Etched Single-Ion-Track Templates for Single Nanowire Synthesis

N. Chtanko,* M. E. Toimil Molares, T. Cornelius, D. Dobrev, and R. Neumann

Gesellschaft für Schwerionenforschung (GSI), Planckstrasse 1, D-64291 Darmstadt, Germany

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Polycarbonate membranes with one pore only are created by the track-etching technique. The shape and size of the pore are determined by the type of etchant as well as by the temperature and etching time. The dynamics of single-pore formation during etching is investigated to determine the breakthrough time and the track-etching rate. The pore is characterized by electrical conductivity measurements and scanning electron microscopy. This kind of template is employed for the electrochemical deposition of a single bismuth wire that is left in the polymer for further measurements of its electrical properties.

Introduction

In recent years, nanowires have attracted considerable attention because of their extraordinary physical properties and enormous potential for applications in numerous fields of research and technology.¹⁻³ Among the methods widely used to create nanowires, electrochemical deposition in the pores of ion-track polymer membranes turned out to be very suitable.^{4,5} These membranes are produced by the irradiation of foils with energetic heavy ions and subsequent chemical etching of the so-called latent tracks (i.e., the extremely narrow damage zones created along the ion trajectories). By varying the ion fluence and the etching conditions, pores of different sizes and geometries and with area densities up to 10^9 pores/cm² are feasible. Because the material deposited in a pore acquires the exact pore shape, this template technique enables the fabrication of wires with various shapes, in particular, conical or cylindrical. The highly selective etching of tracks in polycarbonate makes it possible to produce membranes with pore diameters down to about 10 nm.6

Until now, most publications presented results concerning the synthesis and study of metallic nanowires deposited in multitrack membranes.^{7–10} The irradiation of a target with one heavy ion only, a technique available at the UNILAC linear accelerator of GSI, provides, after track etching, membranes containing a single channel. This article reports procedures suitable for the fabrication of single-channel templates with diameters ranging from 400 down to 50 nm and with well-defined geometry. Electrochemical deposition in these membranes allowed us to generate and contact single nanowires with low-ohmic contact resistances. We chose Bi because exceptional electronic features are expected to occur with decreasing wire dimensions.^{11–12} The first studies of how electrical properties of Bi nanowires differ from those of the macroscopic bulk were presented recently.²¹

Experimental Methods

Polymer foils were irradiated normal to the surface by Xe, Au, and U ions of energy 11.4 MeV/u at the UNILAC. The samples consisted of stacks of either four Makrofol KG foils of thickness 20 μ m or three Makrofol N foils of thickness 30



Figure 1. Schematic of the cell used for cylindrical pore etching and wire electrodeposition. (a) Etching in 2 M NaOH at 40 °C, applying 400 mV. (b) Electrochemical deposition of a Cu layer after the sputtering of a gold layer. (c) Bi single-wire deposition.

 μ m (both materials from Bayer AG, Leverkusen). Predetermined by the technology used for production (cast process), the foils had a glossy (smooth) and a matte (rough) side.

To produce membranes containing one single pore, a metallic mask with a circular aperture of diameter 0.1 mm at its center was placed in front of each sample. The signal of a semiconductor detector behind the sample, created by the first ion passing through the foil stack, was used to prohibit the impact of further ions by blocking the accelerator beam within 15 ms.

To achieve cylindrical pores, we irradiated each foil prior to etching with UV light, thus increasing the track etching selectivity (i.e., the track-to-bulk etch-rate ratio, V_T/V_B .)⁶ The etching and electrodeposition processes were both performed in an electrochemical two-compartment cell (Figure 1). After inserting the foil, we filled both compartments with aqueous 2 M NaOH solution and kept them at 40 °C; we then applied a voltage of 400 mV between two Au electrodes immersed in the etchant on both sides of the foil as shown in Figure 1a. The process of pore opening and growth was monitored by recording the electrical current. After etching, the cell was flushed with distilled water, subsequently filled with 1 M KCl (pH 7), and the electrical conductance was measured using Ag/AgCl electrodes. Assuming a cylindrical shape, the result was used to

^{*} Corresponding author. E-mail: n.chtanko@gsi.de. Phone: (49) 6159-71-21-71. Fax: (49) 6159-71-21-79.



