ADVANCED ELECTRONIC MATERIALS

Supporting Information

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Effects of Size Reduction on the Electrical Transport Properties of 3D Bi Nanowire Networks

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Effects of size reduction on the electrical transport properties of three-dimensional Bi nanowire networks

Michael Florian Peter Wagner[*], *Anna Sarina Paulus, Joachim Brötz, Wilfried Sigle, Christina Trautmann, Kay-Obbe Voss, Friedemann Völklein, and Maria Eugenia Toimil-Molares*[*]

Structural stability of nanowire array and nanowire network after polymer removal

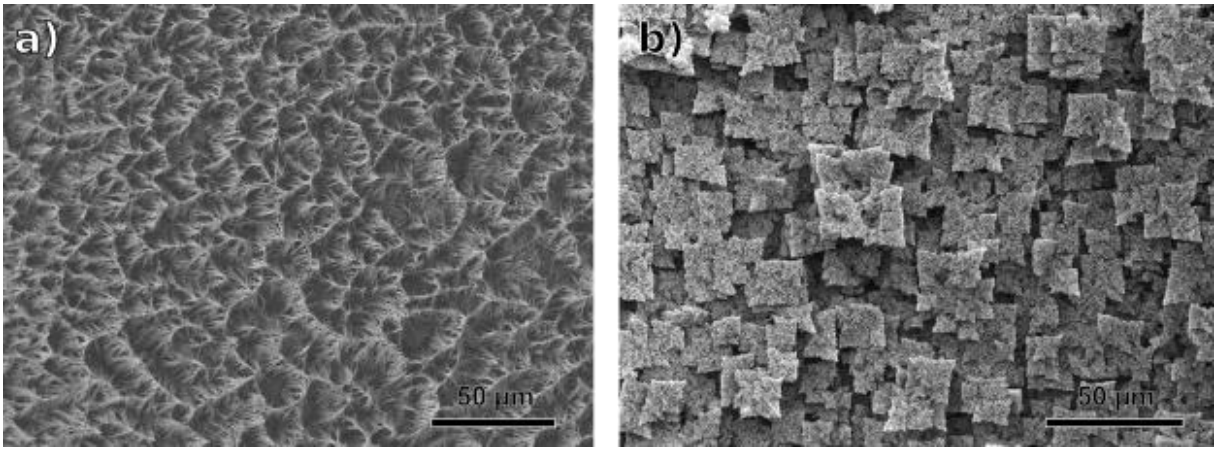


Figure S1. SEM image of a Bi nanowire array a) and a Bi nanowire network b) after template removal. In both cases the nanowires have a diameter of 100 nm. Nanowire density is 10^8 wires·cm^{-2} and 1.4×10^9 wires·cm^{-2}, for the nanowire array and network, respectively. Whereas the wires in case of the array bend under their own weight, the wires within the network form mechanically self-supporting structures after template removal.

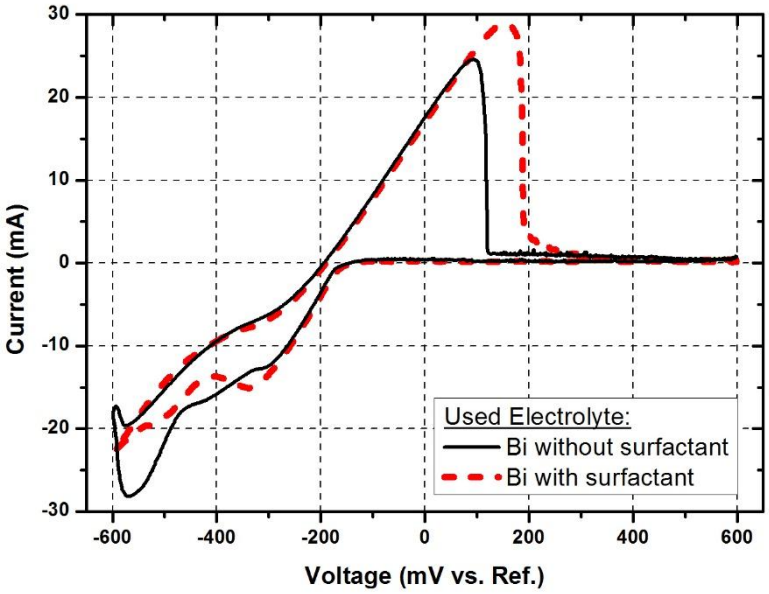


Figure S2. Second cycle of a cyclic voltammogram of Bi electrolytes at 40° C with and without surfactant on an Au disk of 8 mm in diameter. The scan rate was 10 mV/s.

