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PREPARATION OF NANOWIRES AND MICROARRAYS*

ZHANG LI-DE(张立德)[a], MENG GUO-WEN(孟国文)[a]†, and F. PHILLIPP[b]
[a] *Institute of Solid State Physics, Chinese Academy of Sciences, Hefei* 230031, *China*
[b] *Max-Planck-Institut für Metallforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany*

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We report on the synthesis of one-dimensional (1D) solid nanostructures and ordered microarrays consisting of nanowires and carbon nanotubes. For 1D nanostructures, several synthesis methods, such as, carbothermal reduction of silica xerogels containing carbon nanoparticles, chemical vapor deposition on mesoporous active carbon with transition metal catalyst nanoparticles inside the pores, and simple physical evaporation with the help of transition metal nanoparticles as catalysts, have been used. For microarrays, anodic alumina membranes (AAMs) with highly ordered honeycomb structure were used as templates, chemical vapor reaction inside the nanochannels, Sol-gel technique, and selective electrodeposition in the channels, have been used to prepare microarrays embedded in AAMs.

Keywords: nanostructured materials, microstructure
PACC: 6146, 6480G

I. INTRODUCTION

Recently, quasi one-dimensional (1D) solid nanostructures attracted considerable interest of scientific research due to their unusual properties.[1−21] Compared with micrometer-diameter whiskers and fibers, these nanostructures are expected to have remarkable optical, electrical, magnetic, and mechanical properties. They have potential applications in mesoscopic physics research, the development of nanodevices and as reinforcements in composites.[1] Different approaches have been used for the synthesis of 1D solid nanostructures. For example, (a) carbon nanotube template-mediated growth method to produce carbide[1] and nitride[2,3] nanorods; (b) vapor-liquid-solid (VLS) growth mechanism to synthesize Si,[4−9] Ge,[4] SiO_2,[10,11] GaAs,[12] InAs,[12] and β-SiC[11,13,14] nanowires; (c) solution-liquid-solid mechanism for the growth of InP, InAs, and GaAs nanowhiskers or nanofibers;[15] (d) physical evaporation to produce Ga_2O_3[16] nanowires; (e) electron-beam (EB) lithography,[17] the etching technique,[18] and scanning tunneling microscopy[19] to produce Si nanowires; and (f) other methods to produce nanowires, such as MgO,[20] PbSe,[21] Ag,[22,23] Au,[24] and ZnTe.[25] Exploration of novel methods for the large-scale synthesis of 1D nanostructures is a challenging research area.

With the development of electronic and photonic devices such as field emission displays and data storage units, high-density, well-ordered nanowire arrays will be needed. It is well known that the anodic alumina membranes (AAMs) grown in acid electrolytes possess hexagonally ordered porous structures[26] with channel diameters ranging from below 10 to 200nm, channel lengths from 1 to over 100μm, and channel density in the range of $10^{10} - 10^{12}$cm^{-2}. These unique structural features and their thermal and chemical stability make AAMs ideal templates for the fabrication of ordered nanostructures. By using AAM as templates, different kinds of ordered nanowire arrays have been fabricated.[27−34]

Our research group has been exploring methods to synthesize 1D nanostructures and their arrays for a few years. Investigations by our laboratory with respect to the preparation of nanowires and microarrays shall be described below. In section II, we will discuss the development of general approaches to the synthesis of nanowires. In section III, several methods to prepare microarrays will be reported.

