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PRODUCTION AND CHARACTERIZATION OF CdTe WIRE ARRAYS FOR HYBRID INORGANIC/ORGANIC PHOTOVOLTAIC CELLS

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A new approach for obtaining hybrid inorganic/organic photovoltaic structures, based on CdTe nanowires and organic dye films is reported. The wire arrays of CdTe (10^6 wires/cm^2) were electrochemically grown using a template method. Ion track polycarbonate foils (30 micrometer thick) were used as templates and the growth conditions for obtaining good quality and stoichiometric CdTe nanowires were identified. After dissolving the polycarbonate template, a CdTe thin film (300 nm) has been deposited by thermal vacuum evaporation onto the wire array before the deposition of ZnPc film as organic absorber. Finally a ZnO thin film was deposited by Electron Pulsed Deposition on ZnPc, working as TCO top electrode. The structural, morphological, electrical and optical properties of each component layer are investigated. Typical parameters of the prepared photovoltaic structures are determined. The external quantum efficiency of the Au/wire array CdTe/CdTe(300 nm)/ZnPc/ZnO structures was significantly increased, with respect to that of Au/wire arrays CdTe/ZnPc/ZnO structures.

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1. Introduction

Using nanostructured materials, hybrid inorganic/organic low-cost photovoltaic cells are produced. A new direction in photovoltaic has emerged, structures based on large arrays of nanowires made of A_2B_6 semiconductors and organic dyes, as absorber layers. A_2B_6 semiconductor compounds are well suited for 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. Template methods [1-5] are 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 [6, 7], sol-gel deposition [8], or, the most widely used, electrochemical deposition. Two types of nanoporous membranes are mostly used as templates: anodic alumina [9-13], and polymer ion track membranes [5, 14-18]. The results on the preparation and transport properties of CdTe nanowires, electrodeposited in large arrays by using a template method, with ion track polymer membranes used as templates are reported here.

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2. Experimental Procedures and Measurements

When preparing the nanowires a template growth method is used. Having as template polycarbonate foils (Makrofol N, Bayer), 30 μm thick, which were irradiated with swift heavy ions at different fluencies in the range 10^4– 10^8 ions/cm^2, the future electrodeposition of the nanowires will be made in the cylindrical pores that have the desired diameters after the chemical etching with aqueous solutions containing 5M NaOH and 10% volume methanol at 50°C. Methanol was added in the etching solution for improving the pore wall smoothness and etching rates. The etching rate of 200 nm/h allows a good control of the diameter of the pores. The next step is consisting 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.
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 deposition of CdTe nanowires was performed in a potentiostatic mode. The reaction mechanism leading to the formation of CdTe nanowires is described by:

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

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

Having a deposition process with Te diffusion limited is a peculiarity of CdTe forming in this case. 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 CdTe film (300 nm) has been used to coat the Au base layer, after exposing the wires by dissolving the polycarbonate template.

Also, over the thin CdTe film, an organic dye thin film (400 nm thick) was deposited by thermal evaporation..

Then, on top of it, a transparent electrode was grown by pulsed electron deposition. Superficial resistivity for ZnO thin film was 88 Ω/cm^2.

Organic dyes such as ZnPc are efficient absorbers in the VIS-UV region of the spectrum. But optical absorption in such materials occurs through an excitonic mechanism, which impedes the charge extraction. Typical values for exciton diffusion length in organic materials are in the range 20 nm – 100 nm.

Using arrays of CdTe wires could lead to an increased dissociation rate of excitons at the D/A interfaces and a better charge photogeneration.

New in the design of this structures is the reduced rate of recombination at the back electrode then increasing the hole collection. A better efficiency of exciton dissociation process was obtained by creating a large area interface between the organic dye and the nanostructured inorganic semiconductor.

Figure 1 summarizes technological steps in producing hybrid A_2B_6 wire array/organic dye photovoltaic structures.