Cyclic voltammograms of used bismuth electrolytes

Filling ratios of nanowire networks grown with pulsed plating

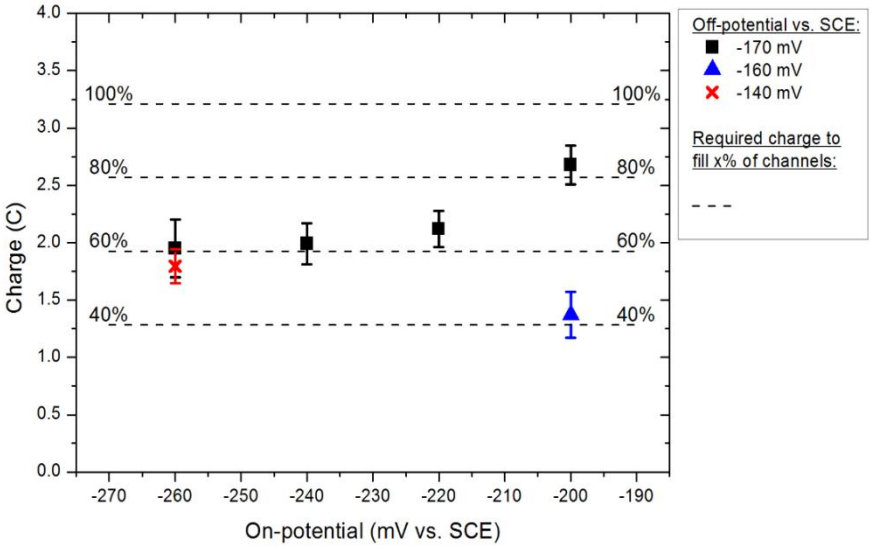
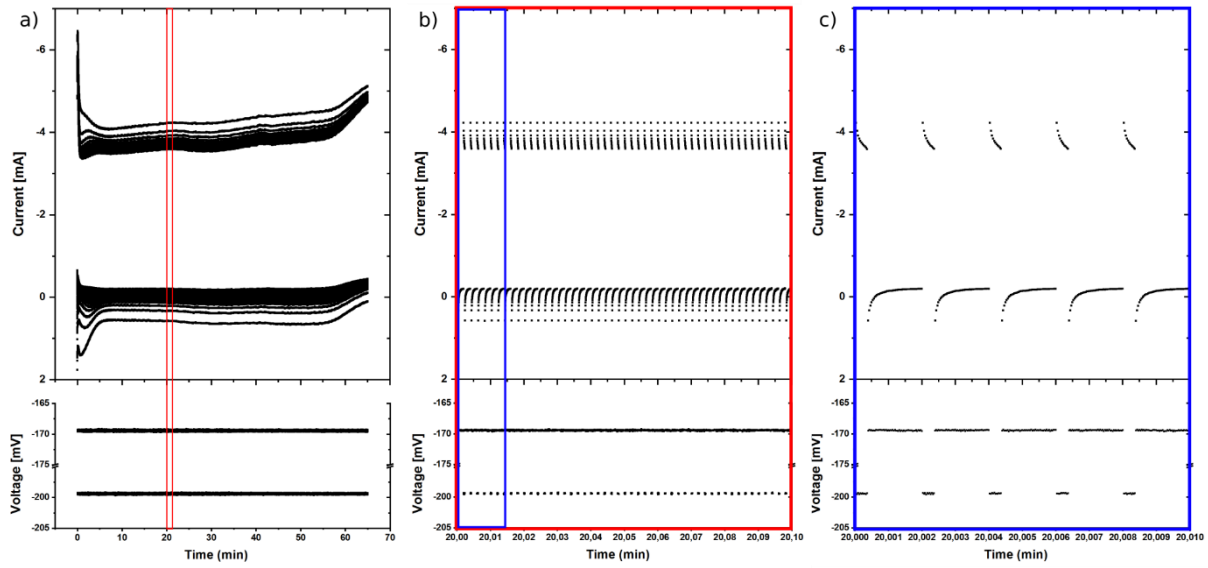


Figure S3. Filling ratio as a function of applied on-potential. The dashed lines indicate different filling states of the templates, which is deduced from the ratio of the required charge to fill all channels with a diameter of 100 nm and the charge that was deposited till cap growth started.



Pulse Plating Data

Figure S4. Exemplary pulse plating data with three different time scales a) Shows the complete current and voltage data collected during a pulsed electroplating of a Bi network. Within the graph it appears that several plots are shown together. However, when zooming in on the data, b) and c), the separate pulses with ON/OFF times of 20 ms/100 ms become visible. The lines in a) are merely an artifact occurring due to the data of the individual pulses being pushed together. Therefore, the lower lines in the current plot in a)-c) correspond to the current response during the OFF-pulse and the upper lines correspond to the ON-pulse.

