

- [10] G. A. Flores, J. Liu, M. Mohebi, N. Jamasbi, *Int. J. Mod. Phys. B* **1999**, *13*, 2093.
 [11] M. Seul, D. Andelman, *Science* **1995**, *267*, 476.
 [12] C. Y. Hong, H. E. Horng, I. J. Jang, J. M. Wu, S. L. Lee, W. B. Yeung, H. C. Yang, *J. Appl. Phys.* **1998**, *83*, 6771.
 [13] K. T. Wu, Y. D. Yao, *J. Mag. Mag. Mater.* **1999**, *201*, 186.

Single-Crystalline Copper Nanowires Produced by Electrochemical Deposition in Polymeric Ion Track Membranes**

By Maria Eugenia Toimil Molaes, Veronique Buschmann, Dobri Dobrev, Reinhard Neumann,* Roland Scholz, Ingrid U. Schuchert, and Johann Vetter

In the recent past, investigations have focused increasingly on confined systems with micrometer and, in particular, nanometer dimensions. Due to their restricted size, these structures exhibit novel physical and chemical properties, and have opened up a large new field of basic research as well as possible applications. Electrochemical deposition is becoming an increasingly attractive method for the synthesis of new materials and nanostructures.

Electrochemical deposition has been used to synthesize nanomodulated ceramic superlattices, suitable for the occurrence of thickness-dependent quantum optical, electronic, and optoelectronic effects;^[1] quantum-confined metal/semiconductor nanocomposites;^[2] and copper(I) oxide films.^[3] Further representative examples of present developments include copper microwires as a new generation of interconnections in high-performance multichip modules^[4] and, with diameters on the nanometer scale, magnetic multilayered wires showing giant magnetoresistance,^[5] macroscopic high-density arrays of parallel nickel needles acting, for example, as infrared polarizers,^[6] and superconducting lead nanowires.^[7]

In several studies, electrodeposition in ion track membranes (template method) has been used to create large two-dimensional arrays of wires and tubes of different kinds of metals.^[8–12] In particular, copper single crystals were grown in template pores of micrometer size at room temperature by using commercial baths and reverse pulse plating in ultrasonic fields.^[13] In this communication, we report the fabrication of cylindrical poly- and single-crystalline copper wires,

by means of the template method, with diameters between 60 and 500 nm and aspect ratios (length to diameter) up to 500. Further, we present the result of a systematic study aimed at determining the critical DC deposition parameters required for single-crystalline growth. These wires provide the possibility of comparing nanometer-scale characteristics of poly- and single-crystallinity with respect to electric current flow, acoustic wave propagation, and other transport phenomena.

The procedure for forming copper nanowires consists of several steps, as illustrated in Figure 1. Polycarbonate foils (Makrofol N, Bayer Leverkusen) of circular shape (thickness

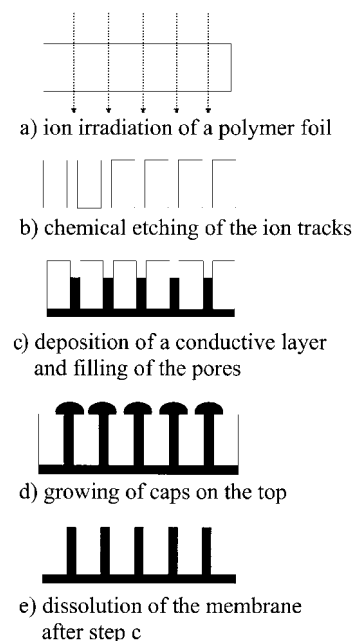


Fig. 1. Scheme of the template method.

30 μm , diameter 5 cm) were irradiated at the UNILAC (Universal Linear Accelerator) of GSI, Darmstadt, with highly charged ^{197}Au and ^{208}Pb ions having kinetic energies of 1–2 GeV and fluences between 10^6 and 10^9 ions/ cm^2 . Due to energy loss through interaction with the target electrons, each ion creates along its trajectory a cylindrical damage zone a few nanometers in diameter. The damaged material can selectively be removed by chemical etching, resulting in pores of cylindrical geometry.^[14] Composition, concentration, and temperature of the etching solution determine the size and geometry of the resulting pores, the pore diameter increasing linearly with the etching time. A 6 N NaOH solution containing 10 % methanol at $T = 50^\circ\text{C}$ was employed for 2–12 min to produce pore diameters between 60 and 500 nm. A thin gold film was sputtered onto one side of the membrane and reinforced electrochemically with copper to obtain a stable substrate, suitable for the growth of the needles. This conductive side served later as the cathode in a two-electrode electrochemical cell.^[8] The inner diameter of a Teflon ring placed on the membrane determined the size of the area in contact with the electrolyte, in our case 8 cm^2 .

