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Physical properties of CdTe nanowires electrodeposited by a template method, for photovoltaic applications

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Nanowires made of CdTe were produced by using a template method. Polymer ion track foils (30 micrometers thick) were used as templates, after a proper chemical etching. Nanowires were electrochemically grown in the resulting pores. A discussion of the observed correlations between the morphological/structural properties of the wires and the growth conditions is given. Electrical properties of the arrays of nanowires were studied in the temperature range of 40 K – 300 K, after contacting them by sputtering a gold layer on top of the membranes. Symmetric, non-linear I-V characteristics were recorded in the voltage range used and an activated electrical resistance was observed in the ohmic regime.

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1. Introduction

In the last decade, quasi-one-dimensional (q-1D) semiconducting structures have attracted a great deal of interest, due to their unique and promising properties, which recommend them for a wide area of applications, from electronics to biology or medicine. Their peculiar electronic and optical properties, induced by the low dimensionality and high surface to volume ratio, make them suitable for applications in nanoscale electronics, such as field effect transistors [1-3]. Increased packing densities and significant reduction of power consumption can be achieved in the case of such devices, due to their small dimensions.

Optoelectronic devices, including lasers [4,5] or active waveguides [6] based on q-1D structures made of A_2B_6 semiconductor compounds have been also successfully produced in recent years.

Successful fabrication of gas sensors with increased chemical sensitivity [7,8] or strain and pressure detectors with large gauge factors (larger than their bulk-material counterparts) has been reported.

Recently, a new direction in photovoltaics has emerged, aiming at producing hybrid inorganic/organic low-cost photovoltaic structures based on large arrays of nanowires made of A_2B_6 semiconductors and organic dyes used as absorber layers. A_2B_6 semiconductor compounds are well suited for all of the above mentioned types of applications. Their wide, direct band gap, the large optical absorption coefficient and their relatively high mobilities of the charge carriers, make them promising candidates for use in electronic and optoelectronic devices, especially for photovoltaic applications.

Several growth methods were proposed and used for fabricating q-1D structures made of A_2B_6 semiconductor compounds. Among them, template methods [9-12] are most widely used to prepare nanowires or nanotubes with high, precisely controlled aspect ratio. As a general principle, they consist in filling of the pores of a template with the material of choice. Concerning the procedures of forming materials in the pores of the template, several techniques have been proposed: chemical vapor deposition [13], sol-gel deposition [14], or, the most widely used, electrochemical deposition. Two types of nanoporous membranes are mostly used as templates: anodic alumina [15-17] and polymer ion track membranes [12,18,19]

In this paper we present our results on the preparation and transport properties of nanowires made of CdTe, electrodeposited in large arrays by using a template method, with ion track polymer membranes used as templates [12,18,19]. It is organized as follows: in the next section details about preparation conditions and experimental methods used for the characterization of nanowire arrays are given. The results regarding their use in hybrid organic/inorganic photovoltaic structures are discussed in the third section. The fourth section summarizes the main conclusions of this work.

2. CdTe nanowire arrays preparation and their characterization results

Nuclear track etched polycarbonate membranes were used as the template for preparation of nanowires. Polycarbonate foils (Makrofol N, Bayer), 30 μm thick, were irradiated with swift heavy ions (e.g. U with specific energy 11.4 MeV/nucleon) at different fluences in the range 10^4– 10^8 ions/cm^2. The foils were subsequently chemically etched with aqueous solutions containing 5M NaOH and 10% volume methanol at 50°C. In the above mentioned etching conditions, cylindrical pores are created. The etching rate of only 200 nm/h allows for a good control of the diameter of the pores. The next step consisted in the deposition of a gold working electrode, 50 nm thick, on one surface of the foils, by sputtering. To complete the closing of the pores and to improve the mechanical stability of the template, a copper layer, 10 μm thick, was electrochemically deposited onto the gold film.

Deposition of CdTe nanowires was performed in a potentiostatic mode using an acidic deposition bath (1 M $CdSO_4$, 0.3 mM TeO_2 at a pH of 1.6 adjusted with H_2SO_4). The reaction mechanism leading to the formation of CdTe nanowires is described by:

$$HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te + 2H_2O \qquad (1)$$

$$Cd^{2+} + Te + 2e^- \rightarrow CdTe. \qquad (2)$$

The peculiarity of CdTe forming in this case is that the deposition process is Te diffusion limited. The polarization curves for the deposition process in a membrane containing 10^8 pores/cm^2 of 80 nm diameter at 74°C are presented in figure 1.

