

## POROUS MATRIXES BASED ON ION-IRRADIATED POLYMER AS TEMPLATES FOR SYNTHESIS OF NANOWIRES

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### ABSTRACT

Irradiation with swift heavy ions is usually used for production of track membranes (nuclear filters). These membranes traditionally used as filters for fine filtration in medicine and biology.

Another application is matrixes for so called matrix synthesis. The idea of this technique is to fill pores by any desired material- metal, polymer, semiconductor and so on.

This work is devoted to formation of membrane for template synthesis, to investigation of filling process and to study some properties of obtained structures.

It was found that filtration track membranes are not the best material for template synthesis –another type of matrixes are needed- with different pores profiles and parallel pores orientation. These parameters could be obtained during irradiation. Different types of etching gave possibility to vary by will the shape of the pores and to obtain pores with conical shape. The process of etching in the alkali solution in mixture of water and alcohol was investigated.

The main part of the work devoted to fabrication of micro- and nanowires via electrodeposition. Different types of metals-copper, silver, cobalt and nickel were used for galvanic deposition of the pores. Two types of the processes- galvanostatic and potentiostatic were investigated.

It was also demonstrated that obtained metallic nanowires could be used as the substrates for deposition of the probe (biological molecules) in mass-spectrometer.

The application of such structures in non-linear optic was also described.

**Keywords:** heavy ion irradiation, porous polymer matrix, template synthesis, conical pores, metallic nanowires

### RESULTS AND DISCUSSION

Nanosized materials are of great interest now. One of the most promising technique for production of these materials is template (or matrix) synthesis: filling of the pores in the special matrix by the desired material. The last one

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can be metal, semiconductor or polymer. We used polymer track membranes or porous polymer material as such matrixes for the filling process. In our work the matrixes with cylindrical and conical pores were utilized and obtained structures (ensembles of metal micro- and nanowires) were used as the emitters for mass-spectrometry analysis.

#### *Obtaining of the matrixes*

Usually commercial TM are used for formation of replicas- nanowires. We used not only commercial TM, but specially prepared polymer matrixes. In this case the polymer films (Polyethyleneterephthalate, PET, thickness 15-20 mcm) were irradiated with swift heavy ions –usually Xe or Ar (for conical pores) with the energy 1-2 MeV/nucleon and surface density  $10^6 - 10^8$  ions per  $\text{cm}^2$ , and perpendicular orientation. All irradiations were done in Joint Institute for Nuclear Research (JINR, Dubna).

For the formation of cylindrical through pores standard etchant (water solution of 5 M NaOH, and treatment (room temperature, a few minutes etching) were used.

We used 3 M NaOH solution in the water-ethanol mixture (with different proportion) for obtaining pores of conical shape (usually: tapered, dead-end pores). It is important that by varying of the etching conditions (composition, temperature and time) we could vary the shape and the size of the pores. It was found that the top angle of pores (and, therefore, the replica cones angle) increases with decrease of temperature of the track etching and with the increase of alcohol concentration. We also demonstrated the possibility of conical pores formation by using the addition of salt ( $\text{BaCl}_2$ ) to etchant (0,25 M KOH+0,1 M  $\text{BaCl}_2$ ).

#### *Investigation of the process of etching of conical pores*

The process of chemical etching of cylindrical pores was investigated in many papers and gave information about structure of latent track area. On the contrary the process of etching of conical pores –in the alkali solution in the mixture of water and alcohol-was not investigated. In our mind this process is different from the first one. So, we investigated the process of etching of conical pores in the mixed etchant (i.e. with the alcohol) by using IR-spectroscopy.

Polymer films (PET with thickness 10 mcm) were irradiated with Ar ions (fluence  $10^9$  ions per  $\text{sq.cm}$ ) at cyclotron in JINR, Dubna. The irradiated films were then etched in 9N solution of NaOH in the mixture of water and alcohol (50:50). The etching temperature was 25°C. The etching times were taken as 10 min, 20 min, 30 min, 40 min and 50 min. After each etching process the etching solution (with the reaction products) was taken for analysis. IR-analysis of etching solution were carried out using IR-spectrometer Specord M80 with computer data development. All obtained spectra demonstrate the changing in

the composition of etchant during the etching. The calculation of these data gave possibility to estimate the quantity of the etching product in solution. It is known that destructed polymer from track areas pass into the solution at the beginning of the etching and this process depends on time. The dependence of two bands ( $1444\text{ cm}^{-1}$  (aromatic) and  $1696\text{ cm}^{-1}$  (carbonil)) intensity on etching time confirms the changing of etchant composition during the first 30 min of etching, than saturation took place. So we have etching of destructed polymer (from track area) during first 30 min, than only non-destructed polymer slowly passed into the etchant. The size of the area of destructed polymer (at the surface) could be estimated as 200 nanometers.

