

SEQUENTIAL DEPOSITION OF MULTISEGMENT NANOWIRES

E. MATEI, N. PREDA, M. ENCULESCU, J.-P. ANSERMET^a,
M. E. TOIMIL MOLARES^b, I. ENCULESCU*

*National Institute of Materials Physics, Magurele-ILFOV, P.O.Box MG. 7,
Romania*

^a*Ecole Polytechnique Federale de Lausanne, Switzerland*

^b*GSI Darmstadt, Germany*

Electrochemical replication of nanoporous membranes represents a facile approach towards the fabrication of nanostructures with tailored properties. By the template method we prepared multisegment nanowires with tailored structure. The first step of the process was the fabrication of the nanoporous template by swift heavy ion irradiation and subsequent selective etching of the ion track. The next step was to fill the pores with the desired combination of materials. In this manner, by sequential electrodeposition steps of metal and semiconductor we prepared Ni – CdTe and Ni – ZnO – Ni nanowires.

(Received October 2, 2010; accepted November 22, 2010)

Keywords: Multisegment nanowire, Ni-CdTe Ni- ZnO, Nanoporous membrane,
Electrochemistry

1. Introduction

During the last decade the main focus in the field of nanotechnology shifted from the pure knowledge driven research towards more complex, application focused work. Thus, in the field of low dimensional structures, initially we dealt with a rush towards discovering new nanoobjects with exotic properties and new nanostructured materials and with reporting a wide range of ingenious methods for their fabrication and characterization. Further, the focus shifted towards refining the fabrication methods in order to develop new functionalities of such nanostructures or nanostructured materials. In the second, more mature step of its development, the research became more complex in both methods and results. The key word at this point is functionality, and with this goal in mind the methods developed in the first years of research were further developed [1-3].

Nanowires are quasi – 1 – dimensional nanoparticles with a huge potential of applications ranging from building blocks of tomorrow electronics to active components of ultrasensitive biological detectors. These nanostructures not only allow extreme miniaturization but, based on their unique morphology low dimensionality and high surface to volume ratio, offer new specific functionalities. The methods used for fabricating nanowires are both physical and chemical, with specific advantages and disadvantages [4 – 6].

The template method is one of the most convenient in order to fabricate nanowires or nanotubes [7-9]. By replicating a nanoporous membrane with cylindrical pores with controlled dimensions, such as polymer ion track membranes or anodic alumina, one is able to obtain nanowires with well controlled morphology and extremely high aspect ratio. Usually the replication of the nanoporous membranes is performed using electrochemical and chemical deposition due to the fact that is more difficult to fill such low diameter pores by employing physical methods. Using this approach metal and semiconductor nanowires were obtained. Further, complex structure nanowires such as multilayered magnetic nanowires with current

*Corresponding author encu@infim.ro

perpendicular to plane giant magnetoresistance were prepared by a simple electrochemical pulsed deposition [3]. Semiconductor electrodeposition advanced steadily during the last two decades opening the possibility that by template replication to fabricate high quality nanowires [10, 11]. Moreover, the next logical step was to prepare more complex structures, either by pulsed deposition when the electrochemical properties of the system make it possible or in a more complicated manner namely by a sequential approach where the deposition bath is changed as a function of the desired result [12].

In this paper we present our results related to the fabrication of metal – semiconductor multisegment nanowires by electrochemical deposition in ion track membranes. Scanning electron microscopy, energy dispersive X-ray analysis and optical spectroscopy were employed to characterize the nanostructures.

By this approach we succeeded in fabricating nanowires with high morphological and structural quality. These can be employed in a wide field of applications, most interesting being the biological molecule (DNA, cancer markers, proteins and so on) detectors. Such nanostructures with controlled properties may also be used in optoelectronics, as photodetectors. By further refining the method and improving the quality of the deposited nanowires one can develop ultra miniaturised light emitting diodes or even laser diodes.

2. Experimental

The first step was to prepare the nanoporous membranes by swift heavy ion irradiation (performed at the UNILAC accelerator of GSI, with heavy ions such as Au or U with specific energy of 11.4 MeV/nucleon) of the polycarbonate foils 30 micrometer thick. The total fluence of irradiation will represent the pore density, taking into account that each ion passing through the sample leaves a defect track. This defect track is further etched with a mixture of an aqueous solution of sodium hydroxide (5M) and 10% methanol at a temperature of 50°C. In these conditions the etching is extremely selective, cylindrical, parallel pores being obtained. The diameter of the pores is controlled by the etching time, a 2 micrometer diameter corresponding to one hour of etching.

