

**FABRICATION AND CRYSTALLOGRAPHIC CHARACTERIZATION OF
ELECTROCHEMICALLY DEPOSITED BISMUTH NANOWIRES**

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For solids of restricted geometry, classical and quantum size effects become observable when their dimensions approach the value of the electron mean free path l_e and the Fermi wavelength λ_F , respectively [1, 2]. For the semi-metal Bi, both these electronic parameters have large values ($l_e = 100$ nm at 300 K and $\lambda_F = 40$ nm) compared to normal metals, enabling the study of these effects in relatively thick nanowires. In particular, the classical size effects cause an increase of the electric resistivity which originates from electron scattering processes at the wire surface [3] and at grain boundaries [4]. In order to separate the influence of the grain boundaries, it is necessary to fabricate a series of nanowires, their structure varying systematically from poly- to single-crystallinity. This requires also a detailed crystallographic examination of the wires.

We fabricate poly- and single-crystalline Bi nanowires by electrochemical deposition (DC and AC) in etched ion-track polycarbonate (PC) membranes. For this purpose, we irradiate PC foils with swift heavy ions at the UNILAC linear accelerator of GSI. Afterwards, the foils are exposed to UV-light and subsequently etched in 6N NaOH at 50 °C. Thereafter, a gold layer (~100 nm) is sputtered on one side of the membrane and reinforced by an electrochemically deposited Cu layer. Both layers serve as cathodes during the then following nanowire deposition. The wires are created at diverse temperatures applying various overpotentials. When the needles reach the opposite surface of the template, caps start to grow on top.

We study the morphology and crystalline structure of the nanowires by means of scanning (SEM) and transmission electron microscopy (TEM), and x-ray diffraction (XRD). In Fig. 1, caps of wires deposited under different conditions are displayed. Compared with Fig. 1 (a), the cap in Fig. 1 (b) shows a remarkable increase of the grain size, caused by the elevated temperature and reduced overpotential during the fabrication. If depositing the wires at 60 °C, applying -20 mV (Fig. 1 c) or rather with reverse pulses (Fig. 1 d), the caps exhibit pronounced facets indicating single-crystalline needles underneath [5]. Depending on whether the fabrication is performed potentiostatically or with reverse pulses, the faceted caps have different shapes, suggesting different crystalline orientations in the wires.

The XRD examinations reveal that potentiostatically deposited Bi nanowires exhibit a (110) texture which becomes stronger for elevated temperature, smaller overpotential, and thinner nanowires. Samples with almost all crystals oriented normal to the (110) lattice plane are obtained for depositions at 60 °C, applying -17.5 mV (Fig. 2). In contrast, Bi nanowires fabricated with reverse pulses possess a (100) texture becoming more pronounced for shorter cathodic pulses and higher anodic voltages. In all cases, the trigonal axis is normal to the cylindrical wire axis, i.e., oriented along the smallest dimension of the structure, as in the case of Bi thin films and wires prepared by pressing liquid Bi into fine Pyrex capillaries [6]. Confirming the XRD results, TEM studies show that the strong textured nanowires, prepared at 60 °C, and -17.5 mV, consist of at least several μm long mono-crystals, the (110) plane being normal to the wire axis (Fig. 3). The direct image displays extinction contours but no grain boundaries.

The conjunction of cap morphology and wire crystallinity enables us to determine the crystal structure of a single bismuth nanowire. Additionally, the single wire creation [7] gives us the possibility to measure quantitatively the influence of the grain boundaries on the electrical resistivity.

References:

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Figures:

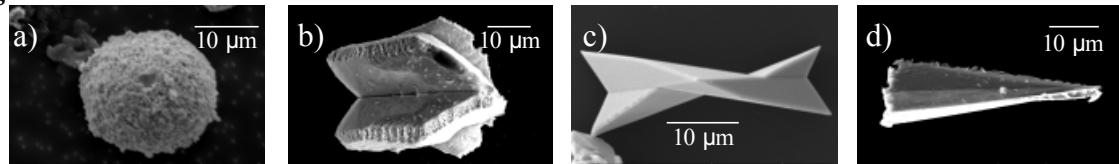


Fig. 1: SEM-images of Bi nanowire caps. a) $d = 300$ nm, room temperature, $U = -40$ mV, b) $d = 300$ nm, $T = 50$ °C, $U = -20$ mV, c) $d = 80$ nm, $T = 60$ °C, $U = -20$ mV, d) $d = 80$ nm, $T = 60$ °C, reverse pulses with cathodic cycle -20 mV (1 s) and anodic cycle 15 mV (0.1 s)

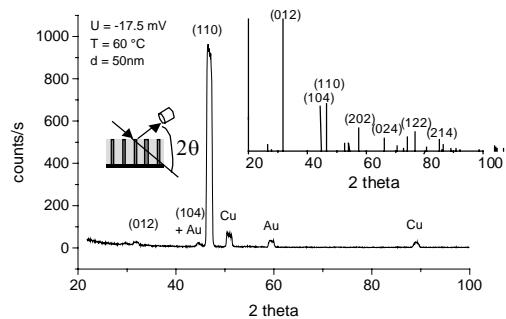


Fig. 2: X-ray diffractogram of 50 nm diameter Bi nanowires deposited potentiostatically at 60 °C, applying -17.5 mV. The right inset shows the diffractogram expected for a standard bismuth powder, the left inset illustrates the experimental arrangement.

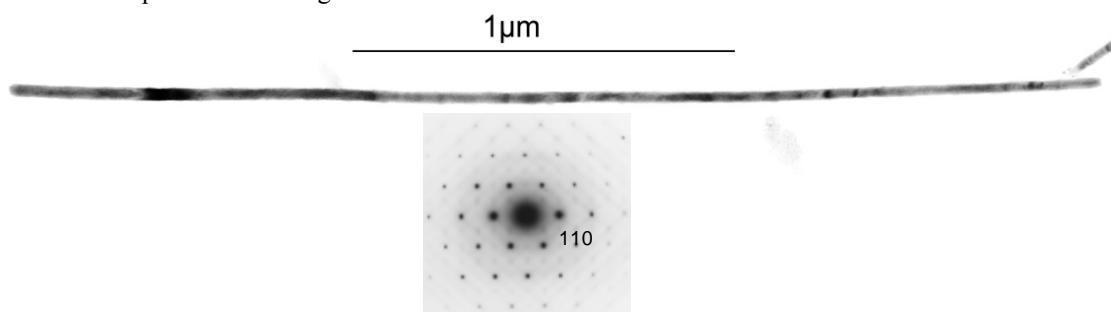


Fig. 3: TEM micrograph and SAED pattern of a ca. 3 μm long single-crystalline Bi nanowire section.