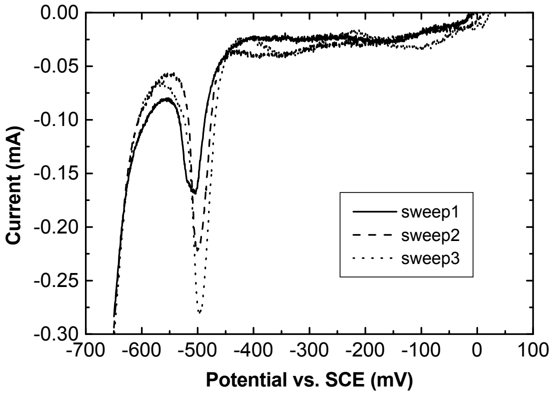


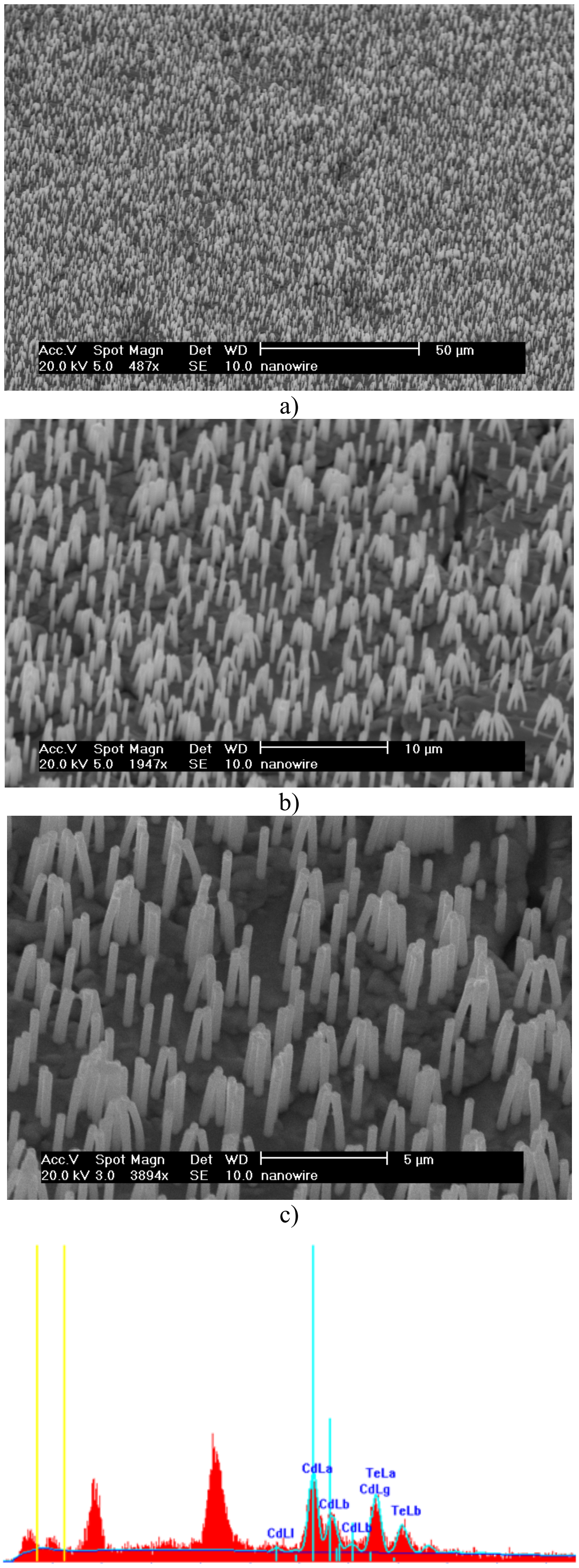
Fig. 1 Polarisation curves for CdTe nanowires deposition. Sweep rate was 5 mV/s.

