Journal of Optoelectronics and Advanced Materials Vol. 6, No. 1, March 2004, p. 121 - 125

ELECTRODEPOSITION OF CdTe NANORODS IN ION TRACK MEMBRANES

M. Sima[a], I. Enculescu[a,b], C. Trautmann[b], R. Neumann[b]

[a]National Institute of Material Physics P. O. Box MG 7, 77125-Magurele Bucharest, Romania
[b]Gesellschaft für Schwerionenforschung, Planckstrasse 1, 64291 Darmstadt, Germany

CdTe nanowires were electrodeposited in ion track membranes with pore diameters in the range 100 – 2000 nm. Acidic and basic baths were tested for obtaining materials with good stoichiometry. The cyclic voltammograms were compared for the case of deposition on a carbon rotating disc and on the porous membrane substrates, the differences being attributed to the additional resistance induced by the pores. For larger pores a tendency of growing hollow structures was observed.

(Received March 4, 2004; accepted March 15, 2004)

Keywords: Cadmium telluride, Electrodeposition, Template method, Nanowires

1. Introduction

Preparation of nanowires and nanowire based devices has attracted more and more interest in the last period of time [1-3]. One of the most convenient method to prepare such quasi 1-D structures is the template replication method. It consists in filling the pores of a membrane (e.g. ion track membranes or anodic alumina) with the desired material, usually by electrodeposition.

During the last twenty-five years, electrodeposition has been more intensively studied in preparing compound semiconductors. The research work of the moment aim to obtain new structures, new functionalities, directly from the electrodeposition step. One can highlight the growth of nanostructured semiconductors in templates in the form of nanowires or nanorods [4-6] or deposition of hybrid structures between semiconductors and organic molecules [7].

Cathodic electrodeposition of cadmium chalcogenides films from aqueous solution are the most studied cases of semiconductor electrodeposition. CdTe is a very interesting semiconductor for the fabrication of the solar cells with a heterojonction of CdTe/CdS, but also for infrared and X-ray detectors. Its direct energy band gap in the range of 1.4-1.5 eV and high absorption coefficient $\sim 10^5$ cm^{-1} makes CdTe suitable for this purposes [8]. Our study presents some results referring to the electrodeposition of CdTe nanorods using a polycarbonate track-etch membrane as template.

2. Experimental

Polycarbonate (Makrofol, Bayer Leverkussen) foils, 30 μm thick, were irradiated with swift heavy ions (e.g. Au ions, kinetic energy of 11.4 MeV/nucleon), fluences in the range 10^6-10^8 ions/cm^2. Each heavy ion produces a cylindrical damage zone chemically more active than the non-irradiated surrounding material. After irradiation the polymer foil is etched in an aqueous alkaline solution (5M NaOH with 10% methanol at 50 °C), uniform cylindrical pores with the diameter depending on the exposure time to the etch bath being obtained. For the experiments described we used membranes with pores diameter in the range 100 to 2000 nm. A thin gold electrode film, which will later play the role of the cathode, was deposited on one side of the membrane by sputtering; this film was reinforced by chemical or electrochemical deposition of copper.

The electrochemical deposition of Cd and Te into the pores was accomplished with a potentiostat/galvanostat PAR 173 conected to a computer. A commercial saturated calomel electrode (SCE) was used as reference electrode and as auxilliar electrode a platinum mesh. In an additional experiment we used a vitreous carbon rotating disk (S=0.125 cm^2) and a Pt wire (0.065 cm^2) as working electrodes to study the electrodeposition of CdTe. After the electrodeposition process the polymer membrane was dissolved in CH_2Cl_2. The nanorods were imaged by scaning electron microscopy and their composition was determined by energy dispersive X-ray analysis (EDX).

3. Results and discussion

CdTe compound semiconductor was electrodeposited using both acid and basic solutions.

The acid solution contains 300 μM TeO_2 and 1 M $CdSO_4$, the pH is 1.6 adjusted with H_2SO_4 and the growth temperature was 80 °C.