Morphology of nanowire networks grown in templates with channels oriented in three different

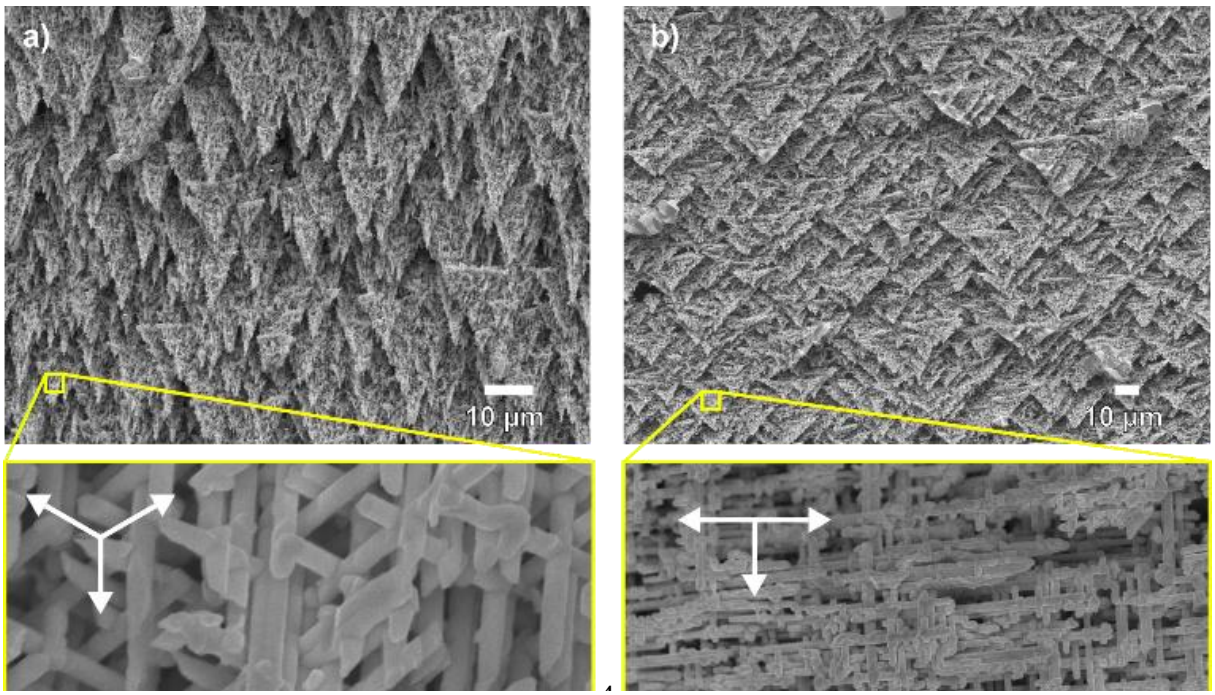


Figure S5. Morphology of Bi nanowire networks grown in templates irradiated from three directions (1×10^{9} ions·cm^{-2} per direction). The irradiation directions are shown as white arrows inside the close ups of the networks. In the case of a) the angle between directions is ~120°, in the case of b) the angle can be 90° or 180°. The diameter of the wires is ~ 100 nm in both cases.