The peak at 500 mV corresponds to the potential where CdTe is deposited. A shift towards more positive potential can be observed at the second and third sweep. This is most probably due to the fact that the deposition is further favorised by the presence in the substrate of Te atoms.

Investigations by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) have shown that, under the above mentioned conditions, homogeneous CdTe nanowires are obtained, with a polycrystalline structure, of würtzite type [12]. It is worth mentioning that the equilibrium crystalline phase of bulk CdTe is the cubic, zinc-blend type, phase. However, the occurrence of the hexagonal phase is not unusual for the materials with a close-packing structure, the variation of the forming energy from the cubic to the hexagonal phase being small.

A series of wire arrays, 300 nm diameters, were deposited at different potentials, in the range -650 mV to -450 mV.

The chemical composition of the wires was measured using energy dispersive X ray analysis (EDX). Figures 2 and 3 show SEM micrographs and the output of EDX investigations.



a)

b)

c)

d)

Fig. 2 SEM micrographs of an array of CdTe wires (10^8 wires/cm^2, 300 nm diameter) deposited at -500 mV vs. SCE and the result of energy dispersive X-ray (EDX) analysis. These wires contain 49% Cd and 51 % Te.

The stoichiometric composition is obtained at about -530 mV vs. SCE. There exists a narrow range of deposition potentials were the (near)stoichiometric compound is obtained, which is a consequence of the Te concentration in solution. Using more negative deposition potentials results in getting wires richer in cadmium.

The current – voltage (I-V) characteristics of CdTe nanowire arrays were recorded at temperatures ranging from 20 K to 300 K. The temperature dependence of the electrical resistance of the wire arrays was measured, at voltages in the ranges were I-V curves show an ohmic behavior.

