

# Optical properties of CdS electrodeposited nanowires

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Electrochemical deposition was performed in order to prepare CdS nanowires. The method employed for preparation of such high aspect ratio nanostructures was template replication. Ion track polycarbonate membranes were used as templates. The nanowires were studied by scanning electron microscopy (morphology characterization), energy dispersive X ray analysis (composition) and optical spectroscopy. Optical reflection spectroscopy was performed in order to determine the band gap value while photoluminescence spectroscopy was used for getting information regarding the point defects in the material.

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## 1. Introduction

The template replication represents a convenient approach for fabricating nanostructures with pre-determined morphology. The approach was successfully employed for preparing high aspect ratio metallic and semiconducting nanowires and nanotubes [1 -3]. The technique consists in filling the nanopores of a membrane with the desired material. The typical method is electrochemical deposition (due to their high aspect ratio it is impossible to fill the pores with methods such as vacuum evaporation or sputtering) but electroless plating represents an excellent alternative for fabricating hollow structures such as metallic tubules [4, 5].

Electrodeposition of semiconductors represents a promising approach for obtaining large area films or nanostructures [6-8]. Its low cost and scalability recommend the method for large scale applications as in e.g. solar energy harvesting. Thus, by this approach one can easily deposit II – VI group semiconductors with good stoichiometry.

In the present paper we report our results regarding the fabrication of highly uniform, high quality CdS arrays of nanowires. We studied the optical properties of the films by optical spectroscopy namely optical reflection and optical photoluminescence. The band-gap determined from the reflection measurements is in the range attributed to CdS. Photoluminescence spectra evidenced the characteristic point defects of such semiconducting nanostructures.

## 2. Experimental

Polycarbonate foils 30  $\mu\text{m}$  thick were irradiated with swift heavy ions and subsequently etched in a sodium hydroxide aqueous solution ( 5 M NaOH and 10% methanol) at 50°C . Further a thin layer of gold was sputtered on one face of the membranes for obtaining the working electrode. This electrode was strengthened with a

copper layer of approximately 10  $\mu\text{m}$  which also completely closed the pores on the electrode side.

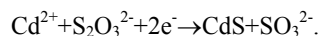
The semiconductor electrodeposition process was carried out in a typical three electrode arrangement with a platinum counter electrode and saturated calomel as a reference electrode. The deposition was performed by a potentiostat controlled by a computer. The electrochemical cell was thermostated and the deposition was performed at 80°C. Continuous stirring was performed during the experiment. An aqueous solution containing  $\text{CdCl}_2$  as a source of Cd ions and  $\text{Na}_2\text{S}_2\text{O}_3$  as a source of sulfur ions was employed. The chemicals, pro analysis grade were acquired from Sigma Aldrich and used as received. Millipore grade (18.2 M $\Omega$  cm) purified water was employed.

In order to image the samples, for morphological characterization, after depositing the semiconductor wires, the polymer foils were dissolved using dichloromethane. Scanning electron microscopy (SEM) and energy dispersive X ray analysis were employed for both morphological and compositional characterization. Optical properties were acquired by reflection spectroscopy and photoluminescence. An integrating sphere was used for measuring the reflection spectra (in a Perkin Elmer Lambda 40 spectrophotometer). In order to measure both the specular and the diffuse reflection the sample was mounted on a support which provided an 8° angle between the normal to its surface and the incident beam. The photoluminescence measurements were performed using an Edinburgh L900 luminescence spectrometer with a 450 W Xe lamp excitation and double monochromators on both excitation and emission. A front face luminescence setup was employed.