The next step of the algorithm was to deposit the working electrode. Thus, a thin layer of gold was deposited onto one face of the membrane and further thickened by electrodeposition of copper. After the metal electrode was prepared, the pores were completely closed on that face of the membrane.

The next step was the electrochemical deposition of the nanowires. In order to do this the membrane was inserted in a thermostated electrochemical cell, with the opened side of the pores facing the electrolyte. One major problem we encountered was due to the fact that polycarbonate is a hydrophobic material this leading to incomplete pore filling with the aqueous electrolyte. For both metals and semiconductors electrodeposition we proved that the addition of polyvinylpyrrolidone (PVP) to the deposition bath increases the ratio of filled pores and leads to highly uniform nanowire arrays [13, 14]. PVP acts therefore as a wetting agent and was employed for all the baths we used in the present work.

The electrodeposition was performed at constant potential using a PC controlled potentiostat and a three electrodes set-up. In order to minimize the contamination and to maintain its temperature as close to room as possible, the reference electrode was connected to the electrochemical bath by means of a salt bridge filled with a saturated solution of KCl. The reference electrode was a commercial saturated calomel electrode and the counter electrode a platinum foil of 1 cm square.

We deposited two types of metal-semiconductor nanowires, with the metal in both cases being nickel while the semiconductor being either zinc oxide or cadmium telluride. Nickel electrodeposition was performed using a typical Watts bath containing nickel sulphate and chloride as source of metal ions and boric acid as pH buffer. CdTe was deposited from a solution containing cadmium sulphate, tellurium dioxide as sources of cadmium and tellurium ions. The pH of the solution was approximately 2. Zinc oxide was deposited from a nitrate bath which contains zinc nitrate as the source of zinc ions.

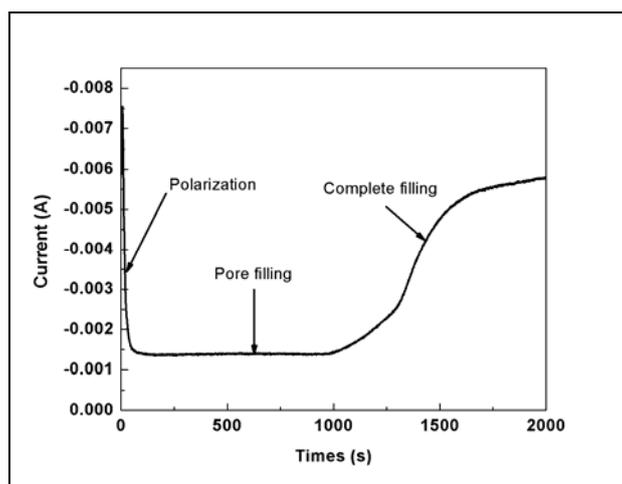
When subsequent deposition was performed two thermostated electrochemical cells were employed and the sample holder containing the sample was moved from one bath to the other. In order to observe the samples and to measure their composition, scanning electron microscopy and energy dispersive X-ray analysis were performed. For this the template polymer was dissolved and carefully washed away in chloroform. For the samples containing a zinc oxide segment after dissolving the template we performed photoluminescence measurements.

3. Results and discussion

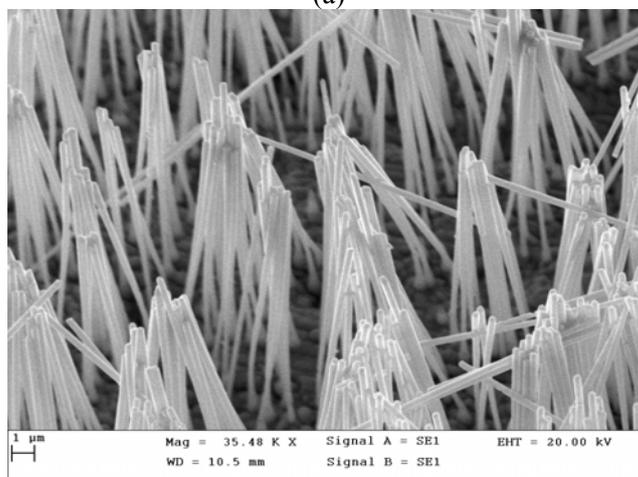
3.1 Deposition of metal segment

Deposition of nickel was performed from a Watts bath containing besides the “classical” components PVP as pore wetting additive. We show in a previous paper [13] that by adding PVP the pore filling efficiency reaches 80%. The deposition temperature was $50^{\circ}\pm 1^{\circ}$ C.

