6.3 Other nanowire assemblies

Several nanowire assemblies exhibiting different kinds of interconnectivity have been produced by direct synthesis or post-deposition processes. These methods are based on electrodeposited nanowires. In this section, the fabrication of various nanowire assemblies is briefly demonstrated.

6.3.1 Two-dimensional nanowire networks by the template method

Two-dimensional (2-D) nanowire networks were obtained by electrodeposition using templates with 2-D nanochannel networks. The templates had been fabricated by irradiating in two steps from two directions. In a typical experiment, the polymer foil is irradiated at an angle of incidence α with respect to the incoming ion beam. Subsequently, the sample is turned by 180° and irradiated again at the same angle. The axis of rotation is perpendicular to the sample surface. Chemical etching leads to the formation of interconnected nanochannels with well-defined orientations. With optimized parameters in terms of nanochannel density, orientation, and dimensions, 2-D nanowire networks can be obtained that are mechanically stable after template removal.

Figure 6.18 shows SEM images of 2-D nanowire networks that were fabricated with templates irradiated at α=45°. In the low magnification image, randomly distributed 2-D networks with dimensions of roughly $1000-5000\ \mu m^2$ are depicted (Figure 6.18a). In addition, caps are visible. In the case of 2-D nanochannel templates, caps grow preferentially in chains. The interconnectivity is revealed at higher magnification (Figure 6.18b). Nanowires are organized into a crossed 2-D array of highly-ordered nanoscale building-blocks. In these assemblies, only one branching geometry is observed, since the wires are always connected by cross-junctions. Each junction interconnects two nanowires at a right angle, because the angle of two wires is defined by 2α (=90°).

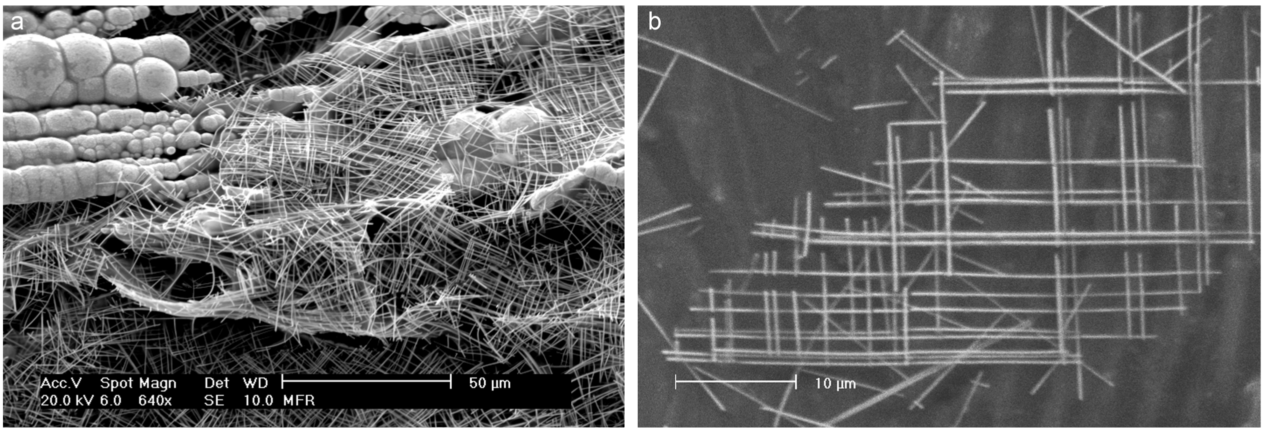

Figure 6.18: FESEM images of 2-D nanowire networks. (a) Randomly distributed 2-D nanowire networks on the substrate. (b) Ordered 2-D nanowire network structure.

6.3.2 Two-dimensional nanowire assemblies by diffusion bonding

The concept of diffusion bonding (DB) is frequently used for joining macroscopic objects. DB is especially suitable for interconnecting noble metal components such as Au, because of rapid self-diffusion characteristic and absence of an oxide skin.[181] While elevated temperatures and high pressures are required for permanently connecting metal components on the macroscale, nanoscale building blocks have been reported to be interconnected by DB at relatively low temperature and ambient pressure. For instance, Gu et al. reported a method for the formation of random nanowire network structures by DB of nanowires in a fluidic medium.[106] DB worked in the presence of various acids at lower temperatures than in their absence.

Here, the method of DB is employed to interconnect nanowires to various 2-D assemblies. The process involves dispersing nanowires on a silicon substrate and subsequent heating. Nanowires in contact with each other coalesce at elevated temperatures.