II. NANOWIRES

A. SiC, Si_3N_4, and SiC/SiO_2 nanowires from carbothermal reduction using carbon nanoparticles as carbon source.

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†To whom correspondence should be addressed. E-mail: gwmeng@mail.issp.ac.cn

Based on micrometer-diameter whisker investigation results, according to which SiC whisker nucleates on the surface of carbon particles during the carbothermal reduction,[35] and an Si_3N_4 whisker nucleates on carbon particles during the carbothermal nitridation[36] of SiO_2, we tried to synthesize nanometer-diameter SiC wires by carbothermal reduction using carbon nanoparticles as carbon source. The sol-gel technique was used to prepare SiO_2 xerogels containing carbon nanoparticles. Pure β-SiC nanowires[37] were synthesized by carbothermal reduction of the sol-gel derived SiO_2 xerogels containing carbon nanoparticles at 1650°C for 2.5h. Large quantities of SiC nuclei and the nanometer-sized nucleus sites, formed during carbothermal reduction, on carbon nanoparticles are both favorable to the formation of β-SiC nanowires. The pure β-SiC nanowires are typically up to 20μm in length with diameters of about 30nm. Figure 1 is a TEM image of the pure β-SiC nanowires. Moreover, β-SiC nanowires sheathed with SiO_2 wrapping layers (β-SiC/SiO_2)[37,38] were also synthesized by carbothermal reduction at 1650°C for 1.5h, and after 1.5h the temperature was steeply raised to 1800°C and held for 30min. The formation of the amorphous SiO_2 wrapping layers results from the combination reaction of the decomposed SiO vapor and O_2 from SiO_2 xerogels. Figure 2 is a typical high magnification TEM image of two individual β-SiC cored nanowires. In addition, Si_3N_4 nanowires[39] were produced by carbothermal nitridation of the sol-gel derived SiO_2 xerogels containing carbon nanoparticles in nitrogen atmosphere at 1450°C for about 6h.

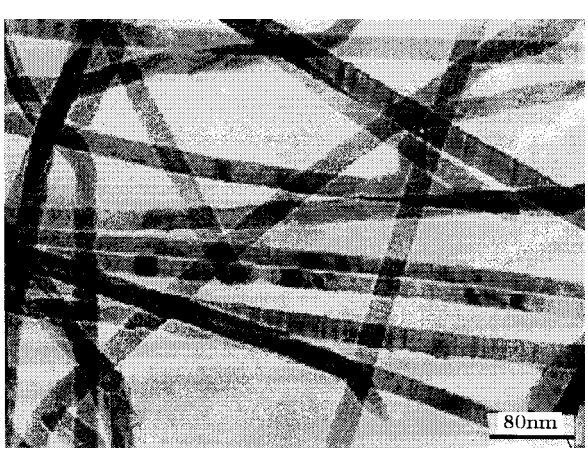


Fig.1. High-magnification TEM image of pure β-SiC nanowires.

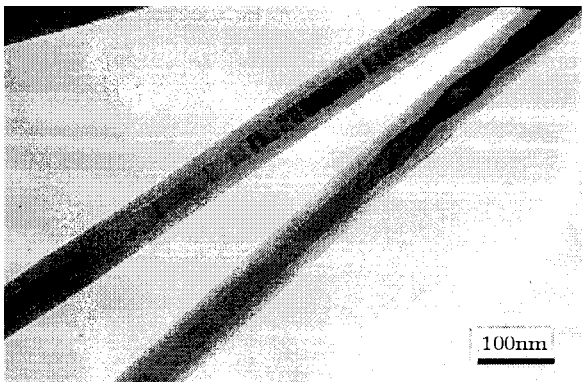


Fig.2. High-magnification TEM image of two individual β-SiC nanowires with SiO_2 wrappers.

B. TiC and SiC nanowires from the VLS growth mechanism with transition metal catalysts embedded in the pores of mesoporous active carbon