In figure 1 (a) one can see the chronoampermetric curve for the pore filling process and a typical Ni nanowires array. In the chronoampermetric curve the three typical steps of the pore filling process are easily observed. Thus, the first step is the polarization region, the second is the pore filling region while the third, characterised by a sharp increase of the current corresponds to the complete pore filling and growth of a metal cap on the surface of the membrane. A typical array of nickel nanowires, after dissolving the polymer template is presented in figure 1 (b).



(a)



(b)

Fig. 1. (a) Chronoampermetric curve measured for nickel nanowires electrochemical deposition at -900 mV vs SCE and (b) SEM image of a Ni nanowire array.

The characteristic chronoamperometric curve allows us to calculate the time necessary to completely fill the pore and from this to calculate the growth rate of the nickel segment. By calculating the growth rate for each component of the multisegment nanowire one is able to precisely control each segment length. For the deposition process of multisegment nanowires we stopped the deposition of the first Ni segment at a chosen moment in order to obtain a metal segment with the desired length of a few micrometers.

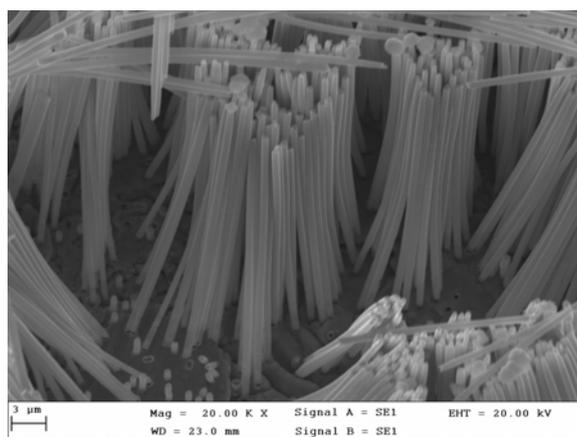
3.2 Deposition of CdTe and Ni/CdTe junctions

CdTe was deposited from an acidic bath. The electrode processes that lead to the CdTe deposit are the following:

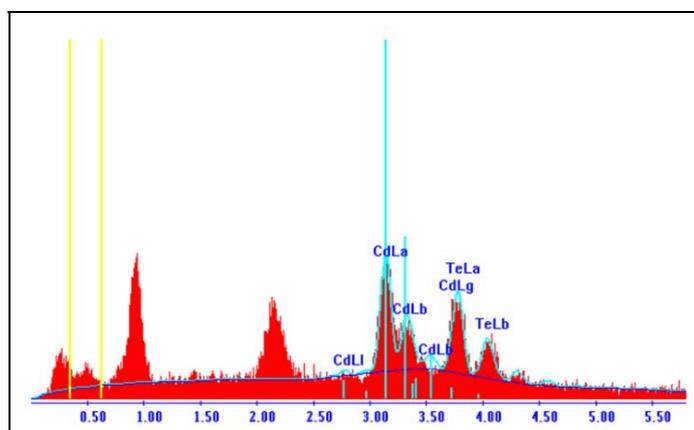


The temperature used for depositing CdTe was of $80^\circ \pm 1^\circ \text{C}$.

We showed in a previous report that the process can be easily tuned in order to obtain stoichiometric deposits of uniform nanowires over large areas [12]. In figure 2 (a) an array of CdTe nanowires is presented together with the corresponding energy dispersive X-ray spectrum in figure 2 (b) which shows the desired stoichiometry of the material.