Figure 6.19 shows SEM images of several Pt nanowires after bonding via DB. The wires are interconnected in different ways to assemblies that vary in number of integrated nanostructures. Various experimentally obtained branching geometries are observed in assemblies consisting of many nanowires (Figure 6.19a), while representative interconnections of only two wires are depicted in Figure 6.19b-c. The micrographs demonstrate stable junctions including a cross-junction and single and multiple y-branched nanowires.

Morphological changes in cylindrical wires by mass transport occurring by surface diffusion are evident. At the interface of two nanowires in contact with each other, diffusion processes proceed at faster rates. The interface disappears as the wires coalesce. Two parallel aligned nanowires in contact form a single nanowire with elliptic cross section.

DB worked already at temperatures below those needed for the formation of morphological changes induced by Rayleigh instability. Nanowires with an average diameter of 74 nm could be interconnected completely by DB at 600 °C, while Rayleigh decay was observed at $T_h \geq 800$ °C. The process is driven by minimization of the surface energy. The surface area, and hence the surface energy, is dramatically reduced, when two parallel aligned nanowires form one nanowire.

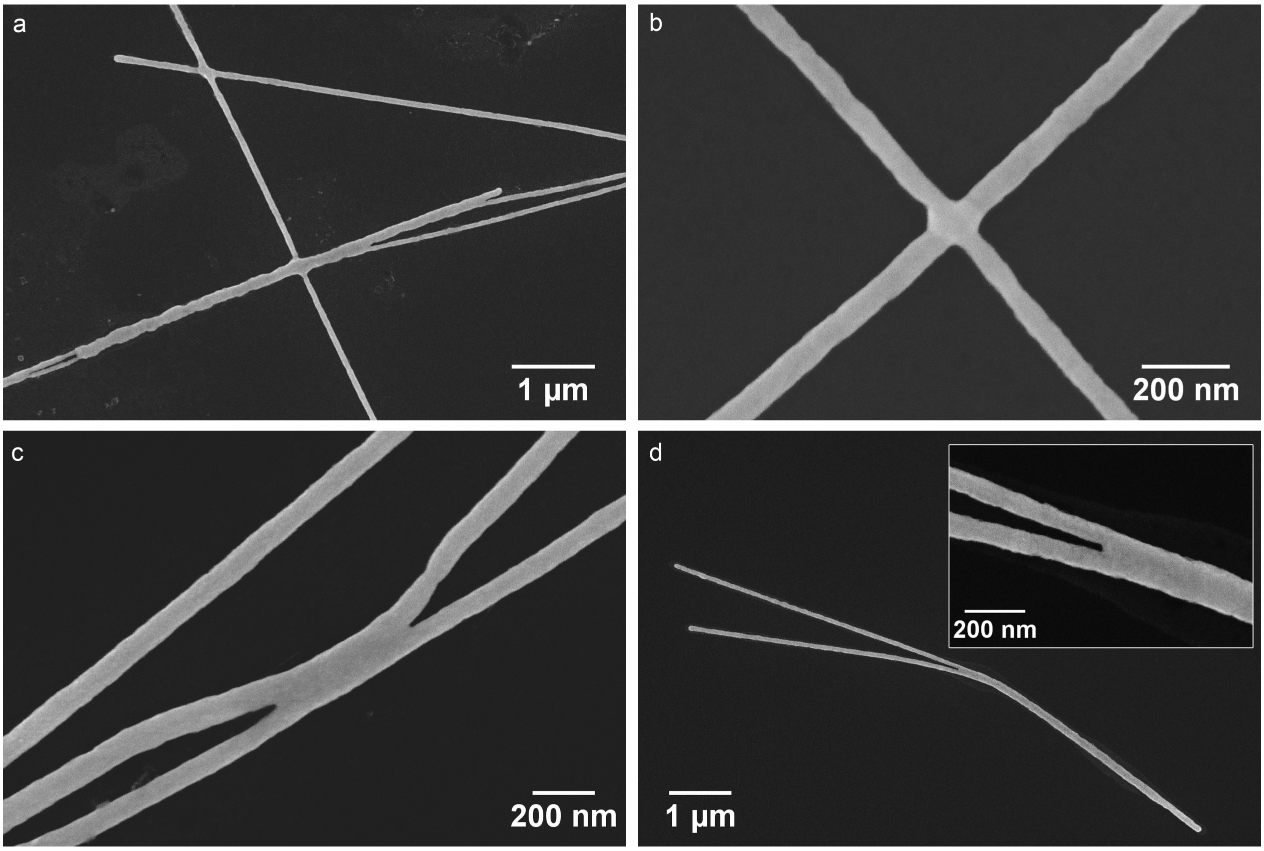

Figure 6.19: FESEM images of 2-D nanowire assemblies formed by diffusion bonding. The nanoscale building blocks have a diameter of 74 nm. (a-c) Nanowires with different branching geometries interconnected at 600 °C. (d) Y-branched nanowire that was made from two nanowires at 700 °C. The inset shows the branching point at higher magnification.