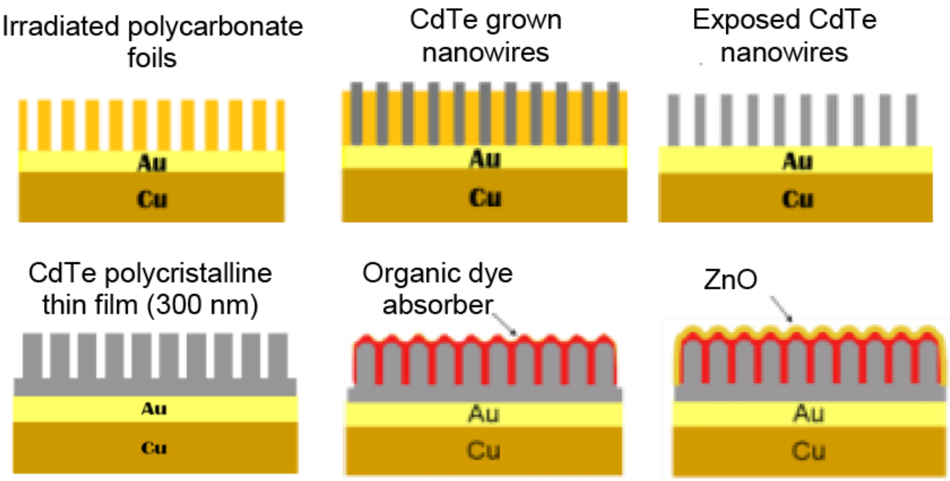

Fig. 1 Technological steps in producing hybrid CdTe wire array/organic dye photovoltaic structures.

Efforts were made to improve the crystalline quality of the organic dye thin films, because that results in larger exciton diffusion lengths. The film shows a good crystalline structure.

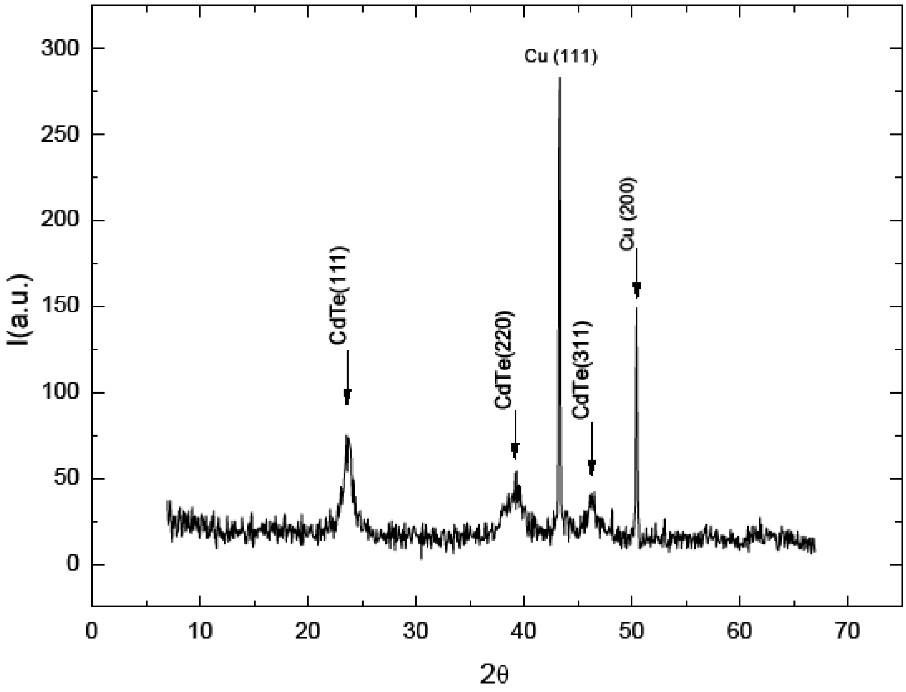

Fig. 2 X-ray diffraction pattern of the CdTe wires

Structural and compositional analysis of the CdTe wires array show a stoichiometric compound containing 50.5% Cd and 49.5% Te in the case of the sample grown at -550 mV with a zinc-blend cubic crystalline structure.

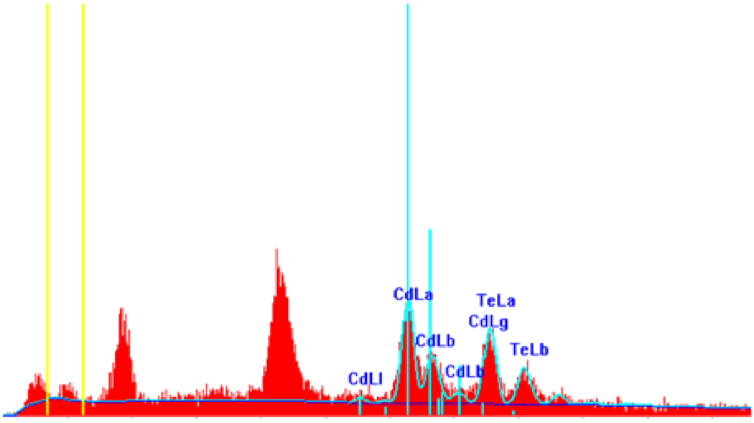

Fig. 3 EDX spectrum of CdTe wires array grown at -550 mV, 50.5% Cd and 49.5% Te

Performing the measurement for the fourth step of the technological process by SEM micrograph we can see the CdTe nanowire array.