directions

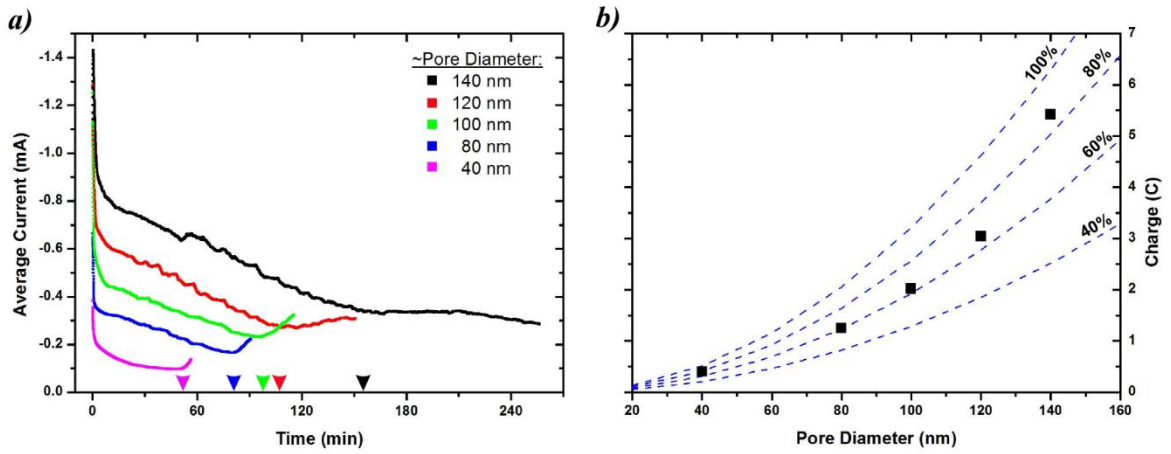


Figure S6. Electrodeposition of bismuth in interconnected channels with various diameters (U_{ON}/U_{OFF} = - 200 mV / - 160 mV, T = 40° C) a) Average current recorded as a function of time. The coloured arrows along the time axis denote the start of cap growth b) Deposited charge obtained from the integrated current during nanowire growth (black squares). The dashed lines represent different amounts of filling of the channels from bottom to top (indicated on the right), calculated by the Faraday law.[47]

Fabrication of Bi nanowire networks with various wire diameters

Figure S6. a) shows the average current recorded as a function of the deposition time during the plating of Bi inside nanochannel network templates (1.4×10^9 channels·cm^{-2}) with channel diameters between 40 and 140 nm. For the same pore density, the increase in pore size leads to a larger area for electrodeposition and thus to larger currents. Increasing the pore size from 40 to 140 nm increases the active area from 2.5% to 26.5%. The average current during plating however does not rise in the same manner, explaining why the times when cap growth starts increase. Figure S6. b) shows the deposited charge recorded during the growth of bismuth NWNWs with different channel diameters until the begin of cap growth. The dashed lines represent the charge expected to fill 40, 60, 80 or 100% of the channels. For most of our samples the experimental charge is in agreement with a pore filling state of 60-80%. The values

are reasonable considering the morphology of the grown networks observed in Figure 2c).