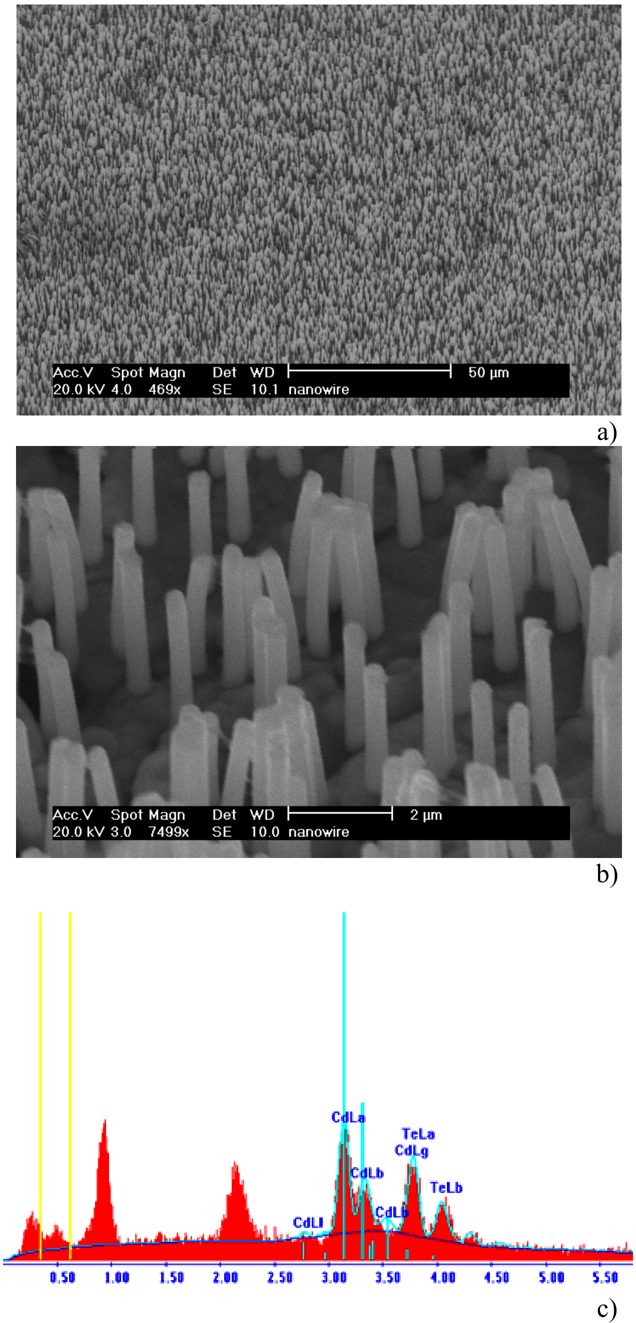


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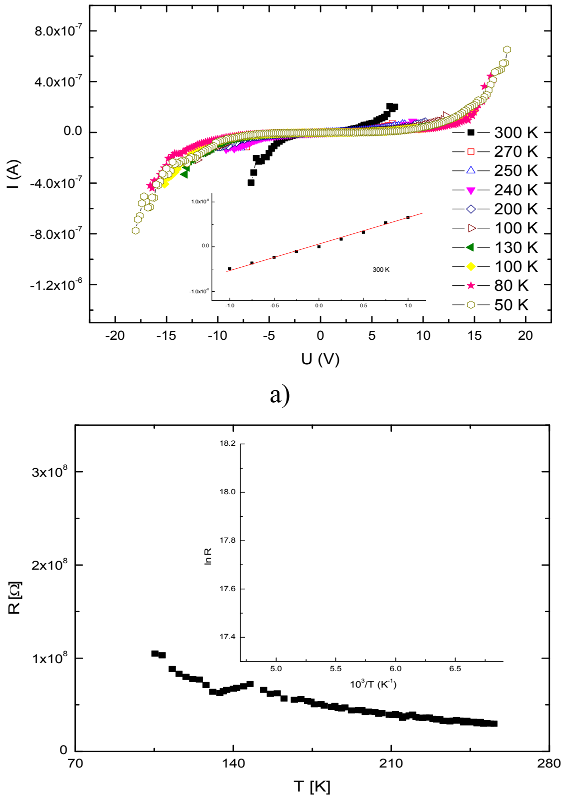
Fig. 3 SEM micrographs of an array of CdTe wires (10^8 wires/cm^2, 300 nm diameter) deposited at -600 mV vs. SCE and the result of energy dispersive X-ray (EDX) analysis. These wires contain 51% Cd and 49 % Te.

It is well known that CdTe has a problem in establishing ohmic contacts with metals, due to its very large work function (5.9 eV). In an attempt to minimize that problem, samples with multisegment wires were produced (300 nm diameter, 10^6 wires/cm^2).

Fig. 4a shows I-V characteristics recorded at different temperatures (listed on graph) for a sample indexed as CT8 (see Table I).



a)

b)

Fig. 4 a) I-V characteristics recorded for a CdTe multisegment wire array (300 nm diameter, 10^6 wires/cm^2). The sequence of the segments is specified in Table I (CT8 sample). b) Temperature dependence of the electrical resistance of the sample, measured at applied voltages in the range where I-V curves were linear.

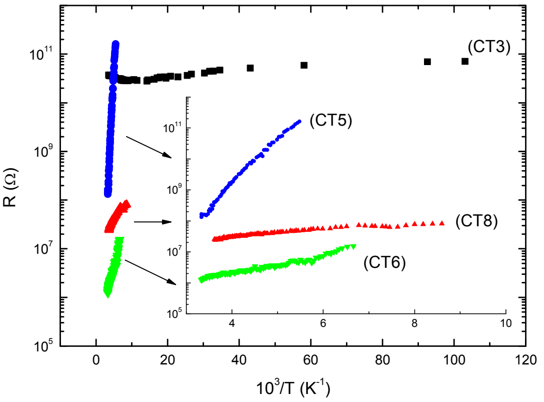


Fig. 5 Temperature dependence of the electrical resistance of the multisegment CdTe wire array samples listed in Table I.

When using potentials more negative that the value corresponding to stoichiometric compound formation (-530 mV), wires richer in cadmium are obtained.

Table I Structure of the multisegment CdTe wire arrays used for electrical characterizations.

