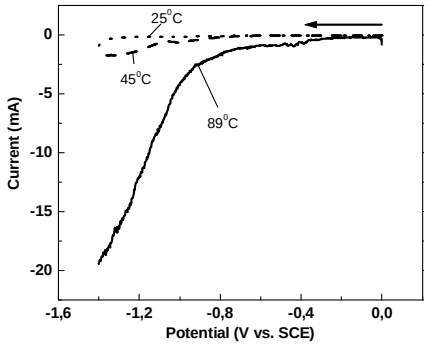
Subsequently the membranes were clamped in an electrochemical cell with two compartments, with the pores exposed to the growth solution. The electrochemical deposition was accomplished using a Voltalab potentiostat/galvanostat connected to a computer.

For subsequent measurements, i.e. electron microscopy and diffraction and X-ray diffraction the membrane was dissolved in dichlor methane (CH_2Cl_2). The micro and nanowires were imaged using a Hitachi S-

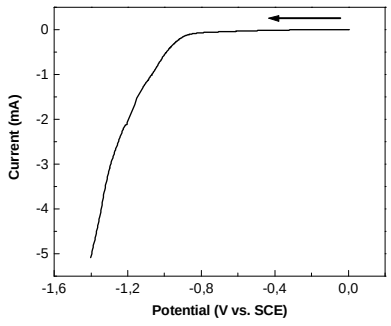
2600N Scanning Electron Microscope having for composition measurements an EDX (energy dispersive X-ray analysis) device from Röntec GmbH. TEM observation and electron diffraction were performed with a JEOL 200CX TEM/SCAN microscope. The X-ray diffraction spectra (XRD) of ZnO samples were recorded with a Shimadzu XRD-6000 diffractometer using CuK_α (λ=1.54056Å) radiation.

3. Results and discussion

Electrochemical deposition in nanoporous membranes allows the preparation of semiconductor quasi 1-dimensional structures. The electrochemical deposits in the case of thin films are in most cases polycrystalline with grain size depending on experimental conditions.



(a)



(b)

Fig. 1. (a) Cathodic sweeping of Pt electrode(1cm^2) potential, at three different temperatures and (b) cathodic sweeping of Au/polycarbonate membrane electrode (0.5 cm^2) at 89 °C in the solution 0.1 M $Zn(NO_3)_2$; sweep rate = 5mV/s.

However, the use of confined spaces, with characteristic dimensions smaller than the average grain size obtained in the case of thin film deposition can increase the ordering degree of the material. The data from literature [12] showed that the electrochemical ZnO deposition takes place in the following steps:

$$2e^- + NO_3^- + H_2O \rightarrow NO_2^- + 2OH^- \quad (1)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO\downarrow + NO_3^- + NO_2^- \quad (2)$$

or global reaction:

$$Zn(NO_3)_2 + 2e^- \rightarrow ZnO\downarrow + NO_3^- + NO_2^- \quad (3)$$

The voltammetric curves recorded during cathodic sweep of the potential for a 1 cm^2 platinum electrode are presented in Fig. 1 (a) for a solution of 0.1M $Zn(NO_3)_2$ at three different temperatures. We notice that the deposition process takes place at a faster rate at higher temperatures and, following the 89°C voltammetric curve we find that the electrochemical process on platinum electrode starts at a potential of -0.25 V/SCE. In Fig. 1 (b) we present a similar curve for the Au/membrane electrode in the solution of 0.1 M $Zn(NO_3)_2$ at 89 °C.

In this last case we used a polycarbonate membrane having 10^7 pores/cm^2, pore diameter 1.5 μm, surface exposed to the solution 0.5 cm^2.

At the Au/membrane electrode the electrochemical deposition process starts at higher voltage when compared with the platinum electrode; a cause for this behaviour is the diffusion of the ions through the polycarbonate membrane pores.