Figure 2. Schematic of the cell used for conical pore etching and wire electrodeposition. First procedure: (a) Electrochemical deposition of a Cu layer after the sputtering of a gold layer on the rough side of the foil. (b) Etching in 9 M NaOH with 30% methanol at 30 °C, applying 100 mV. Second procedure: (c) Etching in 2 M NaOH with 40% methanol at 50 °C with stopping solution from the opposite foil side (rough side with the gold layer). (d) Electrochemical deposition of a Cu layer. (e) Bi single-wire deposition in both procedures.

calculate the effective diameter $d_{\rm eff}$ of a single pore according to¹⁸

$$d_{\rm eff} = \left(\frac{4l}{\pi\kappa R}\right)^{1/2}$$

where l is the thickness and R is the resistance of the cell and κ denotes the specific conductivity of the 1 M KCl solution, amounting to 10.2 S m⁻¹ at 20 °C. The uncertainty of the pore diameter ($\Delta d_{\rm eff}$) was calculated, taking into account the errors of contributing experimental parameters (current, voltage, foil thickness, and specific conductivity). The sample was taken out of the cell, rinsed, and dried, and a gold layer was sputtered on the matte side using an Edwards Sputter Coater S150 B. Afterward, the foil was returned to its former place in the cell. A Cu layer was then deposited electrochemically (Figure 1b) onto the gold and served as a cathode during the subsequent electrodeposition of Bi. The deposition into a single pore was performed at 50 °C using a Bi electrolyte with a Bi anode immersed into it at voltages from 20 to 50 mV between this anode and the copper layer (Figure 1c). The resulting wires were almost cylindrical, confirming a large $V_{\rm T}/V_{\rm B}$.

Two procedures were employed for the generation of conical Bi nanowires (Figure 2). In both cases, we decreased V_T/V_B by a controlled increase of $V_{\rm B}$. The first technique allowed us to obtain single conical wires with a large opening angle. After sputtering a 100-nm gold layer on the rough foil side, the sample was inserted into the electrochemical cell, and the gold layer was reinforced with several micrometers of Cu (Figure 2a). Then, the single track was etched from the uncoated side with 9 M NaOH in H₂O + CH₃OH (7:3 or 8:2 v/v) at 30 °C, applying 100 mV with the positive potential at the Au electrode in the etchant (Figure 2b). To obtain a single pore with small opening angle, we used a second procedure as follows. After sputtering gold on one side of the PC foil, we filled one-half of the cell with 2 M NaOH in $H_2O + CH_3OH$ (6:4 or 7:3 v/v) and the other half with $KCl + H_2O + HCOOH$ (Figure 2c) that was in contact with the gold-coated side and served as stopping solution.¹³ In both cases, etching was stopped when registering



Figure 3. Typical etching curve of single ion track. Etching occurred from both sides of the foil (20- μ m Makrofol KG) in 2 M NaOH at 40 °C and a voltage of 400 mV. The arrow indicates the breakthrough.



Figure 4. Current (a) and charge (b) as a function of time for Bi wire deposition in a cylindrical single pore (diameter 130 nm) in polycarbonate Makrofol KG, thickness 20 μ m. The deposition occurred at 30 mV at 50 °C.

a certain current through the etched pore. After etching, a Cu layer was deposited on the gold (Figure 2d). In both procedures, bismuth nanowires were electrodeposited potentiostatically (Figure 2e) in the single pores at 50 °C using the following electrolytes: the Bi solution contained 0.2 M BiCl₃, 0.3 M tartaric acid, 0.2 M NaCl, 1.3 M HCl, and 100 g/L glycerol;¹⁴ the Cu solution consisted of 238 g/L CuSO₄·5 H₂O and 21 g/L H₂SO₄; the stopping solution was prepared by mixing 2 M KCl and 2 M HCOOH (1:1 v/v). The water contact angles were measured for original polycarbonate foils using an optical microscope (model Biolam, LOMO, Russia). The current flowing between the two electrodes was monitored by a Keithley 6485 picoammeter.

Results and Discussion

1. Etching of Single Cylindrical Pores and Bi Wire Deposition in Makrofol KG. The main disadvantage of polycarbonate templates is the hydrophobicity of these materials



Figure 5. Morphologies of caps on top of Bi single wires ($d_w = 200$ nm) deposited at 50 °C and different voltages: (a) 50 mV, (b) 20 mV.