The solution contains the ions Cd^{2+} and $HTeO_2^+$. The cathodic reactions for CdTe deposition are:

$$HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te + 2H_2O$$

$$Cd^{2+} + Te + 2e^- \rightarrow CdTe$$

Fig. 1 presents the cyclic voltammogram of carbon rotating disk electrode and of the membrane/AuCu electrode respectively. For the carbon rotating disc electrode the hysteresis observed between potentials –0.68 and –1.0 V indicates that the reduction of Cd occurs more readily on the CdTe surface than on the carbon surface. This hysteresis does not appear in the cyclic voltammogram of Au-Cu electrode deposited on the polycarbonate track-etch membrane in the same solution; probably, this behavior is due to the additional resistance, which appears into the membrane nanopore.

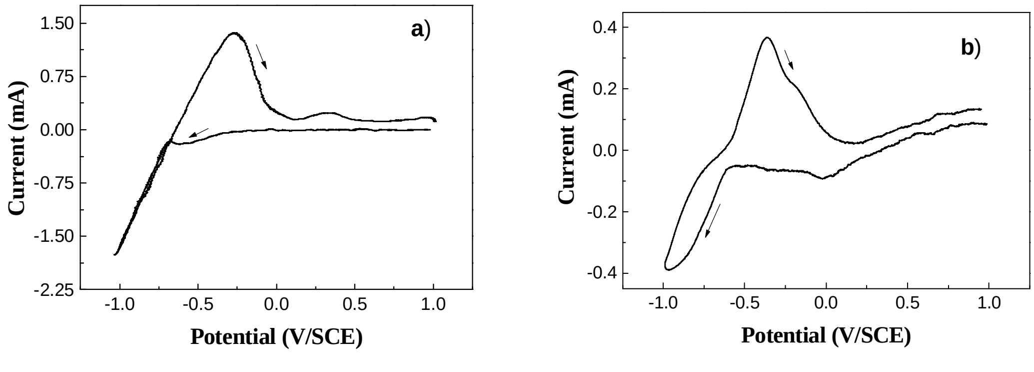


Fig. 1. Cyclic voltammograms on vitreous carbon rotating disk electrode (a) and on membrane substrate (b) in a solution containing 300 μM TeO_2 and 1M $CdSO_4$ (pH=1.6); sweep rate=50 mV/s, T=80 °C, rotation rate=500 rpm.

Deposition of CdTe in the pores of the membrane starts at a potential of about -0.6V versus SCE. In the reverse scanning the re-oxidation peak is observed at a potential - 0.36 V/SCE. We assume that this is a superimposition peak of CdTe and elemental cadmium.

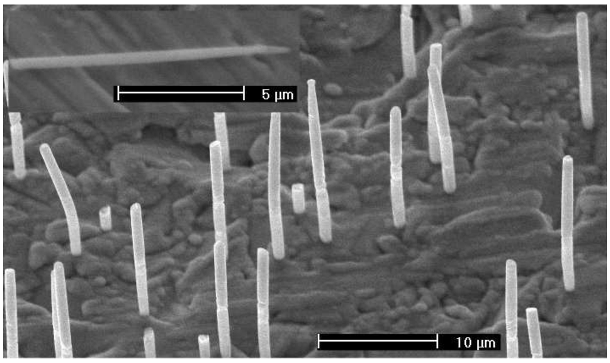


Fig. 2. SEM image of an array of standing CdTe wires 1000 nm diameter prepared by potentiostatic electrodeposition in track-etch membrane at -0.75 V/SCE, inset shows fragment of nanowire of about 500 nm diameter.

We deposited CdTe from this acid solution in the membrane nanopores at two different potentials -0.63 and -0.75 V/SCE A typical morphology of these CdTe nanorods is shown in the SEM image in Fig. 2. It is shown that CdTe nanorods have uniform diameters. After the dissolution of the membrane the thicker rods are still standing and their length is equal to the thickness of the foil. The thinner rods were more brittle so during and after the dissolution of the membrane the rods were broke (Fig. 2. inset). We noticed that the nanorods are uniformly distributed on the whole sample area of 1 cm^2.

The EDX measurements showed in atomic percent, a Cd/Te ratio of 9/1. It is known that the composition of CdTe films depends on the deposition potential. In reference [9] composition studies reveal that deposition in a narrow range of 95 mV, between -0.53 and -0.625 mV with respect to a silver-silver chloride (saturated) reference electrode, employing the same solution results in stoichiometric films. Films deposited at more negative potentials have excess Cd and at more positive potentials, excess Te. We assume that the difference in composition for the case of porous membranes when compared to the deposition of films is given by the fact that the volume of the $HTeO_2^+$ ion is much larger than the Cd^{2+} ion. This will mean that also a large difference in the diffusion coefficients of the two ions inside the pores is expected, this being the reason for the large differences in composition obtained between the deposition of a thin film and of the nanowires.