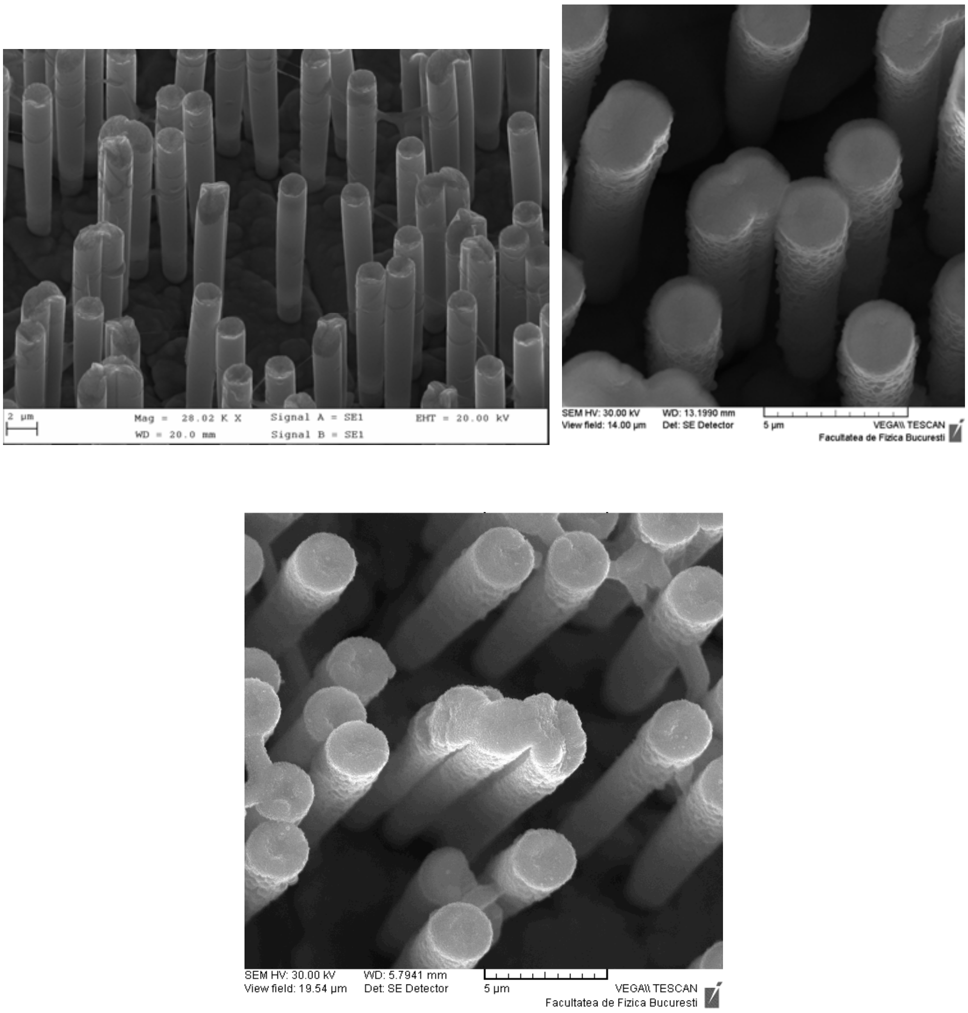

Fig. 4 (a) SEM micrograph showing the CdTe wire array after dissolving the polycarbonate membrane, (b) SEM image after covering CdTe wires with CdTe thin film (300 nm) and ZnPc (400 nm),(c) SEM CdTe wires covered with CdTe film, ZnPc and ZnO (300 nm)

The typical parameter when discussing about a photovoltaic devise is the external quantum efficiency. EQE is a characteristic quantity of a photovoltaic structure, representing the fraction of electron-hole pair collected at the electrodes to number of incident photons, measured in short-circuit conditions. It does not consider reflected or transmitted photons.

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

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

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:

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

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

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

The spectral dependence of the external quantum efficiency (EQE) of two photovoltaic structures, CdTe wires/ZnPc and CdTe wires/CdTe (300 nm)/ZnPc are shown in figure 5 and figure 6, respectively.