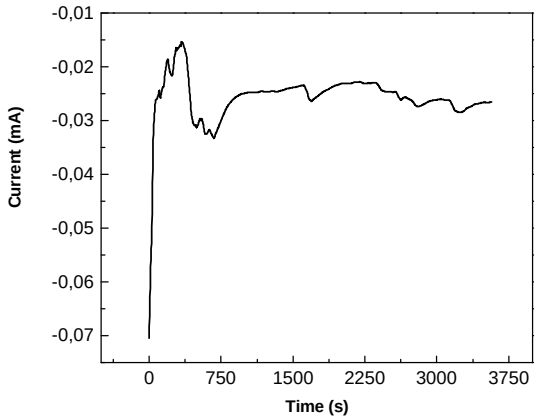
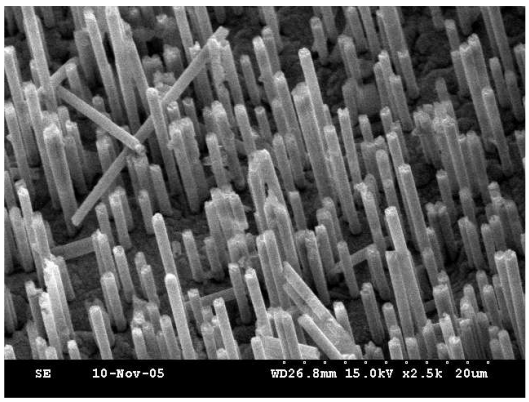


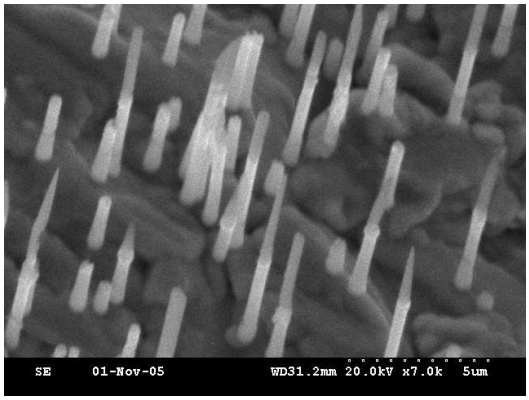
Fig. 2. Chronoamperometric curve registered during the deposition of ZnO wires (0.1M $Zn(NO_3)_2$, at 89 °C, 10^7 pores/cm^2, 1.5μm diameter).

The chronoamperometric curve for the deposition process at constant potential (-0.8V/SCE) and 89 °C temperature is presented in Fig. 2. The growth current presents some variations due to formation of vapor bubbles on membranes surface at this temperature.

In the case of micron size pores the deposition of ZnO at -0.8 V vs. SCE leads to the formation of hollow structures similar to what we observed in the case of other semiconductors. For the case of smaller pores the rods are not hollow anymore. In Fig. 3 SEM micrographs of such structures obtained in pores with diameter of 1.5 μm and 330 nm respectively can be observed.



(a)



(b)

Fig. 3. ZnO wires obtained at 89 °C in membranes with pores diameter of 1.5 μm (a) and 330 nm (b); for micron sized pores hollow structures are obtained.

In Fig. 4 the diffraction spectrum for 1.5 μm hollow structures is presented. The spectrum corresponds to a polycrystalline sample. Besides the diffraction peaks corresponding to ZnO, diffraction maxima corresponding to the substrate can be observed.

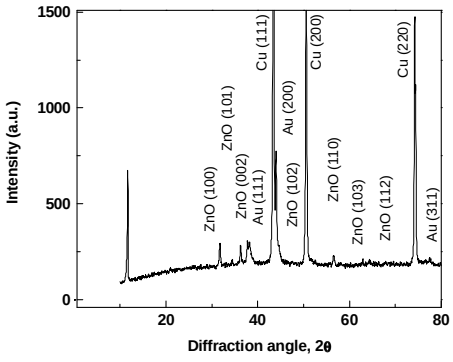
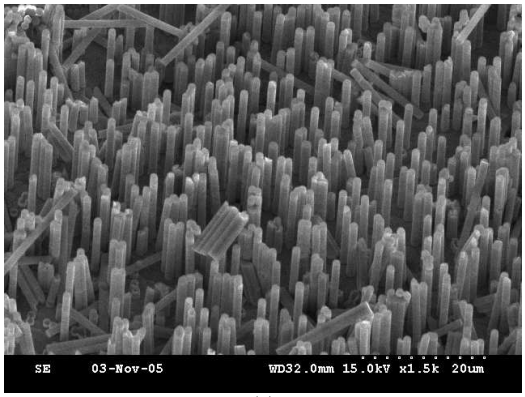
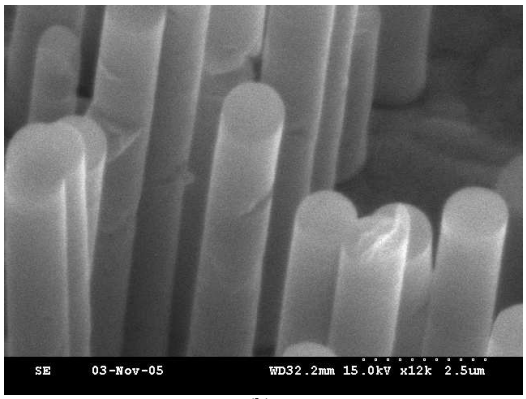


Fig. 4. Diffraction spectrum for a system containing ZnO microtubes.