[*] Prof. R. Neumann, M. E. Toimil Molaes, Dr. D. Dobrev, I. U. Schuchert, Dr. J. Vetter
 Gesellschaft für Schwerionenforschung (GSI)
 Planckstrasse 1, D-64291 Darmstadt (Germany)
 E-mail: r.neumann@gsi.de

Dr. V. Buschmann
 Technische Universität Darmstadt
 Petersenstrasse 23, D-64287 Darmstadt (Germany)

Dr. R. Scholz
 Max-Planck-Institut für Mikrostrukturphysik
 Weinberg 2, D-06120 Halle (Germany)

[**] Financial support from the Deutscher Akademischer Austauschdienst (DAAD) is gratefully acknowledged by one of the authors (METM).

It is known that for flat anodes the metal is deposited preferentially at the outer border areas of the cathode.^[15] This effect was avoided by using a conical copper (containing traces of phosphor) anode, leading to a noticeably more homogeneous copper distribution over the whole cathode surface. During the deposition process, the copper bath was mechanically stirred using a small motor. Two different solutions were tested: a commercial electrolytic copper bath (Cupatierbad, Riedel Company) and a simple-salt electrolyte that consisted of an aqueous solution containing 238 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 21 g/L sulfuric acid. A high concentration of CuSO_4 was used to supply a sufficiently large number of ions inside the pores during the deposition. Sulfuric acid was added to increase the conductivity of the solution and to lower the cathode over-voltage.^[16] The electrodeposition was performed potentiostatically at temperatures between 25 and 70 °C with low over-voltages applied. The low overvoltages avoided side reactions such as hydrogen evolution. Subsequently, the membrane was dissolved in dichloromethane in order to image and characterize the copper nanowires by scanning electron microscopy (SEM). In the case of the thinnest wires, after removing the membrane, we folded the sample in such a way that the wires located at the kink became accessible to transmission electron microscopy (TEM).

In order to follow the deposition process, the current was recorded as a function of time. Figure 2a shows the current versus time curves for different voltages applied between cathode and anode at $T = 50\text{ °C}$. The measurements were performed on membranes irradiated under the same conditions and etched simultaneously (fluence 10^6 ions/cm², pore diameter 500 nm). Typically, four different zones (I–IV) can be distinguished as indicated in the inset of Figure 2a. After immersion of the sample in the electrolyte, no external voltage is applied until the open-circuit voltage between cathode and anode stabilizes at a value of about -10 mV. Then, when a potential is applied, the current exhibits a sharp increase (I) that is ascribed to the charge of the electrical double layer. The reduction of Cu^{2+} ions directly located at the cathode surface creates a concentration gradient that causes a flux of ions towards the cathode. In this process, the decrease of current indicates the formation of the diffusion layer.^[17] During the growth of the copper needles in the pores, the current remains nearly constant (II) until the wires reach the polymer surface. When this happens, caps start to grow on top of the needles (see Fig. 1d), and owing to the increased surface the current increases (III). Once caps are growing on the surface, the current continues to increase very slowly (IV). It approaches the value obtained when Cu is being deposited at the same voltage on an electrode with the size of the polymer surface exposed to the electrolyte. The $I-t$ curves displayed in Figure 2a reveal these four distinct zones. As given by Faraday's law, the integral of the current versus time curves between the beginning of the deposition and the transition to zone III corresponds in all cases to the total charge necessary to fill up all the pores. This dependence was used as an indication that homogeneous growth occurred on the whole sample.