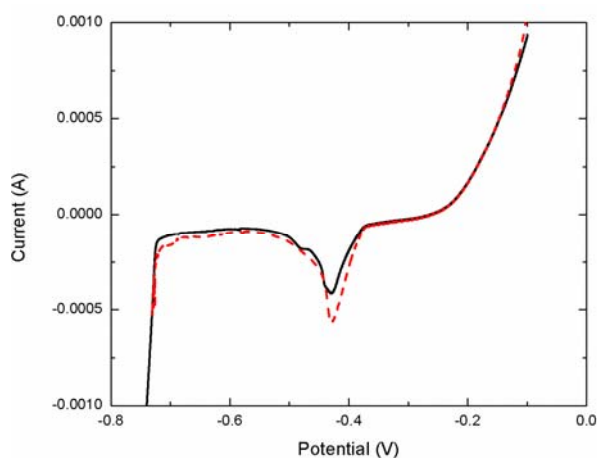
## 3. Results and discussion

Electrochemical deposition of CdS was performed using a solution containing 200 mM  $\text{CdCl}_2$ , 10 mM

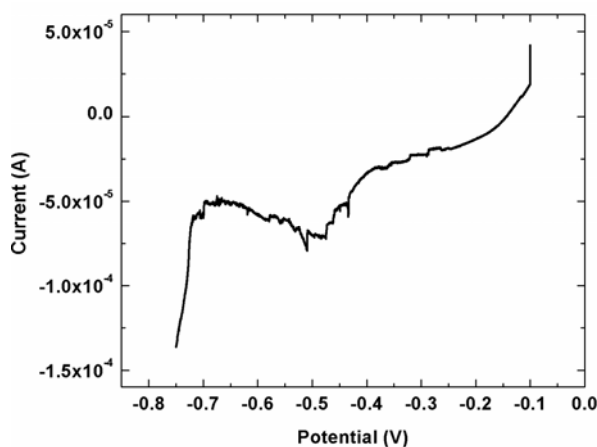
$\text{Na}_2\text{S}_2\text{O}_3$  at a pH of 2.3. The global reaction taking place at the electrode is:



In Fig. 1 (a) are presented electrochemical polarization curves for the case of membranes containing  $10^8$  pores/ $\text{cm}^2$  of 300 nm diameter. The sweep rate for the deposition process was 1 mV/s.



(a)



(b)

Fig. 1. Electrochemical polarization curves for: (a) membrane containing 300 nm diameter  $10^8$  pores/ $\text{cm}^2$  (b) 100 nm diameter  $10^9$  pores/ $\text{cm}^2$ . Sweep rate was 1 mV/s.

As one can notice, at an overvoltage of approximately -350 mV, as a function of the reference electrode, the current increases strongly. A maximum can be noticed, followed by a plateau of approximately 300 mV. This plateau is associated with the stoichiometric deposition, in this range the compound semiconductor being deposited. At more electronegative overvoltages a steep increase of the current is observed corresponding to the predominant deposition of the metallic cadmium. We

performed two consecutive sweeps, with same parameters, in order to establish how the deposition is influenced by the substrate. We noticed that the two curves corresponding to the two sweeps are very similar, the plateau range and the sharp increase of the current taking place at the same overpotential values. In order to determine the influence of the pore diameter on the deposition process we performed the measurements on a membrane containing 100 nm diameter pores. As one can notice comparing the data in the two plots there is a slight tendency of shifting the plateau and the corresponding maxima towards more electronegative potentials.

This tendency can be explained taking into account that we deal with pores with smaller diameter and the diffusion process becomes slower. This means is more difficult to bring ions near the electrode and, as a consequence, there is a lower concentration of ions in the vicinity of the cathode.

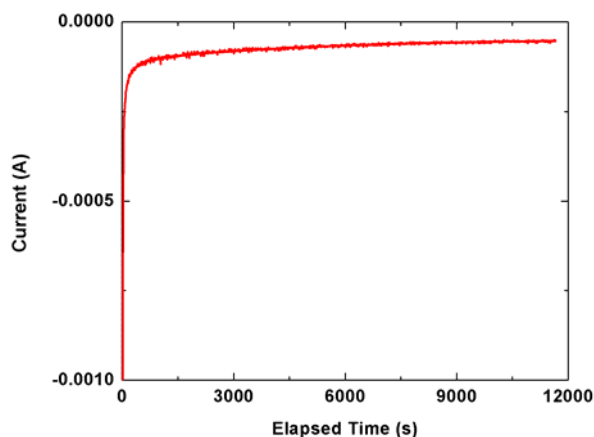


Fig. 2. Typical chronoamperic curve for the growth in a membrane with 500 nm diameter  $10^8$  pores/ $\text{cm}^2$ . Deposition was performed at -600 mV.