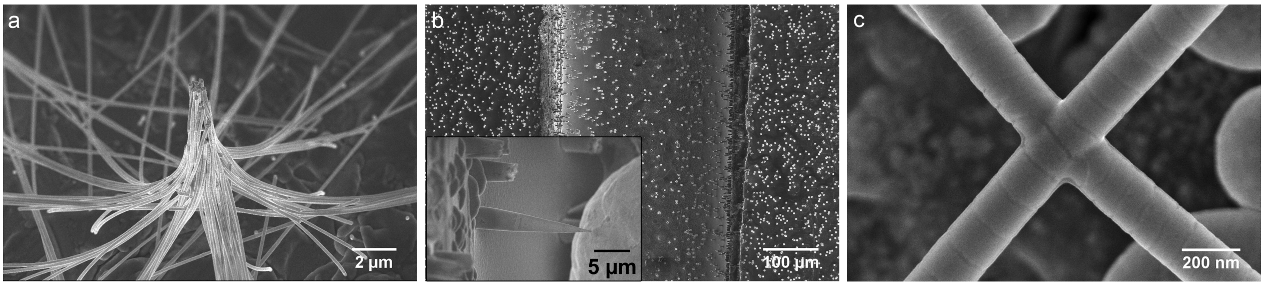

Figure 6.20: FESEM images of various Pt nanowire assemblies. (a) Clustered nanowires for field emission. (b) Nanowires in a thermoformed microchannel. The inset reveals the conical wire shape. (c) Segmented network nanowires.

6.3.3 Nanowire assemblies for field emission

For field emission measurements, regular patch arrays of Pt nanowires were fabricated. During ion irradiation, a mask with square arrays of holes, each with a diameter of 50 µm, was used. Pt nanowires electrodeposited in these templates intend to agglomerate into bundles after template removal. Figure 6.20a depicts a representative FESEM image of clustered nanowires. The formation of these structures probably occurs by bending facilitated due to their high aspect ratio. The regular Pt nanowire bundles were systematically investigated with field emission scanning microscopy by A. Navitski (Universität Wuppertal).[182] Similar gold structures have been demonstrated previously.[183]

6.3.4 Nanowires in thermoformed micro structures

Microthermoforming is a microfabrication process that allows forming of polymers without loss of material coherence.[184] It has been demonstrated that previously applied material modifications including ion-track etching can be preserved.[185]

To prove the feasibility of generating nanostructures by template electrodeposition in a thermoformed template, a track etched polymer membrane was post-processed using microthermoforming to create a microchannel. Electrodeposition in the microstructured template resulted in the formation of conical nanowires growing in the replicated microchannel. Figure 6.20b shows a top view of the nanostructured microchannel imaged by FESEM after polymer dissolution. The inset reveals the conical structure of the wires. Thermoforming experiments were performed by S. Giselbrecht (Institute for Biological Interfaces, Karlsruhe Institute of Technology).

6.3.5 Hierarchical nanowire structures

Hierarchical nanowire structures were obtained by template electrodeposition inside specifically designed templates. The template fabrication was modified to generate a hierarchical nanochannel structure as schematically illustrated in Figure 6.21a.

In a typical experiment, a 30 µm thick polymer foil was irradiated from one side with a low fluence of $1\text{x}10^4$ ions/cm^2 at an angle of incidence normal to the polymer surface. The ion range was adjusted to approximately 15 µm. Consequently, the ions did not fully penetrate the polymer foil. Subsequently, the polymer was irradiated from the other surface in four steps from different directions, as described for nanowire network template fabrication, with α=45° and a total fluence of $1.4\text{x}10^8$ ions/cm^2. The ion range was again decreased not allowing the ions to through-irradiate the foil. Prior to wire growth, a conductive metal layer was sputter deposited on the template side, from which the low fluence irradiation had been performed.