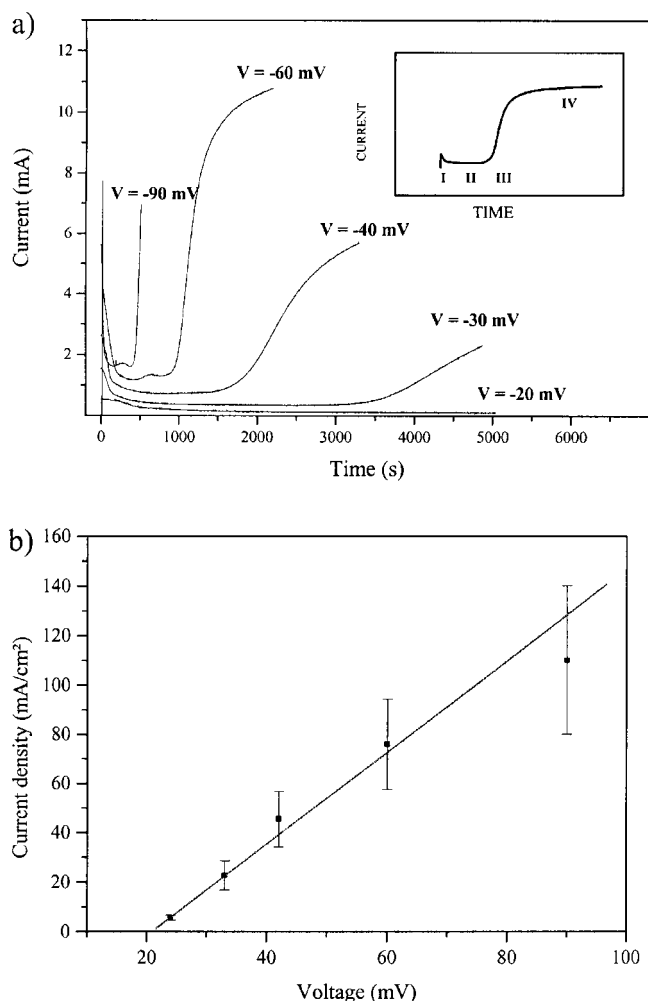


Fig. 2. a) Current versus time curves for different applied voltages at 50 °C. The inset indicates four distinct zones: I) charging of the electrical double layer and formation of the diffusion layer; II) filling of the pores; III) start of growth of caps on the wires protruding from the foil; IV) lateral growth of metal on the polymer surface. b) Current as a function of the cell voltage during the growth of the needles inside the pores. The errors originate mainly from uncertainties in S_{eff} .

The transition between growth of the wires and macroscopic growth on the polymer surface is, as expected, faster the higher the voltage applied between the electrodes. The current densities measured at different voltages during the deposition of copper in the pores were calculated by dividing the current in zone II by the effective surface, $S_{\text{eff}} = fsS$ (where f denotes the pore density, s the cross-sectional area of one pore, and S the polymer surface exposed to the electrolyte). Figure 2b illustrates the linear increase of the current density for low voltages. This voltage range represents the region of significance for the production of single crystals.

During electrochemical growth of the copper needles, two mechanisms occur simultaneously: i) growth of existing nuclei and ii) nucleation followed by formation of new grains. For the creation of single crystals the first process should dominate. The two processes compete with each other and depend on several parameters.^[18] In the experiments reported here, the influence of current density, temperature, and type of

electrolyte on the resulting crystallinity of the needles has been studied in detail. Figure 3 shows SEM images of the tips of three different needles obtained after dissolution of the

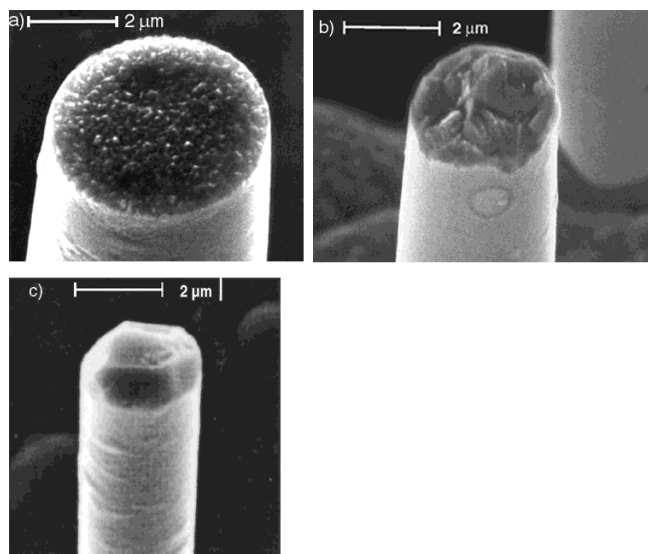


Fig. 3. Copper needles formed at a current density of 15 mA/cm². Different morphologies were obtained at different temperatures: a) polycrystalline needles at room temperature, b) larger grain sizes at $T = 40\text{ }^{\circ}\text{C}$, c) single-crystalline morphology at $T = 60\text{ }^{\circ}\text{C}$. Scale bars: 2 μm .