In another set of experiments, aqueous basic electrolyte containing 50 mM $CdSO_4$, 10 mM Na_2TeO_3, 4M $NH_3(aq)$, 0.5M $(NH_4)_2SO_4$ (pH=10.7) was used for the electrodeposition of CdTe.

In this case the cathode reactions are:

$$TeO_3^{2-} + 6H^+ + 4e^- \rightarrow Te + 3H_2O$$

$$Cd(NH_3)_4^{2+} + Te + 2e^- \rightarrow CdTe + 4NH_3.$$

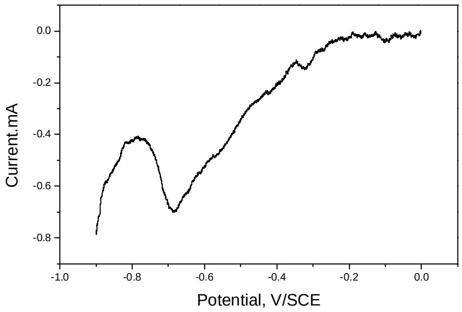


Fig. 3. Polarization curves for deposition of CdTe on Pt electrode (0.065 cm^2) from aqueous basic electrolyte containing 50 mM $CdSO_4$, 10 mM Na_2TeO_3, 4M $NH_3(aq)$, 0.5M $(NH_4)_2SO_4$; T=73 °C; sweep rate=6 mV/s.

Fig. 3 presents the cathodic part of the cyclic voltammogram for this ammoniacal bath. The CdTe deposition process starts at about -0.4 V/SCE.

The deposition was performed in membranes with pores diameters in the range 100 – 2000 nm using a potentiostatic regime at -0.8V/SCE.

For the large diameter pores we have noticed a tendency to grow hollow structures instead of rods (Fig. 4). We assume that this can be attributed to the large pores diameter of the used template and, consequently, to a larger deposition current appearing on the pore walls due to a higher value of the electric field.

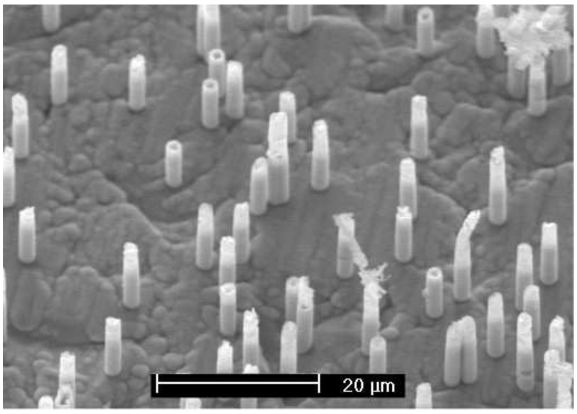
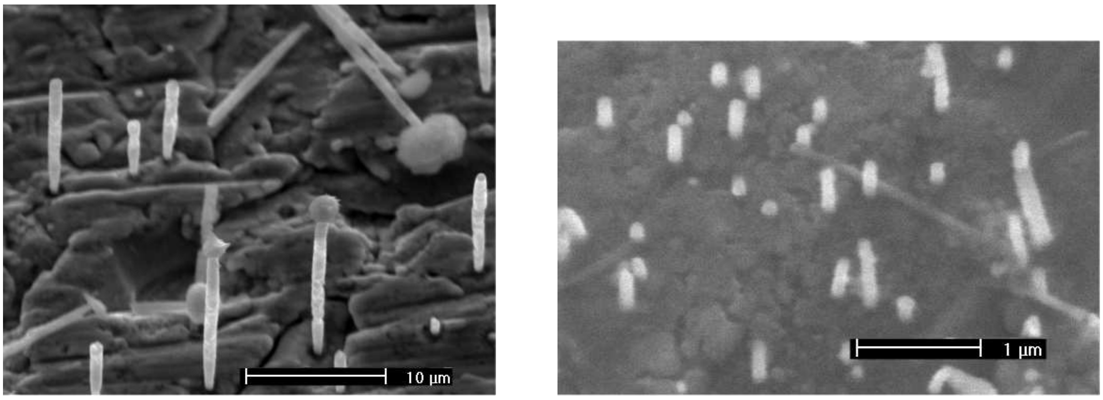


Fig. 4. Array of CdTe hollow structures grown in a membrane with 2 μm diameter pores.