We developed a new method for chemical vapor deposition of carbide nanowires by using mesoporous active carbon loaded with transition metal catalyst nanoparticles inside the pores. In this process, mesoporous active carbon was used both as carbon source material and template to generate nanometer-sized catalyst particles that define the size of the wires produced by the vapor-liquid-solid (VLS) growth mechanism. β-SiC nanowires[13] were successfully prepared using the above method, in which Si vapor coming from the reaction of $SiCl_4$ and H_2 was used as silicon source material and Fe nanoparticles reduced from the $Fe(NO_3)_3$ embedded in the pores of active carbon were used as catalysts. TiC nanowires[40] were also produced by using the VLS growth mechanism on mesoporous active carbon with embedded Ni nanoparticles inside the pores. Mesoporous active carbon loaded with $Ni(NO_3)_2$ nanoparticles inside the pores was calcined for 5h at 450°C to obtain nickel oxide nanoparticles embedded in the pores, and then placed into the hot zone of a quartz tube furnace. The nickel oxide was reduced at 500°C and 180 Torr in 9% H_2/Ar (110cm^3/min) for 4h to obtain nickel nanoparticles. Subsequently, dry hydrogen (0.1MPa) was bubbled at a rate of 160ml/min through $TiCl_4$ liquid in a bottle. The feed gas mixture of $TiCl_4$ and H_2 was introduced into the chamber and the reaction was carried out at 1180°C for 1.5h. The black sponge-like products deposited on the surface of active carbon are TiC nanowires. Figure 3 is a general over-view of the TiC nanowires, and Figure 4 is a lattice-resolved image of a TiC nanowire.

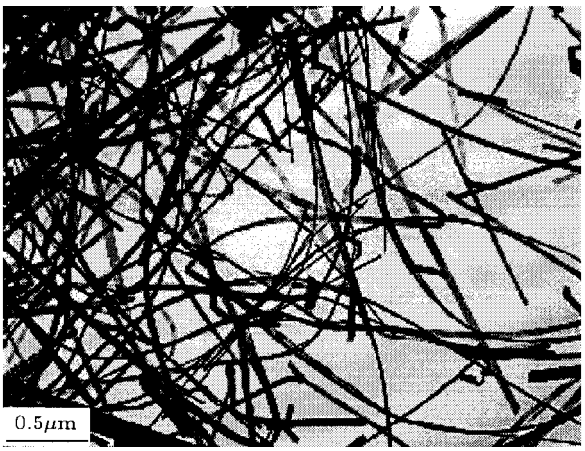


Fig.3. A general overview of the low-magnification TEM image of TiC nanowires.

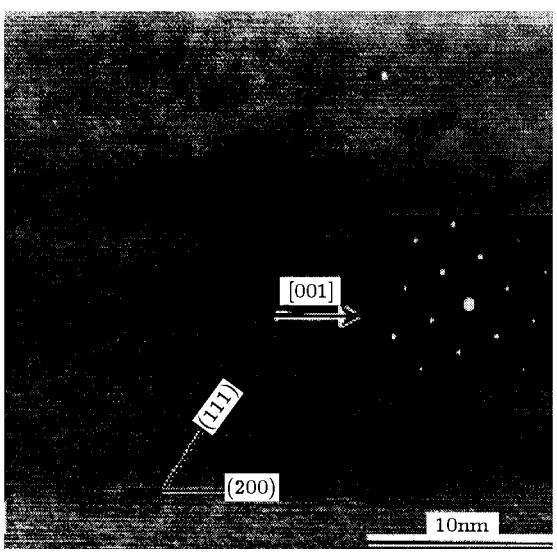
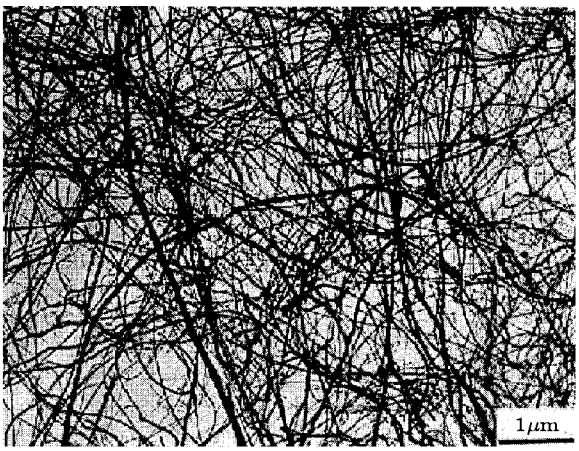
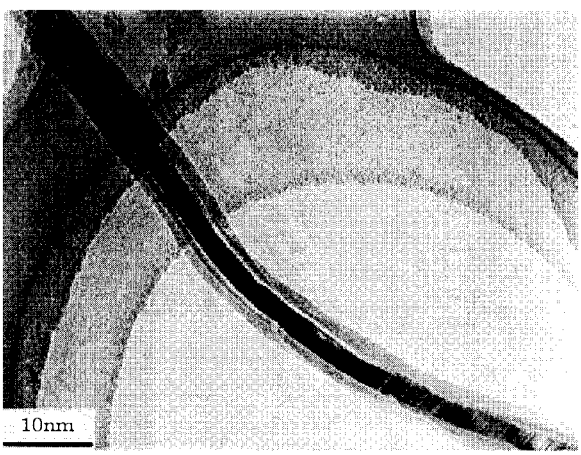


