THREE DIMENSIONAL NANOWIRE NETWORKS FABRICATED BY ION TRACK NANOTECHNOLOGY AND THEIR APPLICATIONS

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Abstract

The existing and future accelerator facilities at GSI and FAIR offer unique opportunities for interdisciplinary research, and in particular, for materials research and nanotechnology. On their way through polymers, swift heavy ions with GeV energy deposit enormous energy densities along their trajectory, causing long nanoscopic damage trails known as ion tracks. Ion-track technology utilizes the small track size (few nm) combined with the extensive track length (up to 100 μ m and more) to synthesize and control the geometry of unique high aspect ratio nanostructures such as tailored nanochannels and nanowires. In particular, electrodeposition and ion-track nanotechnology provide an excellent platform for developing unique 3D networks of nanowires with controlled dimension, composition and crystallographic properties. Here, a summary of recent results obtained on the synthesis and characterization of stable 3D architectures of semiconductor and semimetal nanowires, and their implementation in the fields of photoelectrochemistry and thermoelectrics, is presented.

1. INTRODUCTION

The implementation of nanowires for applications such as thermoelectrics, catalysis, plasmonics, or photoelectrochemical water splitting for hydrogen generation requires both, an excellent control on geometry, crystallinity and composition of the individual nanostructures, as well as its successful assembly into 2D and 3D architectures.^{1,2,3,4,5,6} Fabrication of 3D nanowire superstructures by e.g. vapour–liquid–solid processes has been reported; however, in most cases the tunability of the relevant parameters is limited.^{7,8} Electrodeposition in etched ion-track membranes with interconnected nanochannels, on the other hand, offers high flexibility in the choice of relevant parameters.

Etched ion-track membranes with parallel nanochannels are widely used as templates for the creation of nanowires.^{9,10,3,11,12} Their fabrication involves two separate processing steps. First, the template material is irradiated with energetic heavy ions creating so-called ion tracks.¹³ High energy heavy-ion beams are provided at large accelerator facilities, such as the universal linear accelerator (UNILAC) of GSI (Darmstadt, Germany). The GSI UNILAC provides heavy ions (up to uranium) of specific energy up to 11.4 MeV/nucleon. Such high energy ion beams have a penetration range in polymers of about 120 μ m, enabling the exposure of foils or stacks of polymer foils with thicknesses between ~ 6 and 100 μ m.⁹ The ion tracks are subsequently selectively dissolved and enlarged into channels by chemical etching. Control over the irradiation and etching conditions enables the production of membranes with channels of predefined geometries, sizes, and aspect ratios, with channel densities varying between a single channel and ~10¹⁰ cm⁻².^{9,14,15,16,2} Beyond the etched ion-track templates with parallel channels, the irradiation of polymer foils under several incident angles in consecutive steps, followed by chemical etching resulted in novel etched ion-track membranes with nanochannel arrays tilted at various angles. Electrodeposition in these nanochannel networks, and subsequent removal of the polymer matrix result in highly ordered 3-D nanowire ensembles of various materials such as Pt, Bi, Sb, Cu₂O or ZnO. ^{2,1,4,17,3,18}

Three dimensional nanowire networks can span over cross-sectional areas of up to several cm^2 . The nanowire networks can exhibit surface areas of up to ~250 cm² on a 1 cm² planar surface. In addition, the junctions between adjacent nanowires render excellent mechanical stability as well as electrical conductivity. The wires mechanically support one another and in case of breakage of individual wires, electrical or thermal transport can still occur via alternative nanowire interconnections. ^{19,2,1,20,6,21}. With several examples, we will illustrate how 3D nanowire networks combine the advantages and easy handling of macroscopic samples with the size-dependent properties of nanowires.



Fig. 1 Irradiation scheme for network templates with intersecting pores. The polymer foils are irradiated sequentially from four different directions (a-d) using swift heavy ions. During each irradiation step the foil is tilted by 45° towards the incoming beam. From M.F.P. Wagner, PhD Thesis, Technische Universität Darmstadt, 2018.^{1,4}

2. EXPERIMENTAL

For the preparation of network templates, stacks of up to 4 polycarbonate foils with a thickness of 30 μ m (Makrofol N, Bayer AG) are irradiated at an angle of 45° towards the incoming beam, consecutively from four different directions, with an angle of 90° between each direction, with swift heavy ions (typically Au or Bi) with a specific energy of 11.1 MeV/nucleon.²²

Prior to chemical etching, the irradiated foils are exposed to UV light using a T-30M Vilber Lourmat lamp (30 W, 312 nm). This process is known to decrease the width of the pore size distribution after etching.^{23,24,25} Selective chemical etching of the ion tracks performed in 6M NaOH solution at 50 °C, resulted in cylindrical channels.^{9,13,24} The nanochannel diameter can be estimated by the radial etching rate (10-12 nm/min).²² Fig. 2 illustrates various geometries that can be obtained by adjusting geometry and parameters of the etching process. They include channels with asymmetric bullet-like (a) and conical shapes (b), as well as symmetric cylindrical parallel (c) and interconnected (d) arrangements.^{14,15,16,3,22} The latter ones are used as templates for the controlled electrodeposition of 3D nanowire networks.