For smaller pore dimension the structures grown are not hollow anymore, in Fig. 5 arrays of wires with diameter of 800 respectively 100 nm, can be observed. The mechanical stability of these nanorods is low due to the high aspect ratio (especially for the 100 nm ones) and so the nanorods are broken when the polycarbonate membrane is removed.



(a) (b)

Fig. 5. Arrays of CdTe nanowires grown from ammoniacal solution: (a) 800 nm wires – both standing and fallen after the membrane was removed and (b) 100 nm wires – only short fragments are still standing after membrane removal, fallen fragments can be observed.

Based on results from literature [10,11] we expected for such bath a near-stoichiometric deposition. Indeed, the EDX measurements revealed a much better stoichiometry when compared to the results obtained by using the acid bath. For the larger wires the Cd/Te ratio was 1/1.4 while for the thinner ones (800 and 100 nm) in the range 1 ÷ 1.1. This may be due to the fact that the volume of the two ions: $Cd(NH_3)_4^{2+}$ and TeO_3^{2-} are similar which should mean similar diffusion coefficients.

4. Conclusions

We prepared rod and tube arrays of CdTe using potentiostatic deposition in polycarbonate ion track membranes from acid and alkaline solutions. SEM measurements have shown the growth by electrodeposition of uniform nanostructures on large surfaces. The deposition using an ammoniacal bath allowed the preparation of a near stoichiometric CdTe compound (EDX measurements).

Hollow structures were obtained for the ammoniacal bath in the cases where large pore diameters were employed.

Preparation of semiconductor nanowires open up the possibility of fabricating electronic devices based on them. The use of the template method can be employed in the fabrication of functional structures as photoconductors, temperature detectors or photodiodes. The next step in our work will be the electrical characterization of such nanowires based on the replication of single pore templates, similar to the characterization of metal nanowires [12]. The great advantage of the method is the fact that no lithographical techniques and no manipulation of the nanowires are necessary.

Acknowledgements

The authors would like to thank Dr. Reimar Spohr for the fruitful and stimulating discussions. Financial support of the EU (Contract No. HPRN-CT-2000) and of the Romanian Ministry of Research and Education (project PN3/2003) is acknowledged.

References

[1] M. E. Toimil Molares, V. Buschmann, D. Dobrev, R. Neumann, R. Scholz, I. U. Schuchert, J. Vetter, Adv. Mater **13**, 62 (2001).
[2] C. R. Martin, Science **266**, 1961 (1991).
[3] A. Blondel, B. Doudin, J.-Ph. Ansermet, J. Magn. Magn. Mater. **165**, 34 (1997).
[4] G. S. Cheng, S. H. Chen, X. G. Zhu, Y. Q. Mao, L. D. Zhang, Mat. Sci. and Eng. **A286**, 165 (2000).
[5] D. J. Pena, B. Razavi, P. A. Smith, J. K. Mbindyo, M. J. Natan, T. S. Mayer, T. E. Mallouk, C. D. Keating, Mat. Res. Soc. Symp. **636**, D4.6.1 (2001).
[6] C. Shen, X. Zhang, H. Li, Mat. Sci. and Eng. **A303**, 19 (2001).
[7] F. M. Pavel, R. A. Mackay, Langmuir, **16**, 8568 (2000).
[8] A. E. Rakhashani, H. A. Ramazaniyan, Phys. Stat. Sol. (a) **172**, 379 (1999).
[9] P. Cowache, D. Lincot, J. Vedel, J. Electrochem. Soc. **136**, 1646 (1989).
[10] K. Murase, J. Electrochem. Soc. **146**, 4477 (1999).
[11] K. Murase, Electrochemistry **67**, 331 (1999).
[12] I. Enculescu, Z. Siwy, D. Dobrev, C. Trautmann, M. E. Toimil Molares, R. Neumann, K. Hjort, L. Westerberg, R. Spohr, Copper nanowires electrodeposited in etched single-ion track templates; Appl. Phys. A **77**, 751 (2003).