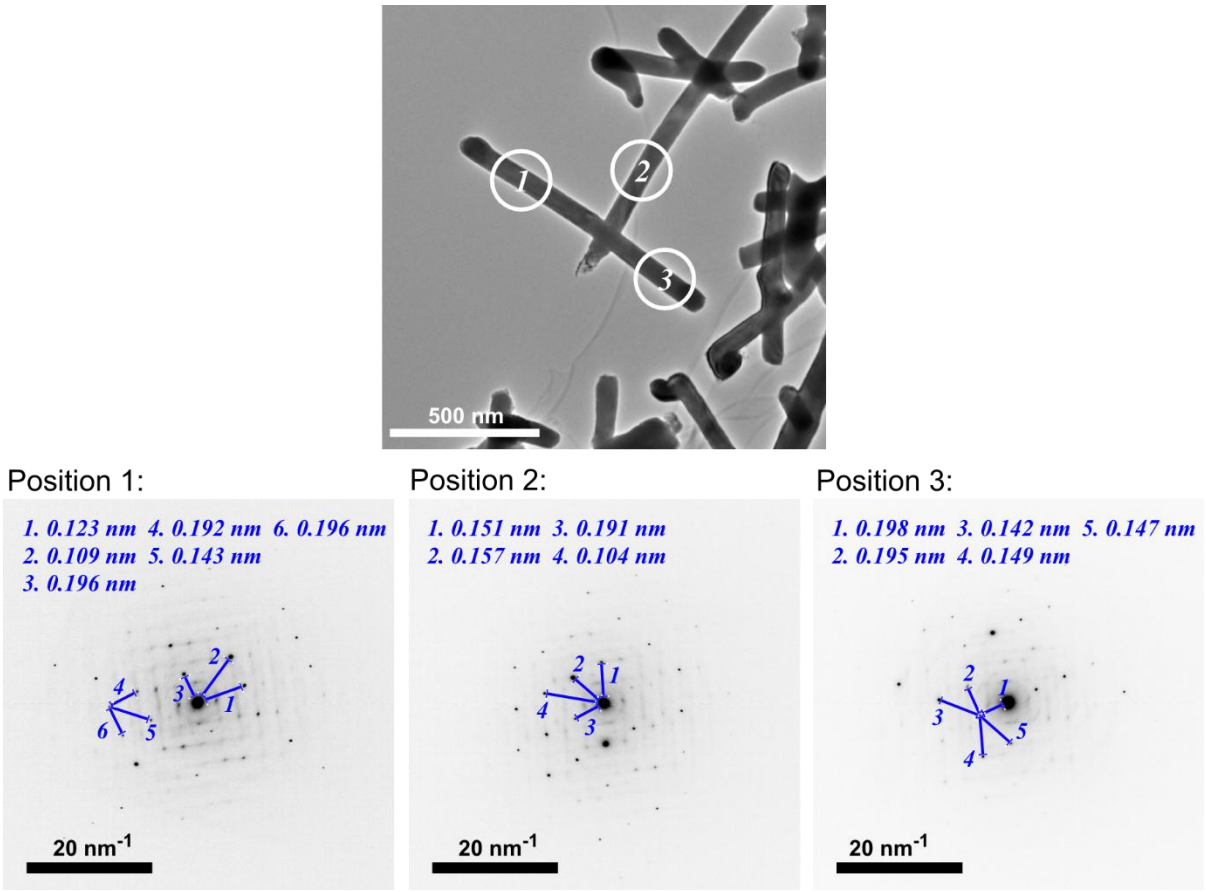


Figure S7. TEM image and SAED patterns of broken Bi nanowire network segments with wires of 80 nm diameter. The crystal structure in front of and behind the intersection differ.

TEM measurements on nanowire network intersection

Irradiation protocol of templates for nanowire networks

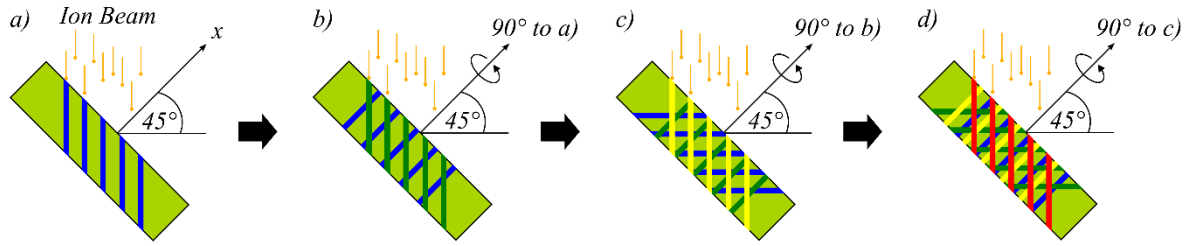


Figure S8. Sequential irradiation for template preparation for NWNWs. a) The template is tilted by 45° with respect to the incoming ion beam, generating ion tracks (blue). b) The sample is then turned by 90° around the foil normal x, tilted again by 45° to the incoming ion beam and irradiated, which generates a second set of tracks (green). This is repeated two more times, to generate tilted tracks from two additional directions (yellow and red) [1, 7, 47, 63].

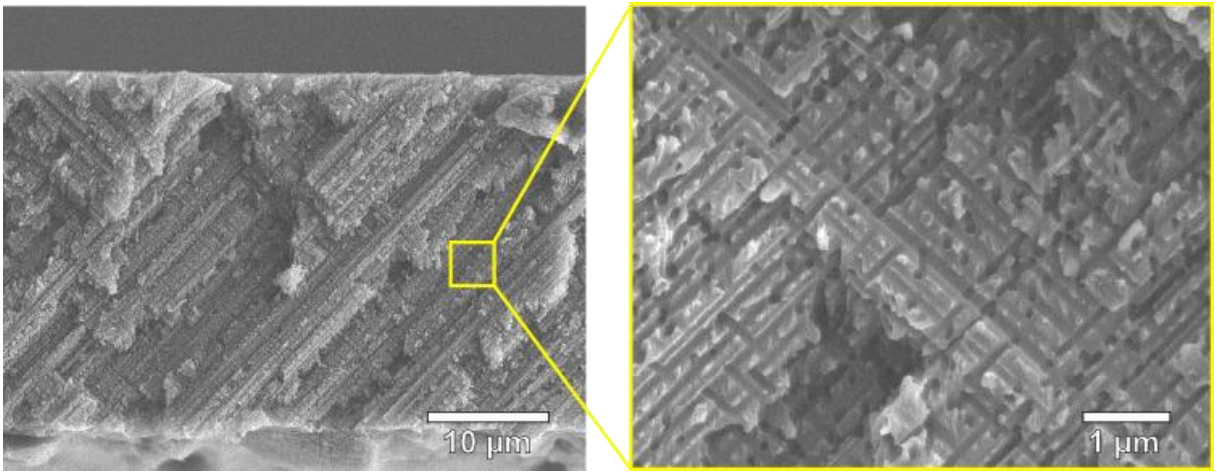


Figure S9. SEM images of a cross section through a nanopore network template with 1.4×10^{9} pores·cm^{-2}.[3]