5 µm

Acc.V Spot Magn Det WD Exp

and, as a result, the difficulty of filling the pores for conductivity measurements and the electrodeposition procedure.^{16,17} Our measurement of the water contact angles for both types of pristine Makrofol resulted in 74 and 84° for KG and N foils, respectively. The Young–Laplace capillary pressure *P* depends significantly on the wetting contact angle according to

$$P = 2\gamma \cos \frac{\theta}{r}$$

where γ is the surface tension, θ is the wetting contact angle, and r is the radius of the capillary. An increase of θ from 74 to 84° changes the capillary pressure by a factor of 5 at the same capillary radius. This means that filling the pores with aqueous solutions would occur much more easily in the case of Makrofol KG. However, one should take into account that the contact angles have been determined macroscopically, whereas on a microscopic scale, θ may fluctuate and thus exceed the critical limit of 90°. Such fluctuations can be due to heterogeneities (in topography and chemical composition) always present at a solid surface.¹⁹ Heterogeneities along the narrow pore can prohibit the imbibition of a liquid into the channel. For these reasons, we selected the more hydrophilic Macrofol KG for the fabrication of single thin cylindrical wires. Because of the wetting problems in pores, the wire diameters were limited to values larger than 80 nm.

The etching behavior of a single ion track is influenced by the fact that the energy loss of the ion along its path is not smooth but fluctuates stochastically. Furthermore, it also depends on the inhomogeneous structure of the polycarbonate



Figure 6. Etching of a single PC track in 9 M NaOH + 30% CH₃OH at 30 °C (a) and 2 M NaOH + 40% CH₃OH (b) with stopping solution at 50 °C, in both cases applying 100 mV.

foil originating from the production procedure.¹⁵ As a result, each single track showed individual behavior with regard to the time needed for perforation, in contrast to many-track samples (track densities of $10^6 - 10^9$ cm⁻²), which exhibited well reproducible current versus etching-time curves due to averaging over the large track number. Additional UV treatment before etching increased the etching selectivity and had a significant influence on the final pore shape and size.⁶ Some authors mention that "hard", thin surface layers on both sides of a polycarbonate foil influence the etching process.^{16,17} A problem that may arise is the occurrence of a "cigarlike" or tapered shape of the resulting pore in the polycarbonate. Such shapes would affect the electrochemical synthesis and properties of the wires. For the foils used in our work, we found this effect to be insignificant for pores with diameters around 100 nm. Our investigations, together with the use of selective etchant (aqueous 2 M NaOH), enabled us to produce cylindrical pores with high aspect ratios.

The curve in Figure 3 displays the current recorded during two-sided etching of a single cylindrical pore. The breakthrough time indicated by a sharp current increase was 3 min, and the track-etching rate amounted to 3.3 μ m/min. For individual single pores etched from both sides, the opening time varied from 3 to 9 min, which corresponded to a track-etching rate $V_{\rm T}$ ranging from 1.1 to 3.3 μ m/min. The bulk etch rate $V_{\rm B}$ was about 1 nm/min, resulting in $V_{\rm T}/V_{\rm B} > 10^3$. A pore opening angle $\leq 0.05^\circ$ was calculated from arcsin($V_{\rm B}/V_{\rm T}$).

The electrodeposition process consisted of several steps. Parts a and b of Figure 4 show the current and charge versus time curves for the growth of single Bi wires of 130 ± 20 nm diameter in 20-µm-thick polycarbonate. At the beginning of the deposition (phase I), the current increased rapidly because of the charging of the electrical double layer. The immediately following decrease in the current indicated the formation of the diffusion layer. During the wire growth inside the pore (phase



Figure 7. Geometrical parameters, D_w (a) and d_w (b), of the Cu conical wires in Makrofol N as a function of etching time in 9 M NaOH at different concentrations of methanol at 30 °C, determined by SEM.

II), the current increased slightly. By registering the current during deposition (Figure 4a), we determined the end of wire formation inside the pore and the starting of cap growth (phase III) characterized by a very fast current increase.