In Fig. 2 we plotted a typical chronoamperic curve measured for the deposition of an array of 500 nm CdS wires. Usually, when the pore is completely filled, a sharp current increase is observed. In the case of CdS nanowire preparation, during the set of experiments reported here, the growth was too slow thus we did not fill completely the pores even after deposition time of more than 8 hours.

Further, we grew wires in membranes pores at different deposition potentials, in the range of the plateau, range where we supposed that the stoichiometric compound is formed.

What we noticed during our experiments was that when compared to the typical case of metal nanowires growth, we need much more time to fill the pores. Even after several hours we did not observe the steep increase in current corresponding to complete pore filling and growth of hemispherical structures on the surface. In Fig. 3 we present SEM images for the wires prepared in the experiment where the chronoamperic curve was plotted in Fig. 2.

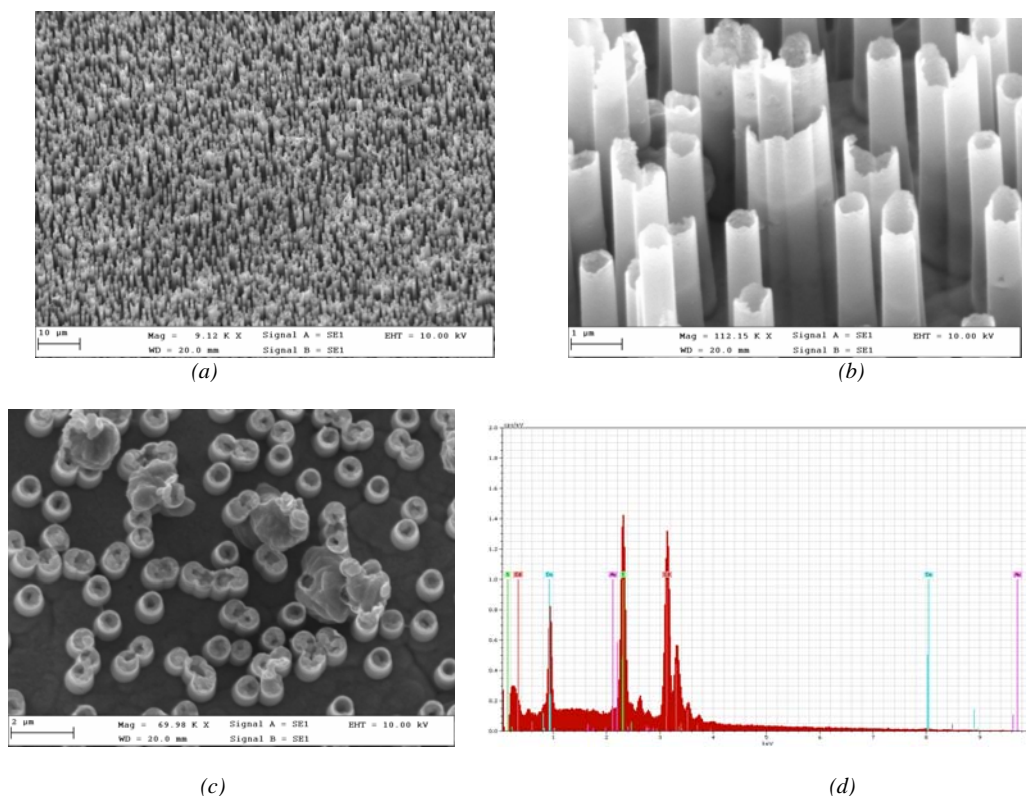


Fig. 3. CdS tubules array fabricated at a potential of  $-600$  mV in a template membrane containing pores with the diameter of  $500$  nm. (a) large area of an array of wires; (b) higher magnification image; (c) top view; (d) EDX spectrum of a nanowire.