When the growth temperature was increased to approximately 94 °C we noticed differences in the morphology of the wires for the case of micrometer size pores. Thus, the number of hollow structures decreases, in most of the cases the growth process leads to formation of rods instead of tubes. Moreover in some regions of the growth area we observed faceted growth, indicating the fact that single crystalline structures are obtained. This behavior is somehow normal, elevated temperatures being employed for the preparation of single crystal metal nanowires [13]. In figure 6. SEM observation of different areas of a 1.5 μm pore diameter template are presented.



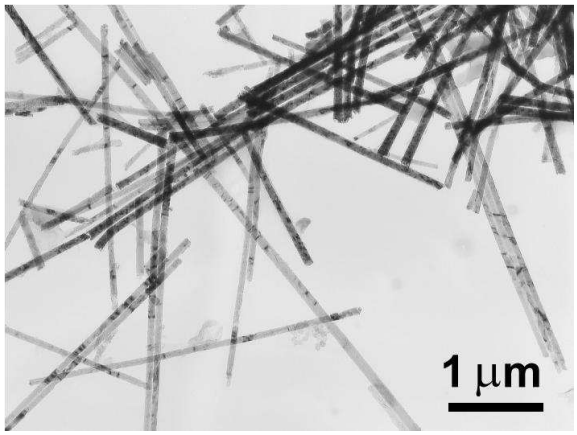
(a)



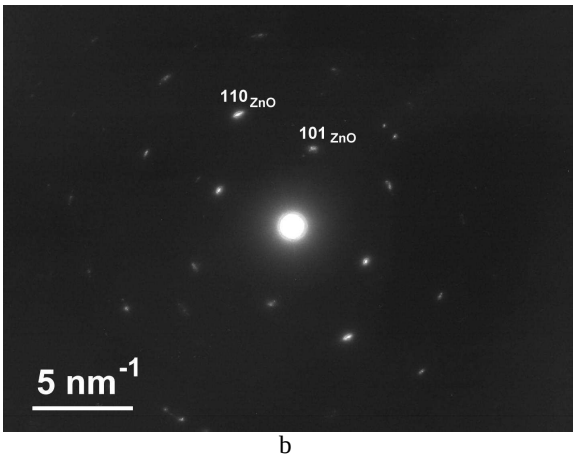
(b)

Fig. 6. ZnO wires obtained at 94 °C in membranes with pores diameter of 1.5 μm. (a) Large area with uniform wire distribution; (b) faceted wires.

For TEM observations, after dissolving the polymer membrane the wires were ultrasonically detached from their substrate into ethylic alcohol. A droplet of alcohol containing the wires was then placed onto a copper grid and the alcohol was evaporated prior to measurements.



a



b

Fig. 7. ZnO wires obtained at 94 ℃ in membranes with pores diameter of 80 nm. (a) TEM observation of a group of wires; (b) selected area electron diffraction pattern.

For nanowires grown at 94 °C TEM observations and electron diffraction showed also good morphological and structural characteristics. In Fig. 7 TEM and selected area electron diffraction for wires grown at this temperature are presented. The SAED pattern shows a high quality of the wires, these presenting single crystal characteristics. The observations made suggest us that by increasing the temperature of deposition higher structural quality wires are obtained.

4. Conclusions

Electrochemical deposition was employed for the preparation of ZnO rods using polycarbonate templates. The flexibility of the method allowed us to prepare both micro and nano structures. SEM observations showed that deposition at 89 °C leads to the formation of polycrystalline tubes in micrometer sized pores, while in submicron pores wires with low morphological quality are obtained. By increasing the deposition temperature, on some areas of the sample faceted wires are obtained while for nanowires SAED reveals single crystalline characteristics.

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