Fig.4. HREM image of a TiC nanowire showing an atomic structure in a two-dimensional lattice, a selected area electron diffraction pattern (insert) corresponds to cubic-TiC with the [1 1 0] axis parallel to the electron beam.

C. Nanowires from simple physical evaporation with the help of transition metal nanoparticles as catalysts

A simple physical evaporation method was exploited to produce nanowires. Mesoporous silica containing Fe nanoparticles was prepared by a sol-gel process. TEOS ($(C_2H_5)_4SiO_4$) (50ml) was mixed with 50ml ethanol, 0.3M $Fe(NO_3)_3$ aqueous solution (40ml), and 10ml deionized water. Subsequently, a few drops of concentrated nitric acid were added. After the gelation of the mixture sol, the gel was dried at 90°C in an oven and then calcined at 140°C for 6h to obtain porous silica xerogels with embedded Fe oxide nanoparticles. The xerogel was crushed into powder





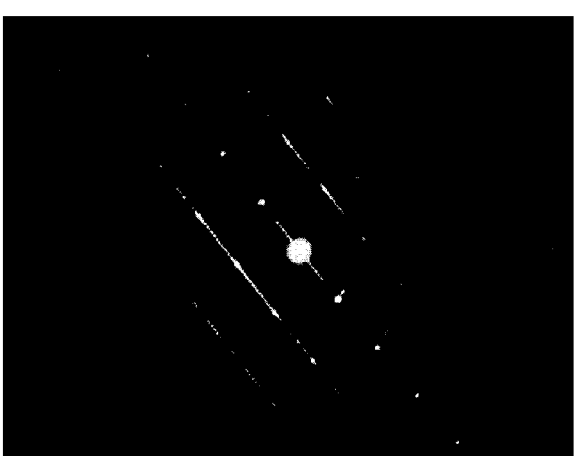


Fig.5. (a) A general low-magnification TEM image of large quantities of β-SiC/SiO_2 nanowires; (b) A representative high-magnification TEM image of an individual β-SiC/SiO_2 nanowire; (c) A corresponding selected area electron diffraction pattern.

and then mixed with active carbon powder. Its quantity was adjusted to obtain a nominal molar ratio of C/Si=4:1. The mixture was heated at 500°C in a flowing high-purity 9% H_2/Ar (110 sccm) atmosphere for 4h to get fresh Fe nanoparticles. Subsequently, the system was heated at 1400°C for 2h

in a flowing Ar atmosphere. Then, β-SiC nanowires wrapped with an amorphous silica layer were produced from the reaction of active carbon and silica xerogels with embedded Fe nanoparticles.[41] In this process the carbothermal reduction and VLS mechanism play an important role. Figure 5 shows TEM images of the nanowires and selected area electron diffraction (SAED). In addition, amorphous SiO_x nanowires with different morphologies were achieved by using simple physical evaporation of the mixture of sol-gel-derived silica xerogels containing Fe nanoparticles and silicon powder.[42]