It is interesting to notice that the structures presented in Fig. 3 are hollow configurations. This aspect of the process is related to the strong influence of the diffusion when compared to the electron transfer processes taking place at the electrode. The diffusion is probably the slowest process and determines probably the kinetics of the entire growth. This is sustained by the fact that the plateau observed in the polarization curves is almost horizontal, when increasing the potential the same current being measured, i.e. a diffusion limited process. One aspect that should be taken into account is that the deposition bath is not very stable at the working temperature. Besides the deposition process which takes place at the electrode CdS is formed in the bath and

precipitates.

The EDX spectrum of the nanowires reveals a quasi-stoichiometric composition namely, in this case, 53% Cd and 47% S. For all the samples prepared in the potential range of the plateau, close to stoichiometric values were obtained. Similar results were obtained for wires with lower diameters. In figure 4 we present scanning electron microscopy images of nanowires with a diameter lower than  $100$  nm. Again the EDX data show a near stoichiometric composition of these nanowires. The spherical structures which can be observed in the SEM images are not grown in the pores but are a result of the precipitation in the solution. Their composition is also CdS.

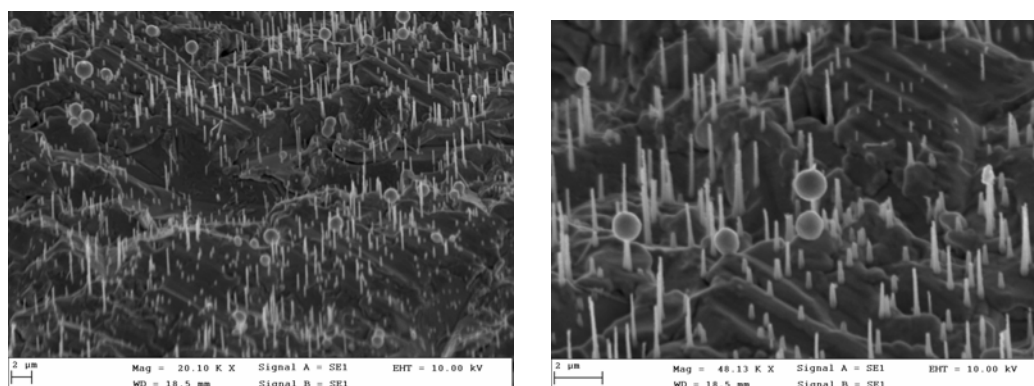


Fig. 4. Array of  $100$  nm CdS nanowires.

Next step in our studies was related to the measurement of the optical properties of the nanowire arrays. Since the substrate is not transparent we performed reflection spectroscopy of the samples. In Fig. 5 one can notice a set of curves corresponding to the reflection spectra of a set of arrays of 300 nm grown at different overvoltages. By applying the Kubelka Munk representation we determined the band gap of the material, of 2.5 eV in the range considered usual for CdS. It is interesting, and can be noticed in the spectra that the deposition overvoltage does not influence this result and that the band gap is independent of this experimental parameter.