(a)

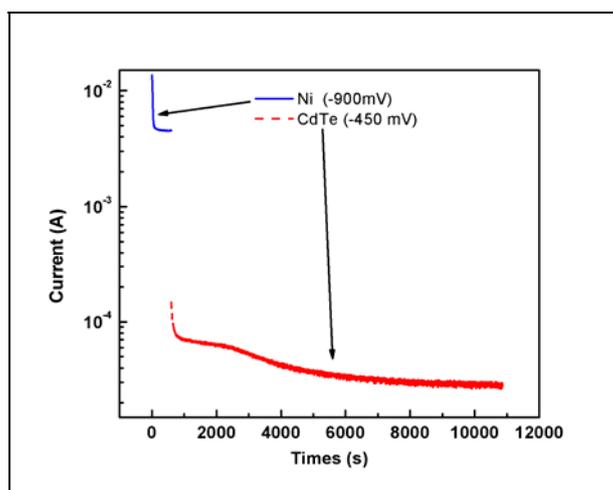


(b)

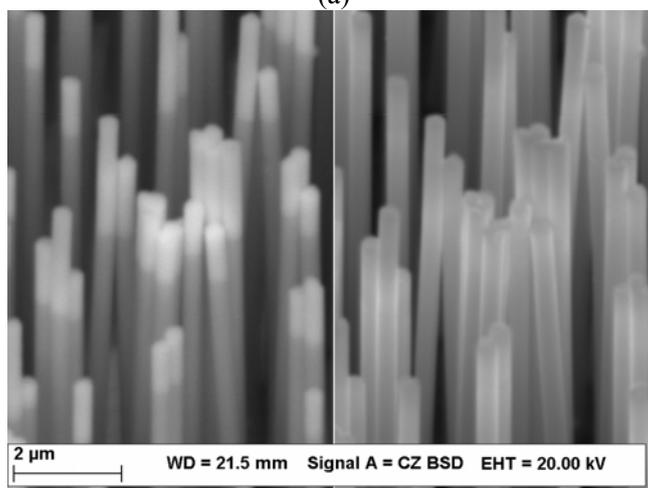
Fig. 2. (a) CdTe nanowire array (b) EDX spectrum showing the stoichiometric composition of the nanowires.

The growth rate for the semiconductor material is much lower than the corresponding rate for the metal due to the lower conductivity of the semiconductor. After finding the appropriate conditions of deposition in terms of bath composition and deposition potential, the next step was to deposit the multisegment Ni – CdTe junctions.

In figure 3 is shown the sequence of chronoamperometric curves corresponding to the deposition of nickel and CdTe and the SEM image of an array of such metal – semiconductor multisegment nanowires.



(a)



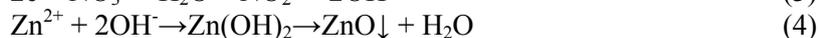
(b)

Fig. 3. (a) Chronoamperometric curves corresponding to the sequential deposition of Ni – CdTe segments; (b) scanning electron microscopy image of an array of Ni – CdTe multisegment wires (left back scattered detector image/ right secondary electron detector image).

The electrodeposition current is two orders of magnitude ratio higher for the deposition of Ni when compared to the case of CdTe (Fig. 3). During the deposition of the CdTe segment the current decreases as a consequence of the high resistance of the semiconductor. In Fig. 3 (b) a split SEM image of an array of multisegment Ni – CdTe wires is presented. On the left one can notice the backscattered electron detector image while on the right side the secondary electrons image is presented. Due to the difference in Z between Cd and Ni the backscattered electron image reveals the two different segments. The secondary electron image evidences the smooth surface of the wires. EDX measurements revealed that the deposition process on a Ni segment takes place in a similar manner as in the case of deposition directly onto the gold/copper working electrode.

3.3 Deposition of ZnO and Ni/ZnO junctions.

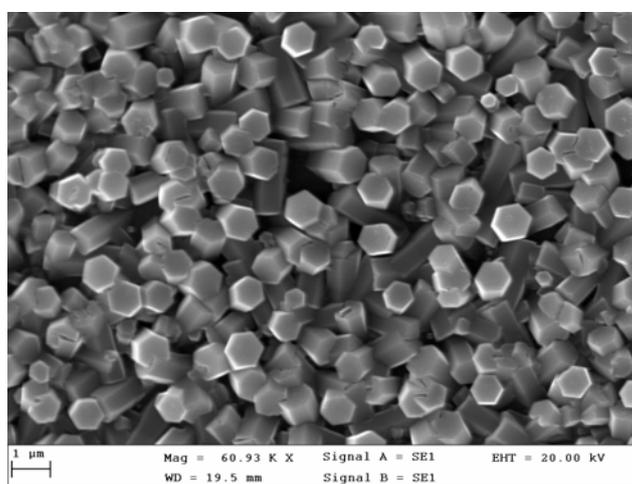
Electrodeposition of ZnO became, during the last decade, a hot topic of research. The mechanism of deposition is slightly more complicated when compared to the electrodeposition of metals. The electrode reactions are the following:



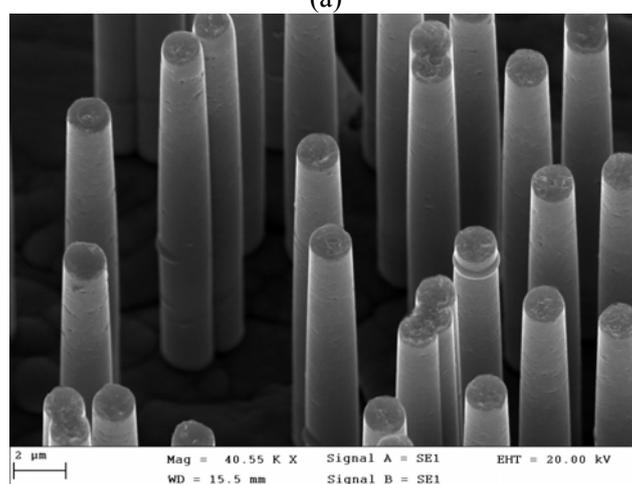
or the global reaction:



Practically the cathodic reduction reaction is (3) representing the nitrate to nitrite reduction. Reaction (4) describes the decomposition of zinc hydroxide with the precipitation of zinc oxide and does not present a charge transfer from the electrode. As a consequence, only the reaction (3) can be monitored through the deposition current.



(a)



(b)

Fig. 4. Electrodeposited ZnO (a) thin film and (b) array of wires.

In Fig. 4 a ZnO thin film and an array of wires deposited on platinum and in a porous membrane are presented. Both images show the high quality of the material. In order to determine the quality of the electrodeposited ZnO and to measure its band – gap, optical spectroscopy measurements were performed. For band – gap measurements the reflection spectra in Kubelka Munk representation were plotted (figure 5 (a)). The calculated band – gap is of approximately

3.2 eV. The photoluminescence spectrum in Fig. 5 (b) shows the typical emission bands characteristic to ZnO prepared in aqueous media, namely the exciton peak centered around 380 nm and the defect related wide band centered at 580 nm and associated with oxygen interstitials.