polycarbonate membrane in CH₂Cl₂. The wires were deposited at the same current density, $j = 15\text{ mA/cm}^2$, but at different temperatures of the commercial bath (Cupatierbad). At room temperature (Fig. 3a), fine-grained polycrystalline needles were created. At 40 °C (Fig. 3b), the needles were still polycrystalline but with larger grains. Finally, at 60 °C (Fig. 3c), the facets on the tip indicate single crystallinity.

The presence of specific additives, for example brightening agents, in commercial electrolytes is well known. They are easily adsorbed at the cathode surface, increasing the electrode polarization (higher cathode over-voltage) and, subsequently, decreasing the grain size of the deposit.^[19] Our results show that this effect of the commercial electrolytes can be compensated by varying the deposition parameters adequately.^[13] The increased temperature obviously leads to a decrease of the cathode polarization, to a more efficient transport of the ions towards the electrode, and to an increase of the surface diffusion. According to our findings, these three factors favor the growth of pre-existing nuclei and therefore the deposition of single crystals rather than the creation of new grains. We assume that the additives are responsible for the large variation of both the growth rate and the crystallinity of the wires between individual pores.

When the simple-salt electrolyte is used, the copper deposition occurs at an approximately constant rate in all the pores over the whole sample, as was pointed out when discussing Figure 2, and all wires show the same crystallinity. Single-crystalline wires were obtained at 50 and 60 °C for current densities below 35 mA/cm². SEM images (see Fig. 4a) of Cu needles deposited under the above mentioned conditions indi-

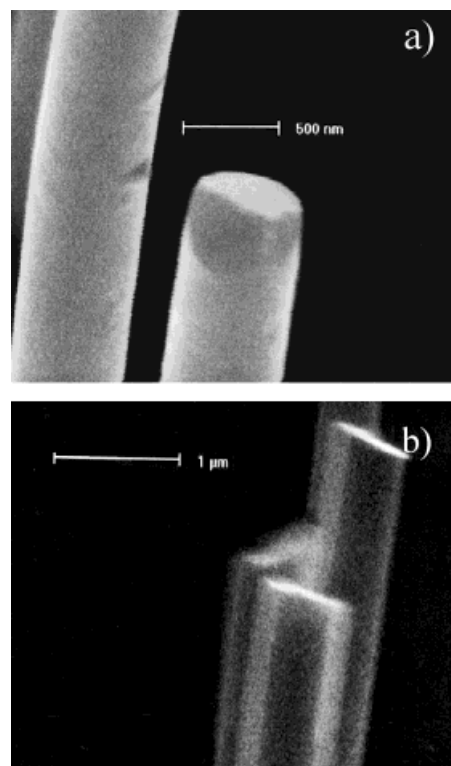


Fig. 4. SEM image of a copper wire indicating a single-crystalline structure. a) Cylindrical geometry (scale bar: 500 nm). b) Faceted geometry showing regular crystallographic structure at the outer faces (scale bar: 1 μm).

cate a single-crystalline structure. Figure 4b shows a special case ($T = 50\text{ }^{\circ}\text{C}$, $j = 9\text{ mA/cm}^2$), where the wire did not adopt the cylindrical pore shape but exhibits cubic crystallographic planes at its side walls. In this case, the metal growth was blocked before reaching the pore walls (perhaps due to passivation of the metal surface). Finally, decreasing the current density is equivalent to increasing the temperature, i.e., the deposition of large crystals is favored in both cases.