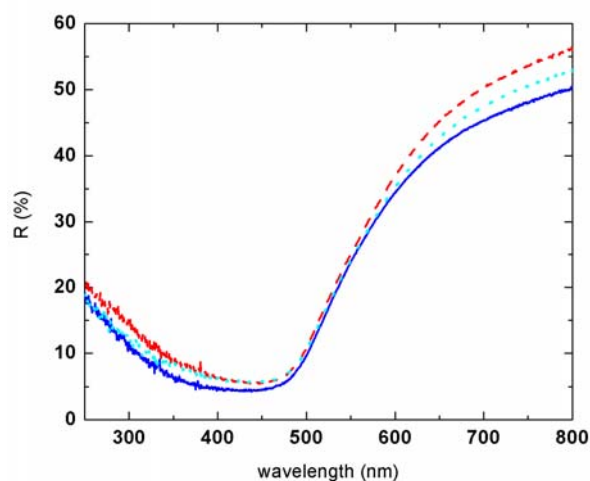


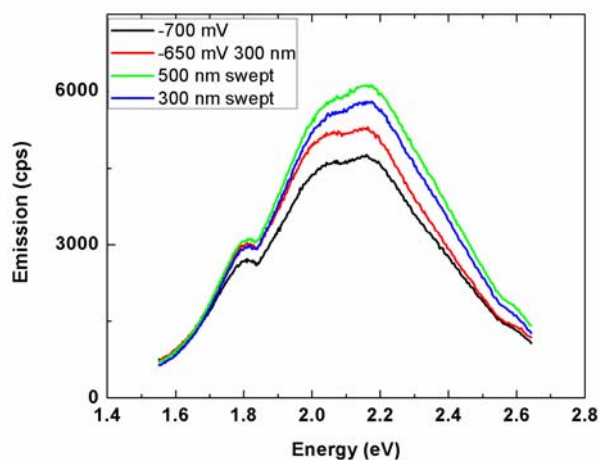
Fig. 5. Optical reflection spectra for three different samples deposited in 300 nm pore diameter membranes at -400 mV continuous curve, -500 mV dashed curve and -600 mV dotted curve.

Photoluminescence spectra were measured for all the samples. It is obvious that for this material grown in membranes nanopores the defect concentration is relatively high. This is the reason for which photoluminescence spectroscopy is important.

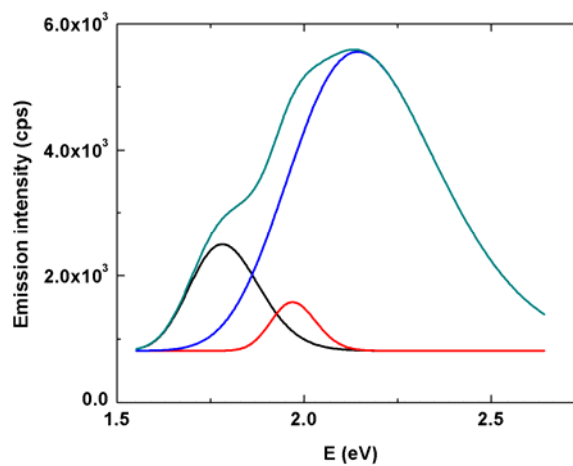
In Fig. 6. (a) we present several emission spectra measured for different arrays of CdS deposited electrochemically in porous membranes with different size of the nanopores and at different overvoltages, including deposition in variable potential (swept).

As one can notice from the peak deconvolution presented in Fig. 6 (b) there are three overlapped peaks which can be associated with different type of defects. The connection to typical defects was made using the excellent systematization of data made by Abken et al. [9] in 2009. All the peaks observed are related to point defects, we do not observe in this case any band to band recombination. Thus, the band at 1.77 eV was observed also for thin films and is considered as corresponding to the transitions between surface states and the valence band [10]. The second peak, centered at 2 eV was noticed but it is not attributed yet to any transition [9]. The third and most intense peak, centered at 2.11 eV, corresponds to levels

associated to interstitial cadmium [11]. The maxima are therefore quite well coincidental to the preparation method and to the morphology of the nanostructures. The nanowires present a high surface to volume ratio and therefore the concentration of surface related defects is high.



(a)



(b)

Fig. 6. Photoluminescence emission spectra (a) from different samples prepared in different conditions, (b) deconvolution of a luminescence spectrum.

Moreover, taking into account that we performed the growth from a solution with high Cd content, is normal that we deal with a high concentration of cadmium interstitials. These defects will further influence the electron transport properties of the nanowires.

#### 4. Conclusions

Arrays of nanowires with different diameters were prepared by electrodeposition in ion track nanoporous membranes. The electrochemical polarization curves show

the stoichiometric plateau, in this range the deposits presenting a near 1:1 composition. The morphology of the structures, determined by scanning electron microscopy presented an interesting characteristic namely that the structures grown in larger pores are hollow while the structures grown in pores with low diameters are rod like, completely filling the pores.

Optical reflection measurements show that the value of the bandgap is of about 2.5 eV typical for CdS. The photoluminescence measurements present three emission peaks, corresponding to point defects. Thus the highest concentration of defects corresponds to surface states and to Cd interstitials. The high concentration of surface related defects is normal due to the high surface to volume ratio of the nanowires while the high concentration of Cd interstitials is probably a consequence of the deposition method. Further research will be dedicated to study the influence of the deposition method on the transport properties of the nanowires.

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