In order to fill the pores by electroplating, first a conductive contact (e.g. ~200 nm thin gold layer) is sputtered on one side of the membrane. This initial layer is further reinforced by electroplating a thicker layer of in most cases gold or copper on top. The conductive layer serves as a working electrode in a three electrode electrochemical cell during the electrodeposition of the material of choice inside the channels. In most cases, the reaction is controlled via the potential (constant or pulsed) in order to avoid the occurrence of side reactions like hydrogen evolution.



Fig. 2 Schematics and SEM images of possible pore geometries in ion track-etched membranes after the etching process. They include channels with asymmetric bullet-like (a) and conical shapes (b), as well as symmetric cylindrical parallel (c) and interconnected (d) arrangements. Partially adapted from L. Burr, PhD Thesis, Technische Universität Darmstadt, 2017 and L. Movsesyan, PhD Thesis, Technische Universität Darmstadt, 2017.

The electrodeposition process is monitored by recording the current between the working electrode and a counter electrode as a function of time. The electrodeposition parameters and the employed electrolytes determine the chemical composition, crystallinity, and crystallographic orientation of the resulting nanowires. The length of the nanowires can be adjusted by varying the electrodeposition time. Detailed descriptions of the fabrication processes for the presented materials can be found elsewhere. ^{9,26,3,27,4,1}

The 3D nanowire networks are typically characterized by a variety of methods, such as XRD, SEM and TEM. When direct access to the nanowires is required, the polymer membranes are dissolved in several consecutive baths of dichloromethane.



Here we show a few representative examples of 3D nanowire networks synthesized by electrodeposition in etched ion-track templates, including their synthesis and characterization.

3.1. ZnO nanowire networks as photoanodes for electrochemical water splitting

The compact design, mechanical stability, and high surface area of semiconducting 3D nanowire-based networks can be advantageous in enhancing the performance of e.g. gas sensors and batteries, as well as facilitating efficient light absorption and charge carrier transport in photoelectrodes.^{5,28,29,30,31,32,33,34,35,36,3} The one-dimensional geometry of nanowires is expected to facilitate the transport of charge carriers to the nanowireelectrolyte interface due to short distances in thin nanowires, which in turn should lead to less charge recombination and an increase in photocurrent. Additionally, the large surface to volume ratio generates a large electrode-to-electrolyte interface. 3,33,34,35 The network structure here allows for a mechanically rigid and electrically reliable model system for which the various geometrical parameters can be adjusted independently.35,3



Fig. 3 Measured generated photocurrents for ZnO nanowire networks and ZnO films with and without a TiO2 protection layer during a linear bias voltage sweep. Yellow areas mark when the samples were illuminated, white areas when the samples were in dark. I think one does not right "copy" from... check the standard sentence. From L. Movsesyan et al., © Nanomaterials 8, 693 (2018).



Fig. 4 SEM images of ZnO nanowire networks with and without TiO2 protection layer after photoelectronchemical experiments. a) After one hour of reaction decay of nanowires and recrystalization of ZnO could be observed. b) After three hours of photocorrosion the network with TiO2 layer shows no or only small effects of photocorrosion. Adapted from L. Movsesyan et al., © Nanomaterials 8, 693 (2018).

To investigate the photoelectrochemical performance of the ZnO networks, the samples were inserted in a photoelectrochemical cell and immersed in 0.1M K₂SO₄ solution with a pH of 5.6. A Ag/AgCl (Sat. KCl) electrode was used as a reference and a Pt-wire as a counter electrode. The sample was then illuminated with an

Arc lamp source with an Xe lamp calibrated at AM 1.5 (1 sun). The illumination generates electron-hole pairs within the material that can be separated by applying a bias voltage. Fig. 3 shows the generated photocurrent density as a function of the linearly sweeped bias voltage for ZnO nanowire networks and ZnO thin films, while the light was periodically switched off and on. The networks all had a wire density of $\sim 5.7 \cdot 10^9$ cm⁻², wire diameter of ~150 nm and a height of $\sim 30 \,\mu m$. Here, the potential is reported versus the reversible hydrogen electrode according to E_{RHE} $E_{ag/AgCl} + 0.059 \text{ pH} + E_{Ag/AgCl}^0$. For both cases also samples with a 20 nm thick TiO₂ layer, that was applied by atomic layer deposition is shown. The TiO2 layer was applied to protect ZnO versus photocorrosion as can be seen in



Fig. 5 Measured generated photocurrents for ZnO/TiO2 nanowire networks with different densities during a linear bias voltage sweep. Yellow and white areas mark when the samples were illuminated or in dark, respectively. From L. Movsesyan et al., © Nanomaterials 8, 693 (2018).