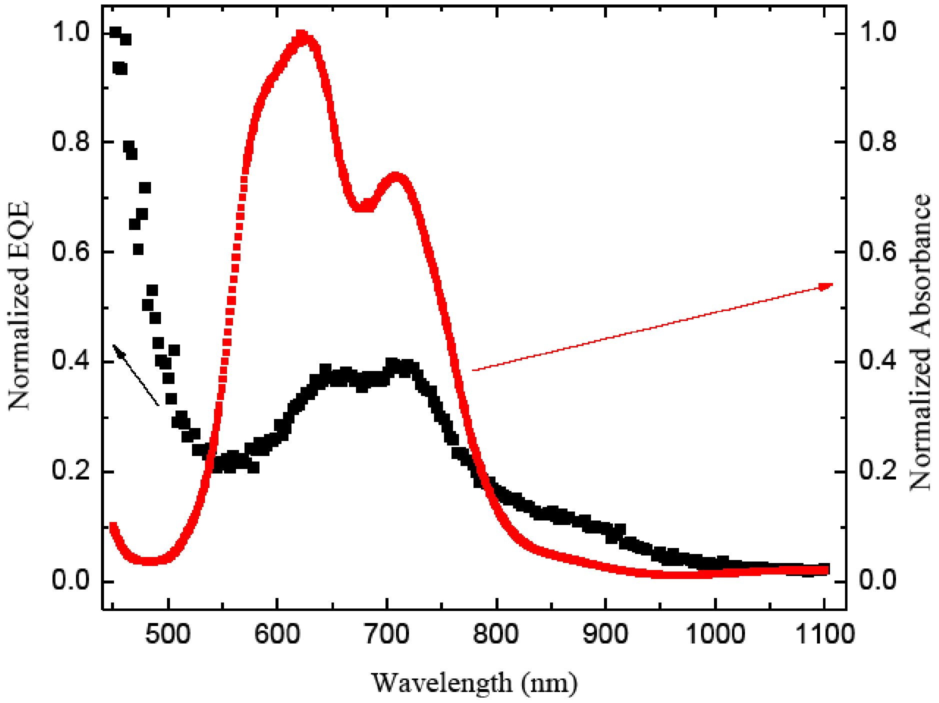

Fig. 5 EQE spectrum of an Au/CdTe (nw)/ZnPc/ZnO photovoltaic structure and the corresponding absorption spectra of ZnPc.

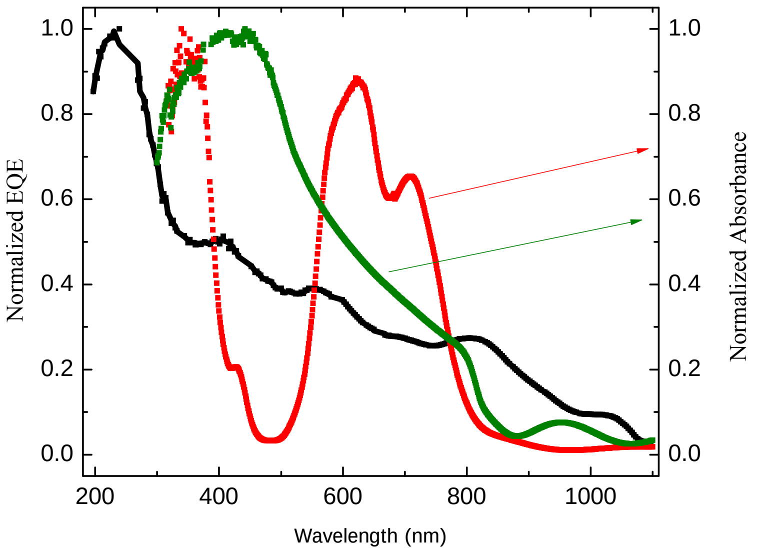

Fig. 6 EQE spectrum of an Au/CdTe (w)/CdTe/ZnPc/ZnO photovoltaic structure (black line); absorption spectra of ZnPc and CdTe films deposited on optical glass in the same conditions (red line, and green line, respectively).

In the case of the structure without the thin CdTe film deposited the external quantum efficiency follows the features in the absorption spectra of ZnPc 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 $\pi-\pi*$ 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). The shoulder at 900 nm is probably due to the onset of light absorption in the CdTe wires.

At the second sample, the external quantum efficiency of the Au/wire array CdTe/CdTe (300 nm)/ZnPc/ZnO structures was significantly increased on the measured range of wavelengths, with respect to that of Au/wire arrays CdTe/ZnPc/ZnO structures and, as it seen in figure 6, it follows the features in the absorption spectra of ZnPc, but also the absorption spectra of the CdTe thin film in the investigated spectral region.

3. Conclusions

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

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. The wires are made of a well formed stoichiometric compound with a zinc-blend cubic crystalline structure.

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.

New in the design of this structures is the reduced rate of recombination at the back electrode then increasing the hole collection.

The external quantum efficiency of the Au/wire array CdTe/CdTe(300 nm)/ZnPc/ZnO structures was significantly increased on the all wavelength range, with respect to that of Au/wire arrays CdTe/ZnPc/ZnO structures.

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