The thinnest wires (diameter < 200 nm) were also characterized by TEM. The results show that most of the wires are single crystalline, possessing very smooth homogeneous cylindrical contours. Figures 5a and 5b show 180 and 70 nm diameter needles, respectively. Selected-area electron diffraction

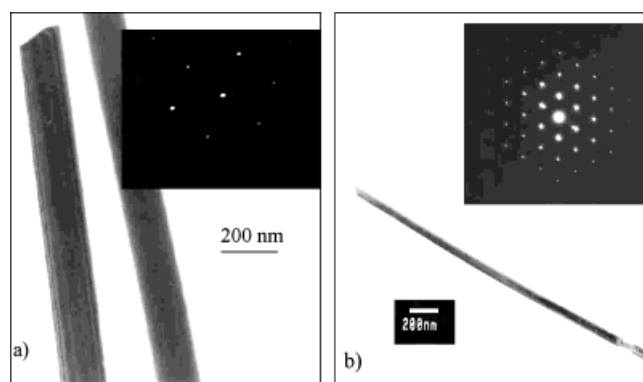


Fig. 5. TEM micrographs of single-crystalline sections of copper nanowires. The diameters are a) 186 nm and b) 70 nm. The electron diffraction patterns give evidence for the single-crystalline structure. Scale bar: 200 nm.

(SAED) patterns (see insets) and bright field/dark field imaging revealed the single-crystalline character of the needles. Figure 6a shows a TEM image of a twinned region, as found in some of the wires. Twinning is a crystal defect characterized

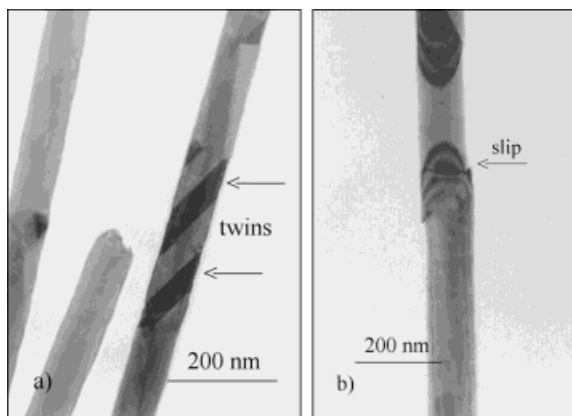


Fig. 6. Lattice defects in single-crystalline copper nanowires. a) Twin structure in a 70 nm wire. b) Slip in a 100 nm diameter needle. Scale bars: 200 nm.

by the partial displacement relative to the matrix of a considerable number of neighboring crystallographic planes,^[20] recognizable by the reduced brightness in Figure 6a. Twins can be created during the growth process or may result from plastic deformation. We also observed slips along the nanowires (Fig. 6b). They typically occur due to plastic deformation^[21] and, in our case, were probably produced when placing the wires on the TEM grid. It should be emphasized that both crystal defects observed here directly influence the mechanical properties of such wires.

To summarize, we have demonstrated DC potentiostatic deposition of single-crystalline copper nanowires in etched ion track membranes using a simple-salt electrolyte. An aspect ratio of 500 has been achieved by growing such needles with length 30 μm and diameters as small as 60 nm. Homogeneous large-density arrays of up to 10^9 wires/ cm^2 were produced on 8 cm^2 . Our method opens up the possibility of comparing the influence of poly- and single-crystallinity on transport processes in nanowires, for example the flow of electric current and propagation of sound waves. The associated sensitivity to corrosion in each case will be another subject of interest.

Received: June 20, 2000
Final version: August 29, 2000

- [1] J. A. Switzer, M. J. Shane, R. J. Phillips, *Science* **1990**, *247*, 444.
 [2] J. A. Switzer, C.-J. Hung, E. W. Bohannon, M. G. Shumsky, T. D. Golden, D. C. Van Aken, *Adv. Mater.* **1997**, *9*, 334.
 [3] Y. Zhou, J. A. Switzer, *Scripta Metall. Mater.* **1998**, *38*, 1731.
 [4] S. Krongelb, L. T. Romankiw, J. A. Tornello, *IBM J. Res. Dev.* **1998**, *42*, 575.
 [5] A. Blondel, J. P. Meier, B. Doudin, J.-P. Ansermet, *Appl. Phys. Lett.* **1994**, *65*, 3019.
 [6] M. Saito, T. Kano, T. Seki, M. Miyagi, *Infrared Phys. Technol.* **1994**, *35*, 709.
 [7] S. Dubois, A. Michel, J. P. Eymery, J. L. Duvail, L. Piroux, *J. Mater. Res.* **1999**, *14*, 665.
 [8] D. Dobrev, J. Vetter, N. Angert, *Nucl. Instrum. Methods B* **1999**, *149*, 207.
 [9] J. Vetter, R. Spohr, *Nucl. Instrum. Methods B* **1993**, *79*, 691.
 [10] J. C. Hulthen, C. R. Martin, *J. Mater. Res.* **1997**, *7*, 1075.