Faraday's law determines the charge Q required to deposit a certain mass m of Bi

$$Q = mz \frac{F}{M}$$
 with $m = \rho \pi r_{\rm w}^2 l_{\rm w}$

where *M* is the molar mass of the deposited Bi, *z* is the valence of the Bi ions, *F* is Faraday's constant, ρ is the metal density, r_w is the wire radius, and l_w is the wire length. Integration of

the area under the experimental curve, shown in Figure 4b until the moment of the fast current increase, provided the total charge $Q_{\text{exp}} = 3.6$ nC. From Q_{exp} , we calculated a wire diameter of 128 ± 16 nm, in good agreement with the pore diameter of 130 ± 20 nm estimated from the conductance of the pore in 1 M KCl. The 16-nm error was mainly due to the uncertainty of the point in time at which the metal deposition into the pore was completed. After the growth of the single wire, the deposition was continued until a micrometer-sized cap was grown on top. As was shown earlier for Cu nanowires, the cap morphology indicates the wire crystallinity.²⁰ We controlled the crystallinity by varying the deposition voltage. Parts a and b of Figure 5 depict the caps of two Bi wires (200 nm in diameter) generated by applying 50 and 20 mV, respectively. A voltage decrease causes a smaller current density and leads to larger grains.

2. Etching of Single Conical Pores and Bi Wire Deposition in Makrofol N. For the fabrication of conical wires, we employed highly hydrophobic Makrofol N. In principle, the conical pore shape may help to eliminate the wetting problems in the process of electrodeposition. For a wetting angle close to 90°, the imbibition of a liquid into the pore is facilitated when the meniscus moves from a wider to a narrower part of the channel. To produce narrow conical channels, a NaOH solution with a certain amount of methanol was employed for the etching of single tracks from one side in Makrofol N. Figure 6a and b shows two etching curves of conical wires created using the procedures depicted in Figure 2. In the case of Figure 6a, a conical pore was etched at 30 °C from one side of the foil, employing 9 M NaOH with 30% methanol. The etching curve in Figure 6b was recorded during etching from one side of the foil at 50 °C in 2 M NaOH and by applying a stopping solution from the other side. The irregular current behavior after the breakthrough displayed in Figure 6b may be caused by the meeting of the etchant and the stopping medium, the fluctuation probably depending on the transient prevalence of electromigration or diffusion fluxes on consumption of highly mobile OH- ions in the neutralization reaction and on convection. After the breakthrough, the stopping solution neutralized the etchant, thus preventing the narrow part of the pore from fast growth. A series of etching experiments were performed with mul-

27.1 μm 50.9 nm 610 nm 610 nm 610 nm 610 nm

Figure 8. SEM image of a conical Bi wire with $D_w = 610$ nm and $d_w = 50$ nm.



Figure 9. SEM image of a slightly conical Bi wire with $D_w = 289$ nm and $d_w = 90$ nm.

tipore membranes under the same conditions as with the singlepore membranes to study the influence of methanol concentration on pore geometry. After the electrochemical Cu deposition and dissolution of the membrane in dichloromethane, the conical wires were imaged with SEM, and the large (D_w) and small $(d_{\rm w})$ diameters were determined. Figure 7 illustrates that the cone angle became larger when increasing the methanol concentration from 20 to 30%. Furthermore, parts a and b of Figure 7 show that for the same etching time a higher methanol concentration resulted in a larger $D_{\rm w}$, whereas there was almost no influence on d_w . The latter result was probably due to the electrostopping effect of a voltage applied between the two electrodes with the positive potential on the etchant side.¹³ We used the graphs in Figure 7 as calibration curves and indirectly deduced the geometrical parameters of single wires. Under these etching conditions, we obtained single conical wires, the narrowest having $d_w = 50$ nm and $D_w = 610$ nm, as illustrated in Figure 8. Etching at 50 °C provided pores with a smaller cone angle (probably due to the partial evaporation of methanol) than etching at room temperature and, accordingly, slightly conical wires as shown in Figure 9, with $d_w = 90$ nm and D_w = 289 nm. The wires depicted in Figures 8 and 9 resulted from multipore membranes.

Summary and Conclusion

In this work, we aimed at the fabrication of bismuth nanowires suitable for measurements of electrical properties, eventually visualizing quantum effects. Different procedures for the preparation of single metallic nanowires were developed. Two types of polycarbonate foils were tested as matrixes for the production of single-ion track templates. The dynamics of single-pore formation in both materials was studied by electrical conductivity measurements. The pore geometry was controlled by the etching mode (one-side or two-side), alkali concentration, and methanol content in the etching solution. Cylindrical and conical single pores with diameters between 50 and 400 nm were filled with Bi by electrochemical deposition. The size and shape of the conical single pores and wires were determined by means of SEM from etching and electrodeposition experiments with multitrack membranes. Bismuth single wires, embedded in polymer, can be employed to find a correlation between diameter and electrical resistance. The creation of single wires with diameters <100 nm should be achievable with more hydrophilic polymers.

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