#### *Fabrication of micro- and nanowires via electrodeposition*

The standard electrodeposition process was used for filling the pores and obtaining of replicas. Different types of metals – Cu, Ag, Ni and Co were used for filling of the pores. Specific features of galvanic processes in these cases were investigated. Different types of cells were utilized and the influence of ultrasound treatment was tested. All the samples obtained had the following parameters (SEM-testing): the diameter -  $0.1\text{--}2.0\text{ }\mu\text{m}$ , the height - up to  $10\text{ }\mu\text{m}$  (for cylindrical wires); the base -  $0.1\text{--}1.5\text{ }\mu\text{m}$ , the height - up to  $5\text{--}10\text{ }\mu\text{m}$  and the cone angle- $5^\circ\text{--}25^\circ$  (for conical wires).

All processes of electrodeposition were done in potentiostatic regimes (at constant potential) with recording the dependence of current on time.

For copper the standard electrodeposition process (electrolyte:  $\text{CuSO}_4$  -  $135\text{ g/l}$  and  $\text{H}_2\text{SO}_4$ - $15\text{ g/l}$ , room temperature) was used for filling the pores and obtaining of replicas. Specific features of electrodeposition into the dead-end pores of conical shape is that in this case we have to carry out all the procedures (vacuum deposition of conductive layer and electrodeposition of metal) at one side of the membrane. A short ultrasound treatment (before the electrodeposition) improved the homogeneity of obtained ensembles- probably because of removing of air bubbles out of the pores. The dependences of current on time for deposition of copper into the matrixes with cylindrical and conical pores were measured.

Other results are for deposition of cobalt into the cylindrical pores of template matrix. In contrast to copper, cobalt is deposited with high cathodic overpotential. Electrodeposition of cobalt can hardly be obtained under low overpotential because of low rate of cobalt ions discharge. However, too high overpotential will cause abundant hidrogen discharge because of low concentration of cobalt ions in the cathodic layer. The higher is the concentration of cobalt, the higher rate of reaction (and overpotential) is allowed, that is why an electrolyte with high concentration of cobalt was used :  $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ - $320\text{ g/l}$ , boric acid- $40\text{ g/l}$ , temperature  $40\text{--}45\text{ }^\circ\text{C}$ . Since the electrolyte has no electro-conductive additives, the ions of cobalt are delivered to the cathode by both

processes: migration and diffusion, so the higher current densities can be reached.

**Dependence on potential.** It was shown that more negative potentials correspond to higher cathode currents, higher growth rate of metal rods and less time required to complete filling the pores with the metal. This dependence is monotonic. Overgrowing time depends slightly on the pore diameter in the examined range of diameters.

**Dependence on the pores diameter.** The growth rate remains approximately constant in the process of metallization of pores with diameter of 0.5 microns at potentials -555, -530, -505 mV, and at more negative potentials (-580, -630, -680 mV) it increases slightly with time. The independence of current on time at this phase indicates that the diffusion of metal ions from the depths of electrolyte being balanced with consumption of discharging ions by the cathodic process. When filling pores of a small diameter the current dependence on time passes through a minimum, especially pronounced for smaller diameter pores, where the relative slowdown is most significant. Thus, in the pores of small diameter (0.1 and 0.2 microns) the effect of deceleration of the wires growth rate is observed in the process of electrofilling the pores. At the same time, the curve "current – time" is linear. It can be supposed that the difficulties, appearing while filling micro- and nanosized pores, are related to the peculiarities of diffusion in narrow channels.

It should be noted also the high current densities, which occur when metal is being deposited into micro- and nano-sized pores – up to  $100 \text{ A/dm}^2$ . At the same time the current density establishes at  $15 \text{ A/dm}^2$  (for growing metal fills the whole surface of the sample). The additional investigation are needed to explain this effect.

The investigation of Co deposition into the conical pores is now in progress.

#### *Mass-spectra, optical properties and stability*

In our previous works the possibility of ion-beam formation (for the molecules of the probe, deposited on such surface with microwires) in the Mass-spectrometer was demonstrated. In this work the peculiarities of this ion emission were investigated. The surfaces with copper wires were used as the substrates for deposition of the probe in mass-spectrometer. We found that using of such a surface leads to increasing of the signal of mass-spectra (to compare with the flat copper surface). Conical wires with rather low surface density and aspect ratio 2-5 demonstrated the highest emission efficiency. It was found that intensity of mass-spectra signal non-linearly increases with increase of probe concentration and the intensity of laser pulse. At the same time this intensity decreases with the increasing of surface density of wires-possible, because of superposition, overlapping of the fields of neighboring wires.

Raman spectra of some probes deposited on such surfaces were also investigated – and increasing of the signal was detected. These effects could be connected with increasing of electrical field tension near the ends of NWs – due to so-called “lighting rod effect”. The effect of the samples destruction, degradation was also found and tested: after 100 pulses we observed melting and bending of wires. This process could be the reason of rather low efficiency and instability of ion emission.

#### *Composite material –AFM investigations*

Just after the deposition we obtain metal wires embedded in polymer matrix – this “composite material” is rather perspective. In our opinion it could be used in some practical application. Moreover it gave an additional possibility to investigate metal wires by AFM: it was done by using tapping and contact modes. For samples with wire diameters 100 nm and 50 nm conductivity was investigated. The I-V dependences (for single wire) were measured and demonstrated the linear character. Using these data two specific resistances were estimated –  $1.8 \cdot 10^{-3}$  ohm · m and  $2.5 \cdot 10^{-3}$  ohm · m (correspondingly).

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