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Micro and nanorods of alkali halides grown in polymer templates

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Porous membranes containing cylindrical pores with diameters ranging from a few tens of nanometers to a few tens of micrometers were prepared by using the ion track technique. Swift heavy ions (e.g. Au with 11.4 MeV/nucleon specific energy) were used for creating the ion tracks in polycarbonate foils. Etching was performed using an aqueous solution of NaOH containing methanol. The growth of the alkali-halides micro- and nanorods was performed by evaporation from a saturated solution. The rods were imaged using scanning electron microscopy. The method opens up the possibility of growing nanostructures with applications as nanolaser media or nanoscintillators.

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1. Introduction

Nanorods and nanowires of a wide range of materials - including a variety of organic and biological compounds, but also inorganic oxides, metals, and semiconductors - can be processed using electrochemical and self-assembly techniques.

Arrays of nanorods, nanotubes or nanowires have potential applications in a wide variety of areas, including optoelectronics, data storage, and sensing [1]. Nanorods with radius from few nanometers to a few tens of nanometers exhibit unique properties relative to bulk structures due to their small size, which leads to large surface-to-volume ratios and size-dependent effects. In close-packed arrays of uniform-diameter nanorods, these properties can be used for applications requiring high signal or density. Assembly of nanorods arrays in polymers templates allows a high degree of control of the structure during growth. Additionally, the arrayed nanorods can be directly incorporated into devices.

The template approach, used for our study, consists in filling the pores of an etched ion track membrane, prepared by heavy ion irradiation and chemical etching, with the desired material by different methods [2-4]. The solution crystallization method which we employ in the present study was already used for the growth of KI micro and nanorods [5].

Alkali halide (KCl and NaCl) cylindrical nanorods were grown in etched track polymers templates from solution by crystallization process. The materials used are very soluble in water and crystallizes in normal conditions. Therefore, their growth behavior was chosen as a model in this investigation for future studies on oriented growth of nanorods and nanowires. The morphological properties of the nano and micro rods were investigated using scanning electron microscopy.

2. Experimental

Polycarbonate foils 100 and 30 micrometers thick were irradiated with swift heavy ions with the specific energy of 11.4 MeV/nucleon at the UNILAC linear accelerator (GSI Darmstadt). The fluences employed were in the range $10^5 – 10^8$ ions/cm^2.

The ion tracks were etched using an aqueous solution of 5 MNAOH containing 10% methanol at 50°C. This resulted in micro and nanoporous membranes containing cylindrical pores with a surface density corresponding to the ion fluence (i.e. for each ion track one pore is obtained) and with different diameters, depending on the etching time.

The growth of the alkali-halide rods was performed from their saturated solutions. The membranes were placed on the surface of the growth solution and left to float. Evaporation occurred under ambient conditions and crystallization of the alkali halides started when a certain supersaturation was obtained. The membranes were removed from the solution after several days and left to dry on filter paper.

The observation of the structures was performed by means of scanning electron microscopy after the partial removing of the growth template by dissolving it in dichloromethane.

3. Results and discussion

The ion track technique allows the fabrication of membranes with uniform pores with different geometrical characteristics. It is a versatile technique which gives the possibility of preparing templates where the diameter of the pore and their surface density can be chosen as suited for the experiment. However the range of diameters for the pores varies from a few tens of nanometers to a few tens of micrometers, i.e. three orders of magnitude. In order to obtain membranes with the highest pore density one has to correlate this two dimensions in order to obtain optimal results. In our experiments we used membranes with pore densities ranging from 10^5 cm^{-2} for pores with large diameters (larger than 10 micrometers) to pore densities of 10^8 cm^{-2} for smallest pore diameters.

We found that for the etching conditions we employed cylindrical pores are obtained for the solution containing 5 M NaOH containing and 10% methanol at 50°C. The addition of methanol to the etching solution is necessary in order to obtain pores with smoother walls, this resulting in rods with higher morphological quality. For the above mentioned composition of the etching bath and etching temperature the diameter of the pores increases with approximately 2 micrometers per hour.