Sample	Structure	Density of pores (cm^{-2})	$E_a^{(*)}$ (eV)	Obs.
CT3	CdTe/CdTe/Ni	10^6	-	-initial CdTe segment deposited at -700 mV -CdTe wire, deposited at -550 mV
CT5	CdTe	10^6	0.13	-CdTe wire, deposited at -550 mV
CT6	CdTe/CdTe/Cd	10^6	0.04	-initial CdTe segment deposited at -680 mV -CdTe wire, deposited at -540 mV -final Cd segment deposited at -680mV
CT8	CdTe/CdTe/Cd	10^6	0.03	-initial segment deposited at -680 mV -CdTe segment deposited at -520 mV -final Cd segment deposited at -680mV

It is known that cadmium in interstitial sites in CdTe lattice acts like a donor [20]. That can explain the observed increase of the electrical conductivity of the samples slightly richer in cadmium (see Fig. 5 and table I). However, if the cadmium content is further increased, the electrical conductivity decreases again, probably due to the segregation of cadmium.

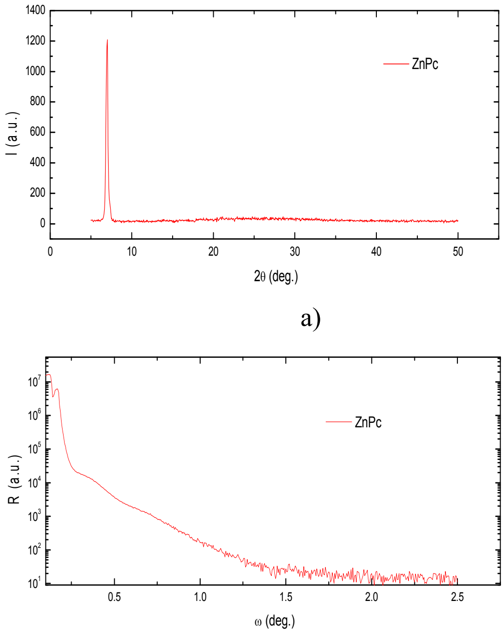
3. Hybrid CdTe wire arrays/organic dye photovoltaic structures

After establishing the influence of growth conditions on the composition and structure of CdTe wire arrays, samples were produced for use in the fabrication of hybrid inorganic/organic photovoltaic structures. A thin film of organic dyes, in our case, either zinc phthalocyanine (ZnPc) or 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPyP), is used as light absorber in such structures.

As compared to "classical", state-of-the-art inorganic solar cells, this type of photovoltaic structures still exhibit rather modest efficiencies. This is essentially due to charge harvesting problems. An excitonic mechanism is responsible for the absorption of the photons in the incident light flux. The problem is that, in spite of the efficiency of the exciton creation process, most of these excitons disappear by direct recombination of the electron-hole pair before reaching an interface where the charge separation can occur.

A better efficiency of exciton dissociation process is expected by creating a large area interface between the organic dye and a nanostructured inorganic semiconductor.

After exposing the wire arrays by dissolving the polycarbonate template, an organic dye thin film (400 nm thick) was deposited by thermal evaporation. Then, on top of it, a ZnO transparent electrode was grown by pulsed electron deposition.



a)

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Fig. 6. XRD pattern, recorded in detector scan regime, (a) and omega/2theta specular reflectivity scan (b) of a ZnPc film grown by vacuum thermal evaporation.

Efforts were made to improve the crystalline quality of the organic dye thin films, because that results in larger exciton diffusion lengths. X-ray diffraction (XRD) pattern obtained for the ZnPc thin film is shown in figure 6a. A Bruker D8 Thin Film high resolution diffractometer was used for structural investigation.

A detector scan method, with incident X-ray beam at 2° incidence angle for maximizing the scattering cross-section of X-photons, has been chosen.

The film shows a good crystalline structure. It consist of a monoclinic β-polymorph of ZnPc, highly textured: only (100) peak at $2\theta=6.9866$ can be observed. The packing b-axis of ZnPc molecules is parallel to the substrate. An interesting feature can be observed in the X-ray reflectivity pattern of the same film, shown in figure 6b. Kiessig fringes corresponding to a 156.7 Å thick layer can be observed at small angles, near the total reflection critical angle. This layer is probably located at the interface with the substrate.

The spectral dependence of the external quantum efficiency (EQE) of two photovoltaic structures, CdTe nanowires/ZnPc and, respectively CdTe nanowires/TPyP measured at ambient temperature (25°C) is shown in figure 7.

