7 Conclusions

7.1 Enhancing ion-track template electrodeposition

In this work, it has been demonstrated that the ion-track template electrodeposition method, which has been used routinely without any significant changes for the synthesis of 1-D nanostructures for several decades, provides excellent possibilities for improvement. In particular, an enhancement of this general method was achieved by identifying and modifying decisive process steps.

The innovation of the approach relies on the modification of template fabrication and the electrodeposition technique, which allows additional control not only over individual nanoscale building blocks but also over the arrangement of nanowires into complex 3-D architectures.

7.1.1 Template fabrication

Template fabrication was modified by exploiting the possibility of adjusting several irradiation parameters, including the number of irradiation steps, angle and direction of incidence, and ion fluence. The optimization of these parameters along with appropriate etching conditions resulted in specifically designed templates featuring controlled arrangements of nanochannels. Although the concept of multistep irradiation for polymer templates has been studied previously, it has not been adopted to produce continuously organized channel structures that enable the use as template materials for the fabrication of complex nanowire structures.[186] In contrast to other current hard-template materials, many structural parameters can be adjusted independently and simultaneously. In addition to excellent control over the nanochannel dimensions, the orientation, integration level, and complexity of the 3-D nanochannel architecture could also be adjusted precisely.

7.1.2 Electrodeposition

The generation of novel structures, including morphology-controlled nanowires and closed nanowire arrays, was mainly achieved on the basis of modified electrodeposition techniques. In addition, structured nanowires such as Co/Pt multilayered nanowires could be synthesized by adopting known methods reported for AAO templates.

Pulse electrodeposition was employed to reduce the growth rate of nanowires and to compensate for the limitations of diffusional mass transport, resulting in homogeneous nanostructure growth across the deposition area. Thus, the size distribution of caps growing on top of the nanowires was significantly reduced.

Furthermore, pulse-reverse deposition was used to manipulate the local electrolyte distribution inside fluidic nanochannels. The combination of a polycarbonate membrane and an alkaline electrolyte solution led to positively charged channel walls, which in turn caused the formation of an electrical double layer with significant thickness. Electrokinetic effects induced by applied electrical fields enabled manipulation of the ion concentrations and controlled deviation from the cylindrical nanochannel shape during the electrocrystallization processes.

7.2 Novel nanowire structures

On the basis of further development of the ion-track template electrodeposition method, novel 1-D nanostructures and advanced assemblies of nanowires were synthesized; they exhibited improved performance and new functionalities. The developed nanostructures are very important for both fundamental nanoscience and nanowire-based devices.

7.2.1 Controlled nanostructuring

Systematic studies on the thermal stability of cylindrical Pt nanowires resulted in significant morphological changes at temperatures much below the melting point of bulk Pt. The observations are qualitatively consistent with previous reports on metal nanowires undergoing Rayleigh decay. Both the spacing and the diameter of spheres formed after Rayleigh decay of a wire are found to be much larger than theoretical predictions by Nichols and Mullins. Several reasons, including anisotropic surface energies, transport mechanisms besides pure surface diffusion, and influence of the substrate, may be responsible for the deviation of the experimentally obtained values from the theoretically predicted values. The results can help to assure satisfactory durability of Pt nanowire-based applications and provide an opportunity to further develop theoretical considerations. Moreover, morphological changes driven by Rayleigh instability facilitate the fabrication of well-defined chains of nanospheres.

As demonstrated frequently, it is possible to produce multilayered nanowires inside nanochannels of a template material. For the purpose of demonstration, the deposition of multilayered Co/Pt nanowires was carried out from a single electrolyte. The extension of existing methods seems to be straightforward and it should readily allow the production of multilayered nanowires consisting of other materials.

Morphology-controlled segmented single-element nanowires were produced by a new concept, allowing a deviation from the continuously cylindrical shape predetermined by the template. Thus, interfaces and voids are obtained between adjacent segments, and pronounced diameter constrictions section the nanowires into length- and sequence-controlled segments. The fabrication of segmented nanowires consisting of only one material via template electrodeposition has not been reported so far. It was shown that the dimensions of the segments can be controlled accurately, and that the texture is a function of the segment length. This study not only contributes to the understanding of the growth process of electrodeposited nanowires predominantly controlled by kinetics but also shows that these wires are powerful tools for investigating transport processes in fluidic nanochannels. The synthetic approach presented for electrodeposited platinum and track-etched polycarbonate membranes can be applied to other selected electrolyte/template systems, and constitutes a general method for controlled nanostructuring. Segmented single-element nanowires may have a great potential for applications because of the possibility to tune their properties by precisely controlling the structure.

7.2.2 Nanowire assemblies

The fabrication of 3-D nanoscale building block assemblies based on the vertical integration of parallel aligned nanowires stabilized between two metal layers has been reported previously.[19] In the present thesis, the method was modified to produce well-defined nanowire microarrays and arrays thereof. A mask was used during ion irradiation to define the area of nanowire growth. With appropriate electrodeposition parameters, large quantities of monolithic nanowire arrays were synthesized in one step. The small arrays can be manipulated and integrated as functional elements into devices by microassembly techniques. They have several potential applications in the field of sensing.

In addition, network structures are promising nanowire 3-D assemblies. A highly effective method was developed to synthesize macroscopically stable nanowire networks with numerous independently controllable parameters such as size, shape, composition, and orientation of the nanowires, and integration level and three-dimensional complexity of the networks. The network structures can be easily manipulated, and they are suitable for efficient incorporation into micro- and macroscopic devices. In the case of Pt, it was demonstrated that NWNs exhibit a comparable or better electrocatalytic performance than Pt nanoparticle catalysts, especially with respect to high catalyst loads. In addition, NWNs are much more durable. The noticeable activity is a direct consequence of the inherent properties of the continuously organized, porous 3-D architecture, which exhibits excellent transport properties and efficient access of reactants to catalytic sites.