Fig. 4. In general, the networks show a larger photocurrent when compared to the film counterparts. Whereas the films exhibit relatively constant photocurrent densities of 0.02 mA/cm^2 and 0.06 mA/cm^2 for at 1.5 V vs. RHE with and without additional TiO₂ respectively, the networks generated 0.1 mA/cm^2 and 0.35 mA/cm^2 that were increasing with increasing bias voltage. The five times increase in generated current of networks was attributed to the geometrical advantages explained above. The higher performance of the TiO₂ coated samples is explained by additional electron-hole pairs generated within the TiO₂ layer and additional contributions to the charge carrier separation by the ZnO-TiO interface, which further helps to reduce the probability of charge carrier recombination.^{37,38}

Additional experiments were performed on networks covered with 20 nm TiO₂ with a lower nanowire number density of $1.4 \cdot 10^9$ cm⁻² and various nanowire diameters, shown in *Fig. 5*. Here, the larger the nanowire diameter the denser the network and, correspondingly, the higher the generated photocurrents. This was attributed to a larger amount of photoactive material in the denser networks. Also the variation of the photocurrents in dependence of the applied bias voltage increases with increasing nanowire diameter. In all cases the generated photocurrents of the networks were higher than the corresponding reference value for the thin films. These measurements showed that using nanowire networks as model systems enables a systematic investigation of the geometrical factors influencing the photoelectrochemical water splitting. Similar results were obtained for Cu₂O nanowire-based photocathodes.¹⁷

3.2. Bi and Sb nanowire networks for thermoelectric applications

The dimensionless thermoelectric figure-of-merit $Z \cdot T = S^2 \cdot \sigma \cdot T / (\lambda_{el} + \lambda_{ph})$ describes the efficiency of the material for thermoelectric applications.^{39,40,41} Here, S is the Seebeck coefficient σ is the electrical conductivity and λ_{el} , λ_{ph} are the thermal conductivities by charge carriers and phonons respectively, of a given material. The interdependency of S, σ , and λ_{el} via the charge carrier density hinders the increase of ZT, and commercial thermoelectric materials nowadays exhibit maximal ZT values of ~1.^{42,43,40,44} However, for widespread applications of thermoelectric modules a ZT of 3 would be required.^{45,46,47}



Fig. 6 Relative electrical resistance and Seebeck coefficient of Sb nanowire networks with a nanwire density of 1.4·10⁹ i/cm² and various wire diameters in dependence of temperature, measured using a custom-build setup introduced elsewhere. Adapted from M.F.P. Wagner, PhD Thesis, Technische Universität Darmstadt, 2018.

The size effects that can occur in nanowires can help to decouple the electrical and thermal transport and thereby open up a route for further improvement of thermoelectric materials.^{43,44,48} Bi_(1-x)Sb_x bulk has already proven its worth for low temperature thermoelectric applications, and the material system is also ideal to study the influence of size effects on the transport and thermoelectrical properties40,49,48,50 because the mean free paths of charge carriers and phonons in Bi and Sb at room temperature are in the order of 100 nm, and the Fermi wavelength in the order of 40 nm.^{43,51,48,52,53} Size effects are, therefore, exhibited already at relatively large dimensions. Potentially, nanowire arrays exhibiting higher ZT values will yield more efficient thermocouples, of great interest for infrared sensor applications.54

Crossplane relative electrical resistivity and Seebeck coefficient of Sb nanowire networks as a function of temperature were investigated using a custom-build setup described elsewhere.55,56,1 Fig. 6 shows the relative electrical resistance and Seebeck coefficient of Sb nanowire networks with $\sim 1.4 \cdot 10^9$ wires cm⁻² and wire diameters ranging between 30 to 140 nm as a function of temperature. The relative electrical resistance exhibits a metallic behaviour in all cases. The electrical resistivity of the nanowire networks with smaller wire diameters is dominated by the scattering of charge carriers with the nanowire surface and on grain boundaries, as theoretically described by Mayadas, Shatzkes, Fuchs, Sondheimer and Dingle, for both thin films and nanowires.^{57,58,59,60} Therefore, with decreasing wire diameter, the electrical resistance is less affected by a decrease in temperature and the corresponding increase in mean free path of the charge carriers. The measured Seebeck coefficient for the Sb networks is in the order of $20 - 25 \mu V/K$. Bulk Sb is



Fig. 7 Measured thermal conductivity of various samples as a function of temperature. The setup and measurement method is introduced elsewhere. From M.F.P. Wagner, PhD Thesis, Technische Universität Darmstadt, 2018.