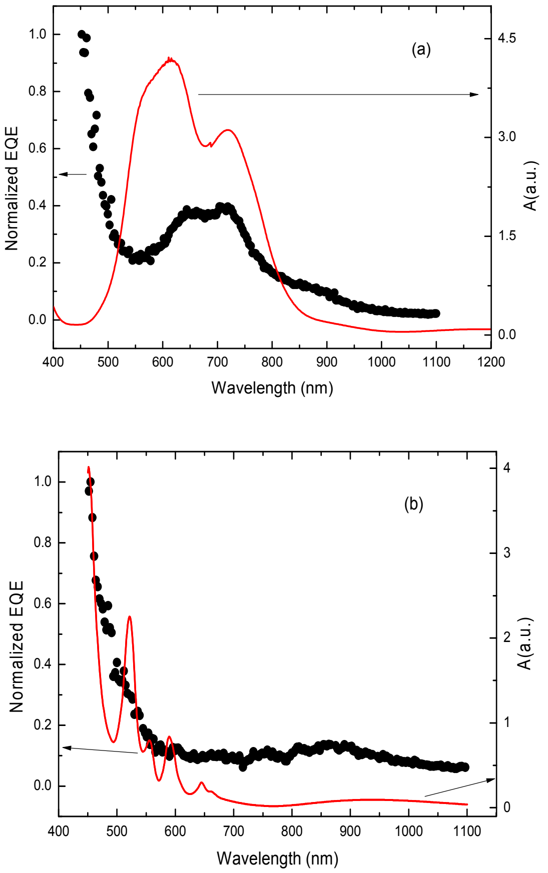

Fig. 7 EQE of a CdTe nanowire array/ZnPc structure (a) and, respectively, of a CdTe nanowire array/TPyP structure (b). For comparison purposes, absorption spectra of ZnPc and TPyP films deposited on optical glass in the same conditions are also given (in red line).

EQE is a characteristic quantity of a photovoltaic structure, measuring the fraction of incident photons for an electron-hole pair collected at its electrodes, in short-circuit condition. It does not consider reflected or transmitted photons.

EQE measured under illumination with monochromatic light having the wavelength λ, is given by:

$$EQE(\lambda) = \frac{I_{sc}(\lambda)}{qS\varphi(\lambda)}, \quad (3)$$

where $I_{sc}(\lambda)$ is the short-circuit current, q is the electron charge, S is the area of the structure and $\varphi(\lambda)$ is the incident photon flux, given by:

$$\varphi(\lambda) = \frac{P_\lambda}{S\frac{hc}{\lambda}}, \quad (4)$$

P_λ being the incident light power, h Planck's constant and c light speed in vacuum. Using eqs. (3) and (4), an expression can be obtained, relating EQE to experimentally measurable quantities:

$$EQE(\lambda) = \frac{I_{sc}(\lambda)\cdot hc}{q\lambda P_\lambda}. \quad (5)$$

In the case of the structure with ZnPc the external quantum efficiency follows the features in the absorption spectra in the investigated spectral region. Those features correspond to Q absorption bands of ZnPc (in the range from 500 nm to 800 nm), associated to π–π* electronic excitations.

Under illumination with higher energy photons (low wavelength) EQE increases abruptly, due to B(0,0) and B(0,1) electronic excitations (Soret B band, extending below 400 nm, not shown in the graphs in figure 7). The shoulder at 900 nm is probably due to the onset of light absorption in the CdTe wires.

EQE spectrum recorded in the case of CdTe nanowire array/TPyP exhibits fewer features, especially in the region of Q absorption bands of the porphyryn macrocycle (500 nm to 650 nm) which are "washed" out. The same increase in EQE at the Soret B band (470 nm) can be observed.

4. Conclusions

Large arrays of CdTe nanowires were successfully produced by electrodeposition, using a template method. Etched nuclear track polycarbonate membranes were used as template.

In each case, the growth conditions resulting in forming of the stoichiometric compounds were identified. The influence of the deposition potential on the chemical composition of the wires has been investigated.

Structural and electrical characterizations of the wire arrays were performed, in order to improve their properties for use in hybrid photovoltaic structures, with thin films of organic dyes as absorbers.

Currently, work is in progress to improve the efficiency of these structures, by increasing the density of the wire arrays, improving the crystalline quality of both the wires and the organic dyes thin films and improving also the quality of the inner interface of the structures.

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