In a more general sense, the networks constitute model systems that facilitate systematic studies on the behavior of increasingly complex nanowire arrangements. NWNs fabricated from different materials are of great interest for electrode materials, catalyst supports, sensors, thermoelectric devices, and other applications, particularly because they can be easily integrated, and they readily provide interfaces between nanostructures and electrical contacts.

Other nanowire assemblies, including 2-D networks, arrays in microchannels, and hierarchical structures, were synthesized to indicate the great potential of the method.

Finally, the synthesis of nanowire assemblies and controlled nanostructuring techniques were demonstrated by producing multilayered Co/Pt and single-element segmented nanowire networks. The possibility of adopting structuring techniques not only highlights the advantages of the method but also affords ways to produce improved nanowire assemblies. Independent control of intrinsic activity and porous architecture, which is highly desirable for catalysis, is possible.

The issue raised in chapter 1, i.e., whether nanowires assemblies, which exhibit different types of interconnectivity, can be created by the ion-track template electrodeposition, was addressed in detail. The presented results will have a value beyond their immediate purpose, that is, to generate precisely controlled Pt nanowire assemblies. Such structures have a practical appeal because their dimensions facilitate manipulation and integration into devices. From the various nanowire assemblies demonstrated in the present thesis, it is clear that the organization of nanowires into systems of much greater complexity results in a considerable improvement in their functionalities and the generation of genuinely new properties. These properties, which strongly depend on orientation, integration level, and interconnectivity, will ultimately be of great technological relevance because they will promote new applications.

In additon, the possibility of synthesizing nanowire assemblies of varying complexity constitutes an important contribution to fundamental nanoscience because it allows systematic investigations of the collective behavior of nanostructure assemblies, depending on their arrangement.

8 Outlook

From the results presented in this thesis, it is clear that nanowire assemblies can show remarkably improved properties. First potential applications were demonstrated. Now it is time to define additional device functions and improve the structures in terms of controlled nanostructuring and architectural design.

In consideration of a particular application, the structures can be improved with respect to the desired functionality. For instance Pt nanowire networks proofed to by an efficient electrocatalyst material although the structure and composition of the nanoscale building blocks had not been optimized at all. Consequentially, the next step could aim for the increase of the fraction of catalyst material being active. This could be achieved by different approaches. To increase the Pt mass activity, networks consisting of porous Pt nanowires, Pt alloy nanostructures or multilayered Pt components (as already demonstrated) can be synthesized. Furthermore, the use of a nanowire network consisting of another conductive material as an advanced support would improve the efficiency of loaded catalyst nanoparticles.

The general method allows the fabrication of nanowire assemblies consisting of other materials than Pt. For applications in the field of catalysis, various active metals and composites are very interesting, while semiconductor structures represent promising functional elements for sensing devices. For example, a sensor architecture is readily accessible by using structured electrodes for nanowire network growth. Two sputter deposited cathode layers separated by a gap could be employed to grow nanowires in a nanochannel network template. Using appropriate conditions nanowires grow across the gap and form stable junctions. Figure 8.1 depicts such a nanowire architecture. Two nanowires that interconnect the electrodes as functional sensor elements are highlighted. A simple sensor setup could of course also be obtained by contacting an existing nanowire network.

Moreover, developed techniques for fabrication of morphology-controlled nanowires resulted in structures, which are expected to exhibit improved properties that might be applicable for real-world devices. The increased surface area of segmented nanowires predestines this structures for applications where the total surface area is important including sensitive sensing and catalysis. In addition, the structured nanowires appear to be of much interest for fundamental nanoscience such as the investigation of transport properties and the thermal stability depending on the morphology. It is planned to explore this properties in detail.

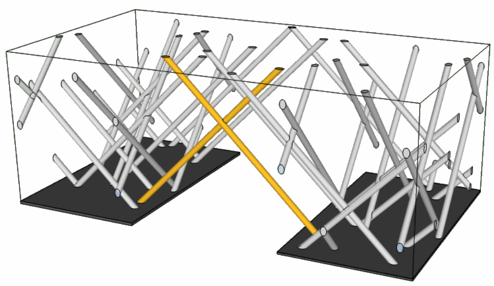

Figure 8.1: Schematic illustration of a nanowire network structure for sensing devices. Two nanowires that interconnect the electrodes as functional sensor elements are highlighted.

8.1 Future trends in nanowire assembly synthesis

Complex nanostructure systems have become the subject of many investigations. Improved functional properties resulting from the organization into advanced architectures have been demonstrated. However, to fully take advantage of these benefits, efficient ways need to be explored, how to use the nanostructures in applications. Many branched and hyperbranched nanowire structures are produced by approaches leading to complex nanostructures with microscale dimensions. Methods for making good electrical contacts to the distributed material need to be developed.

Continuously organized, stable nanowire structures of macroscopic dimensions can readily be integrated into devices and provide electrical contacts. Consequently, array and network structures that can be manipulated are very attractive for device integration. For distributed hierarchical structures, growth-in-place methods might by an alternative way to avoid subsequent integration.

Hard-template based methods proved excellent control over the nanostructure dimensions but are difficult to scale up. Nevertheless, hard template methods are important for fundamental nanoscience and allow fabrication of quantities that are sufficient for many applications.

In the long term it will be desirable to learn how to make nanowire structure more efficiently and controllable by approaches which are amenable to scale up. Materials, which are not considered today for certain applications, may become much more important and new applications that best utilize complex nanowire assemblies will be discovered.