Fig. 8 Seebeck coefficient of Bi nanowire networks with a wire density of $1.4 \cdot 10^9$ i/cm² as a function of temperature measured using a custom-build device introduced elsewhere. From M.F.P. Wagner, PhD Thesis, Technische Universität Darmstadt, 2018.

very anisotropic and exhibits a maximal Seebeck coefficient of ~47 μ V/K⁴⁰ for transport along the binary axis. According to XRD measurements the Sb networks exhibited a {01.2} texture, while also the {10.4} and {11.0} planes could be observed.²² Due to this the Seebeck coefficient is smaller than ~47 μ V/K, but comparable to the Seebeck coefficient of Sb bulk for other crystal orientations. The nanowire networks with smallest diameters exhibit a slightly higher Seebeck coefficient at room temperature, which might be due to small changes in crystallinity for the different wire diameters.^{61,62,63} With decreasing temperature, the values monotonously decrease towards zero, as expected.^{39,40} Fig. 7 shows the thermal conductivities of the polycarbonate template material as well as Sb nanowire arrays and nanowire networks measured using a method described elsewhere.⁴ As comparison, also the well-known thermal conductivity of a Borofloat glass was measured. The thermal for bulk Sb ($\lambda = 24$ W/mK), which is attributed to enhanced phonon scattering at the nanowire's surfaces.^{40,20,21,64} Since the Seebeck coefficient is similar to bulk and thermal conductivity is significantly suppressed, the thermoelectric efficiency ZT is most probably increased for the networks when compared to the bulk material, making nanowire networks promising materials for thermoelectric applications. To demonstrate this, absolute values of the electrical resistance should be measured in the future.

Fig. 8 shows the Seebeck coefficient of Bi nanowire networks with different wire diameters as a function of temperature. The Seebeck coefficients at room temperature are similar to previously reported values for nanowires and are comparable to theoretical values assigned to the bisectrix axis in Bi nanowires.^{48,65} The Seebeck coefficient measured at room temperature decreases with decreasing nanowire diameter, due to the limitation of the mean free path of the charge carriers, ans possibly also to the influence of surface states which is more important for higher surface-to-volume ratios.^{65,56,66,67} With decreasing temperature, the Seebeck coefficient decreases, exhibiting a change of sign which was not observed in the case of Sb nanowires. The data show that the temperature at which the sign changes occurs depends on the diameter of the nanowires, namely the temperature shifts to higher values with decreasing nanowire diameter. A similar behaviour was theoretically predicted by Murata et al. for Bi nanowires with crystals oriented along the bisectrix axis.⁶⁷ According to Murata et al. this sign change can be attributed to a different dependence of hole and electron mobility on nanowire diameter and temperature. In semimetals the Seebeck coefficient S is made up of contributions of holes and electrons according to $S = (S_n \sigma_n + S_p \sigma_p)/(\sigma_n + \sigma_p)$, where $S_{n,p}$ and $\sigma_{n,p}$ are the Seebeck coefficient and electrical conductivity of electrons and holes, respectively.⁴⁰ Under the assumption that both charge carrier densities are similar this means that at the transition temperature the mobility of holes becomes larger than the one of electrons.⁶⁵ At small dimensions also topological surface states can additionally contribute to transport.^{56,66,67} As the properties of topological transport in bismuth and antimony are still under discussion, further transport measurements will unravel new and exciting effects on the transport behavior of tailored Bi and Sb nanostructures.68

4. CONCLUSION

Selected examples have been shown to illustrate how three dimensional nanowire networks, with macroscopic sizes (~cm), exhibit size-dependent properties. We predict that such well-defined tailored networks will serve as model systems to elucidate the behavior of porous materials, leading to the improvement of novel devices in several technological fields such as thermoelectrics, photoelectrochemistry, sensing, or catalysis. The combination of ion-track nanotechnology and electroplating yields nanowire networks of a large variety of technological relevant materials, while providing excellent control on their chemical, structural and morphological properties. The large number of well-defined interconnections between adjacent nanowires render the samples a remarkable mechanical stability even without a supporting matrix, as well as an excellent electrical connectivity.

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