After preparing the porous membranes these are placed on the surface of the growth solution (a saturated solution of KCl respectively NaCl). After left in ambient conditions for several days, due to evaporation the crystallization occurs both in the solution and also on the surface of the membrane and inside the pores.

In Fig. 1 one can observe crystals of KCl grown on the surface of a porous membrane, on top of the alkali halide nanorods.

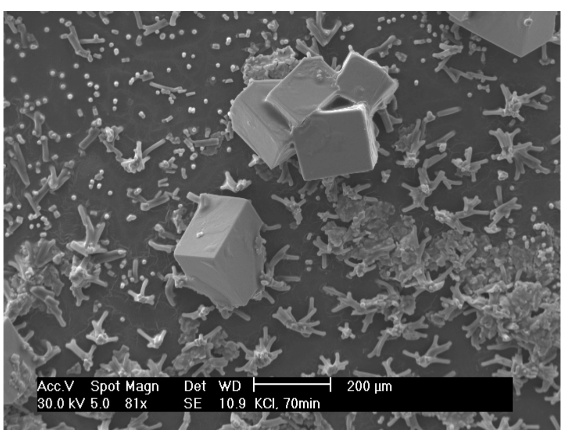


Fig. 1. KCl crystals grown from solution on the surface of a porous membrane.

The same growth process takes place inside the pores of the membrane. In Fig. 2 arrays of alkali-halide rods are presented. Some plastic properties appeared on alkali halide rods of micrometrical size. During the dissolving of the polymer matrix the rods can be mechanically bent as it is shown in Fig. 2. b.

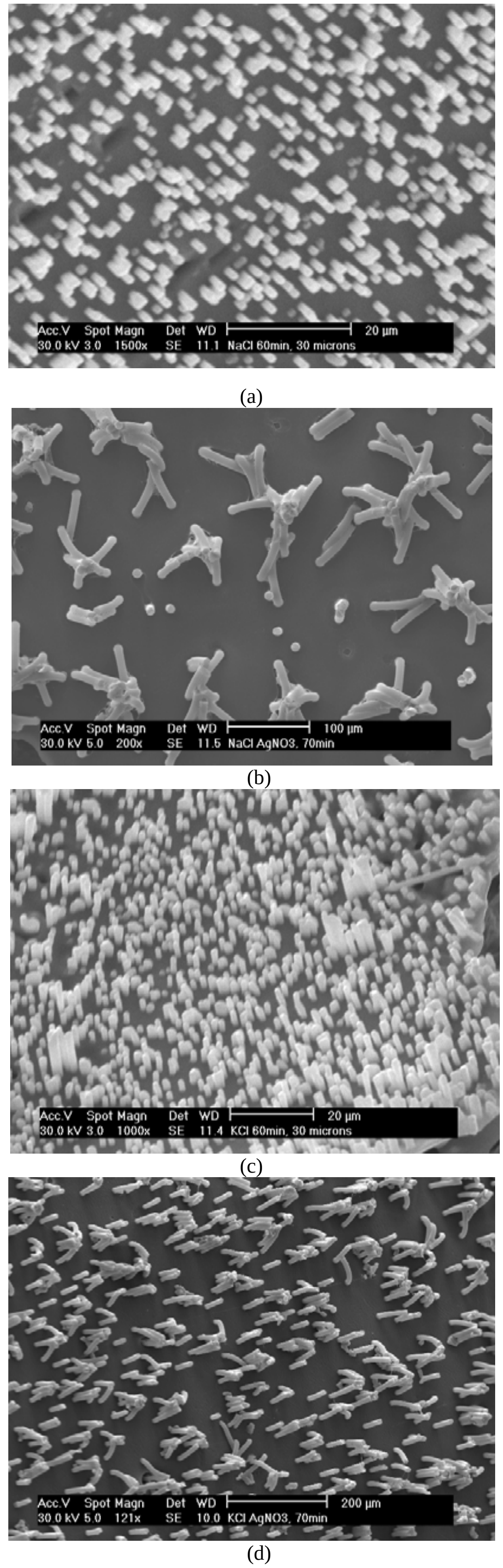


Fig. 2. Arrays of NaCl (a), (b) and KCl (c), (d) rods grown from solution in porous membranes.