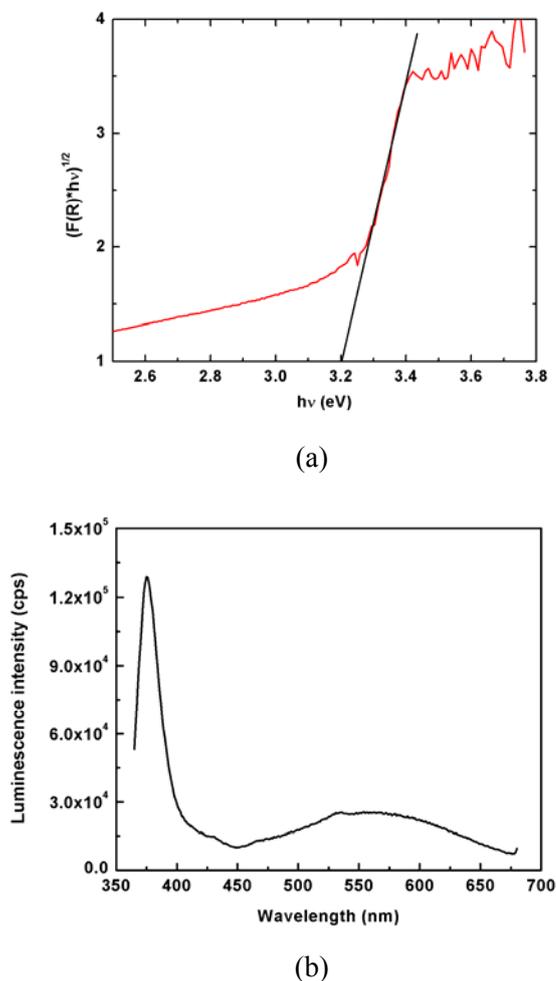
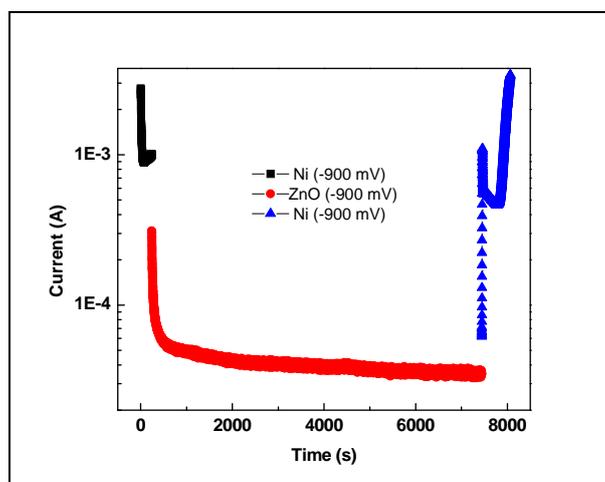
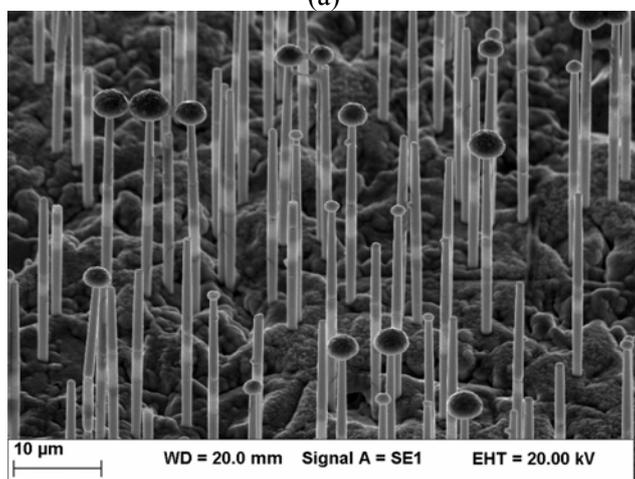


Fig. 5. (a) Reflection spectra of an electrodeposited ZnO film and (b) luminescence emission spectrum of a ZnO array of nanowires.

Deposition of a ZnO segment in a multisegment nanowire was performed just as in the case of CdTe after a short segment of nickel was deposited. Again the deposition rate of the ZnO segment is much lower when compared to the deposition rate of the metal segments. In figure 6 (a) the chronoamperometric curves corresponding to a three segment wire array is presented. The first and the last segments are nickel while the segment in the middle is ZnO.



(a)



(b)

Fig. 6. (a) Chronoamperometric curves measured in the case of deposition of a multisegment Ni – ZnO – Ni array of nanowires, (b) array of Ni – ZnO - Ni nanowires

An important thing to be noticed is the fact that also in the case of ZnO segment deposition the current decreases steadily, similar to the case of CdTe deposition. Moreover, for the second segment of Ni deposition, where the caps grew, one can observe that the average current is much lower than in the case of the first segment, again a consequence of the higher resistivity of the semiconducting segment. The SEM image show high quality wires, completely filling the pores, with several caps being already grown. The semiconducting segment is lighter in the secondary electron image. No contrast was observed in the back scattered electron image since Ni and Zn have close Z .

EDX mapping was performed in order to evidence the semiconductor segment. In figure 7 (a) a typical EDX map of an array of multisegment nanowires is presented while in Fig. 7 (b) the map is presented for a single nanowire.