- [11] C. J. Brumlik, V. P. Menon, C. R. Martin, *J. Mater. Res.* **1994**, *9*, 1174.
 [12] L. Piroux, S. Dubois, E. Ferain, R. Legras, K. Ounadjela, J. M. George, J. L. Maurice, A. Fert, *J. Magn. Magn. Mater.* **1994**, *135*, L17.
 [13] D. Dobrev, J. Vetter, N. Angert, R. Neumann, *Appl. Phys. A* **1999**, *69*, 2333.
 [14] R. Spohr: *Ion Tracks and Microtechnology, Principles and Applications*, Vieweg, Braunschweig **1990**.
 [15] J.-C. Puipe, F. Leaman, *Theory and Practice of Pulse Plating*, American Electroplaters and Surface Finishers Society, Orlando, FL **1986**.
 [16] *Gmelins Handbuch der Anorganischen Chemie*, Verlag Chemie, Weinheim **1955**.
 [17] A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, Wiley, New York **1980**.
 [18] E. Budevski, G. Staikov, W. J. Lorenz, *Electrochemical Phase Formation and Growth*, VCH, Weinheim **1996**.
 [19] *Modern Electroplating* (Ed: F. A. Lowenheim), Wiley, New York **1974**.
 [20] G. Gottstein, *Physikalische Grundlagen der Materialkunde*, Springer, Berlin **1998**.
 [21] C. Kittel, *Introduction to Solid State Physics*, Wiley, New York **1976**.

Phosphorescence in Conjugated Poly(*para*-phenylene)-Derivatives**

By Dirk Hertel, Sepas Setayesh, Heinz-Georg Nothofer, Ullrich Scherf, Klaus Müllen, and Heinz Bässler*

Phosphorescence in organic molecules is due to the radiative decay of triplet excitons.^[1] Since this involves the spin-forbidden transition from the first excited triplet state (T_1) to the singlet ground state, the lifetime of T_1 is long compared to that of the singlet state (S_1). Unfortunately, trapping at defects, or bimolecular reactions of the triplet excitons (triplet-triplet annihilation, TTA) during the long lifetime often prevent efficient phosphorescence which has a spectrum red-shifted from the fluorescence by the amount of the exchange energy. Although electron-electron interactions are significant in conjugated polymers, phosphorescence, as one manifestation of such an interaction, is still a rare event, the exception being in the class of organometallic polyynes,^[2] where the enhanced spin orbit coupling through the heavy metal atom increases the intersystem crossing (ISC) rate. In conventional conjugated polymers information concerning the generation of triplet excitons and their properties has been inferred from triplet-triplet absorption experiments^[3-5] and optically detected magnetic resonance (ODMR) experiments.^[6] Considering the important role the triplet state plays as a non-radiative decay channel which limits the quantum efficiency of fluorescent light emitting diodes (LEDs), it is necessary to obtain information about the energetic position of T_1 and its

[*] Prof. H. Bässler, D. Hertel
 Institut für Physikalische, Kern- und Makromolekulare Chemie und
 Wissenschaftliches Zentrum für Materialwissenschaften
 Philipps-Universität Marburg
 D-35032 Marburg (Germany)
 E-mail: baessler@mail.uni-marburg.de
 S. Setayesh, H.-G. Nothofer, Dr. U. Scherf, Prof. K. Müllen
 Max-Planck-Institut für Polymerforschung Mainz
 Ackermannweg 10, D-55128 Mainz (Germany)

[**] We thank the Stiftung Volkswagenwerk and the Fond der Chemischen Industrie for financial support of this work. D. H. thanks Dr. A. Köhler for making [21] available prior to publication.