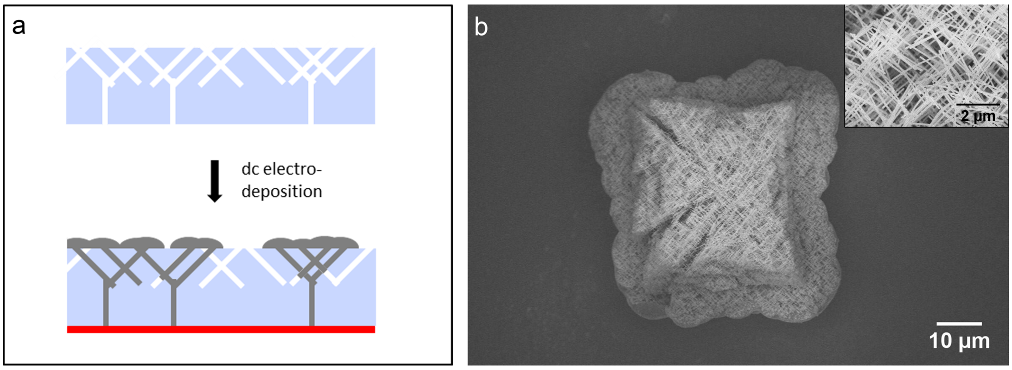

Figure 6.21: Images of hierarchical nanowire assemblies. (a) Scheme of the fabrication process. (b) Hierarchical nanowire network structure (top view on lower side of a cap formation). Nanowires forming the interconnected structure become visible at higher magnification as shown in the inset.

The track etched template was electrochemically filled using dc deposition resulting in the formation of hierarchical Pt nanowire structures. Because the growth process proceeded at the diffusion limited regime, the nanostructure growth directions are determined by mass transport processes. As a consequence, tree-like nanostructures are formed. As the deposition is continued, caps grow on top of these nanostructures. Figure 6.21b shows the lower side of such a cap formation. The hierarchical nanowire structure started to grow in the very center of the assembly arising from one nanowire.

6.4 Structured nanowire assemblies

In section 6.2 single-element nanowire networks with smooth surfaces and cylindrical nanowire geometry produced by dc deposition were presented. Different structuring techniques reported for interconnected nanowires can be adopted to fabricate segmented and multilayered nanowire networks.[2,36]

6.4.1 Segmented nanowire networks

Controlled deviations from the cylindrical wire morphology can be introduced by pulse-reverse electrodeposition, which influences the local electrolyte distribution during the growth process inside nanochannel network templates. Consequently, also nanowire networks consisting of single-element segmented nanowires were fabricated. The applied electrodeposition parameters are similar to those used for segmented nanowire arrays. In Figure 6.20c, a network node formed by two crossing segmented nanowires from a network structure is depicted. The segmented structure is clearly visible and can be used to analyze diffusion and growth processes.

6.4.2 Multilayered nanowire networks

The possibility to produce multilayered structures can also be adopted for NWNs. By using the method demonstrated in section 5.2.1 (page 53) multilayered Co/Pt NWNs were synthesized. Figure 6.22 shows a part of a multilayered NWN imaged by STEM. The segments of different composition can be identified. In the inset, interconnected nanowires are depicted at higher magnification.

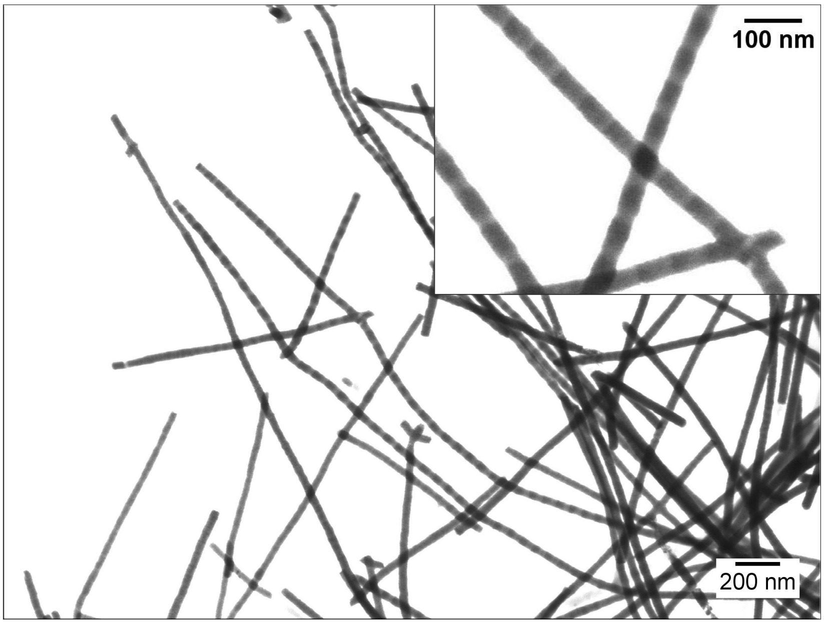

Figure 6.22: STEM image of a multilayered Co/Pt nanowire network fabricated by pulse electrodeposition from a single electrolyte. The picture was taken at a thin edge of the network. Interconnected nanowires are depicted at higher magnification in the inset.