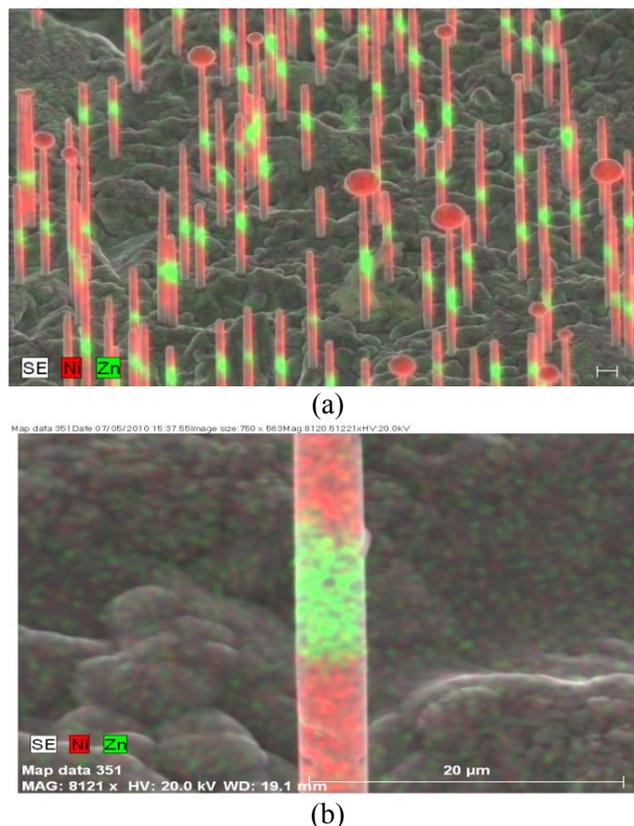


Fig. 7. Composition map for the two metallic elements Zn and Ni: (a) Array of multisegment wires and (b) single wire.

As one can notice from both secondary electron and mapping images, the multisegment wires shows a high morphological quality, with smooth walls and cylindrical shape, as expected.

4. Conclusions

Electrochemical deposition and template method allows the preparation of wires with a complex structure by sequential deposition in nano and microporous polymer membranes. In this manner directly from the deposition process one is able to prepare semiconducting devices. The method has several major advantages, the most important being the fact that it allows the preparation of wires with diameters ranging from several tens of nanometers to several micrometers and huge aspect ratio (up to 1000). Another major advantage of the method is the fact that the wires can be characterized in a straightforward manner without the need of manipulation. In order to provide the wires with electrical contacts, a second electrode on the surface of the membrane, on top of the caps has been deposited.

The next step will be to fabricate semiconductor junctions based on a similar approach, namely sequential deposition of two semiconductor segments.

Acknowledgements

The authors gratefully acknowledge the financial support of the Romanian Education and Research Minister (contract PN II D 11 060/2007) and of the Swiss National Science Foundation (SCOPES contract).

References

- [1] Xia Y.N.; Yang P.D.; Sun Y.G.; Wu Y.Y.; Mayers B.; Gates B.; Yin Y.D.; Kim F.; Yan Y.Q., *Adv. Mater.* **15**, 353 (2003).
- [2] Cui Y.; Wei Q.Q.; Park H.K.; Lieber C.M., *Science* **293**, 1289 (2001).
- [3] Enculescu I.; Toimil-Molares M.E.; Zet C.; Daub M.; Westerberg L.; Neumann R.; Spohr R. *Appl. Phys. A*, **86**, 43 (2007).
- [4] Morales A.M.; Lieber C.M., *Science*, **279**, 208 (1998).
- [5] Martin C. R., *Science* **266**, 1961-1966 (1994)
- [6] Rechtes M., Gazit E., *Science*, **300**, 625-627 (2003)
- [7] Possin G. E., *Physica (Utrecht)*, **55**, 339-345 (1971).
- [8] Li D.D., Thompson R.S., Bergmann G., Lu J.G., *Adv. Mater.*, **20**, 4575-4578 (2008).
- [9] Liang C.; Terabe K.; Tsuruoka T.; Osada M.; Hasegawa T.; Aono M., *Adv. Funct. Mater.*, **17**, 1466 (2007).
- [10] I. Enculescu, M. Sima, M. Enculescu, M. Enache, V. Vasile and R. Neumann, *Optical Materials*, **30**, 72 (2007).
- [11] Enculescu, I.; Matei, E.; Sima, M.; Neumann, R.; Granville, S.; Ansermet, J. – Ph.; *IEEE Trans. On Magn.*, **44**, 2678-2680 (2008).
- [12] Matei E., Ion L., Antohe S., Neumann R., Enculescu I., *Nanotechnology*, 2010, 21, 105202
- [13] Matei E., Enculescu I., Enculescu M., Neumann, R., *J. Opt. Adv. Mat.* 2008 10 508-511
- [14] Enculescu I., Matei E., Sima M., Enculescu M., Sima M., Ghica C., *Surf. Interf. Analysis*, **40**, 556-560 (2008).