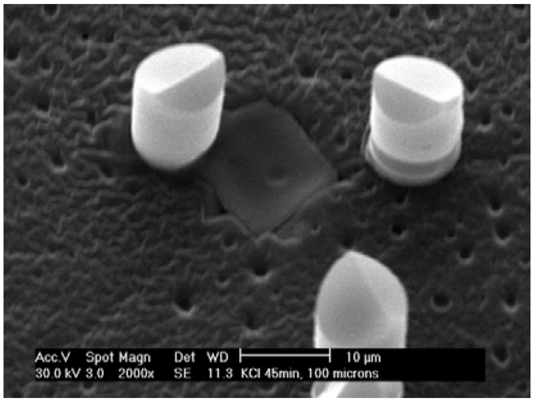
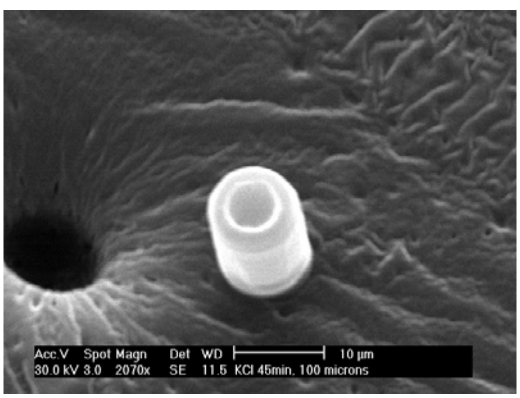


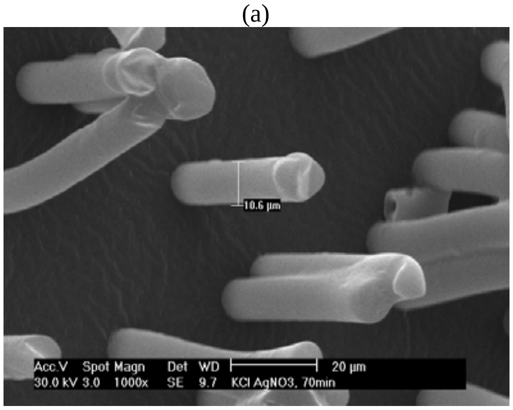
Fig. 3. Facets show single crystal growth tendency for restricted pore geometry (KCl rods).

Due to the restricted geometry of the pores, for such materials where the single crystal growth tendency is high, we expect to obtain also single crystal rods inside the material. Indeed, we observed facets for the micro-structures which are a clear indication of high ordered growth (Fig. 3).

Some interesting phenomena which were observed earlier by Dobrev and coworkers [5] for KI rods were observed also in this case. Thus, in some cases hollow structures were formed due to some morphological instabilities of the growth, while for some of the structures bending occurs after dissolving the template (Fig. 4).



(a)



(b)

Fig. 4. (a) Hollow KCl rod; (b) microrod array where a bended KCl structure can be observed.

4. Conclusions

The template method is a versatile approach in preparing highly uniform micro and nanostructures. The method was usually employed in performing electrochemical growth of micro and nanowires of metals and semiconductors.

We applied solution growth to fabricate micro and nanorods of alkali halides, namely NaCl and KCl.

The growth process shows a strong tendency towards single crystalline structures. In some cases tubes were obtained. The behaviour of such microscopical objects, with high aspect ratio is in some cases different when compared to the case of bulk crystals. As an example bent rods were observed after dissolving the polymer template.

Such structures have high potential impact. One example is the possibility to fabricate micro and nano lasers as it was recently proven for ZnO nanowires [6].

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