D. GaN nanowires on the surface of an anodic alumina membrane through gas reaction

The AAMs were fabricated by a two-step anodization process as described below. The first anodization process was conducted under constant voltage in three types of aqueous solutions, sulfuric, oxalic, and phosphoric acids, in a thermally insulated electrochemical cell at different temperatures for 3 h. Then, the produced alumina layer was removed by wet chemical etching in a mixture of phosphoric acid (6 wt%) and chromic acid (1.5 wt%) at 60°C for 3 h. The second anodizaton process was carried out using the same parameters as in the first process. After coating the surface of the porous alumina film with a protective layer, the remaining Al substrate was removed in a saturated $HgCl_2$ solution. A subsequent etching treatment was carried out in a 6 wt% phosphoric acid at 30°C for 70min to remove the barrier layer on the bottom side of the AAM.

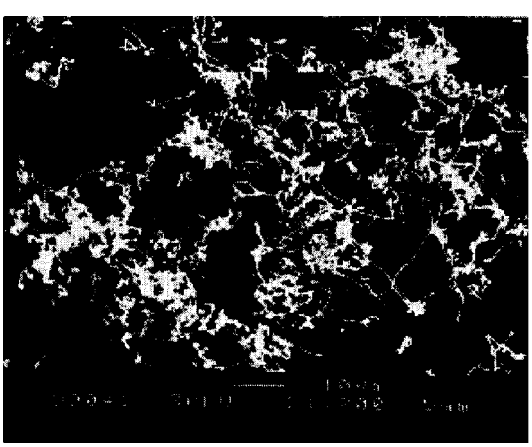


Fig.6. Low-magnification SEM image of GaN nanowires on the surface of an alumina membrane.

The reaction of Ga_2O vapor with ammonia took place in a horizontal quartz tube furnace. The AAMs were first put on the top of the mixture (Ga and Ga_2O_3 with a molar ratio 4:1) and then placed in a quartz tube and held in a constant flowing ammonia atmosphere (300 sccm) at 1273K for 2h. Afterwards, single crystalline GaN nanowire,[43] were obtained on the surface of the AAM. The GaN nanowires with hexagonal wurtzite structure were about 14nm in diameter and up to several hundreds of micrometers in length. Figure 6 shows a SEM photograph of GaN nanowires on the surface of AAM. Figure 7 shows a TEM image of a GaN nanowire and selected area electron diffraction.

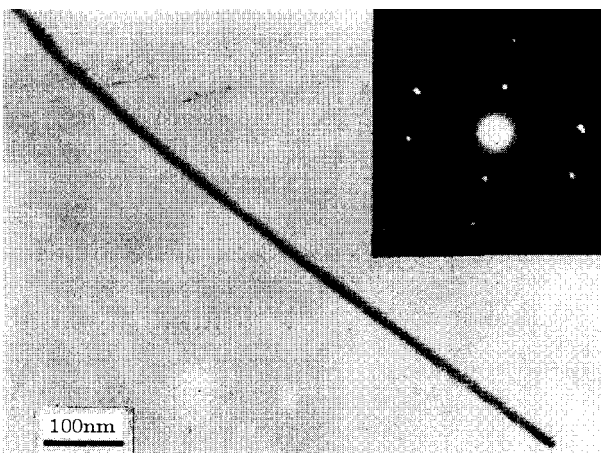


Fig.7. High-magnification TEM image of an individual GaN nanowire. The insert shows the selected area electron diffraction pattern [331] of the nanowire.

Ⅲ. MICROARRAYS

A. Gas reaction in the nanochannels of AAM to produce microarrays

Ordered single crystalline GaN nanowire microarrays embedded in a honeycomb structure of AAM were synthesized through a gas reaction of GaO_2 vapor with a constant ammonia atmosphere at 1273K in the presence of a nanosized metallic indium catalyst on one side of AAMs.[44] First, metallic indium was evaporated in vacuum on one surface of the AAMs to form the nanosized indium nanoparticles at the bottom of the uniform pores. Then, AAMs with indium nanoparticles on one side were put on top of the mixture (Ga and Ga_2O_3 with a molar ratio of 4:1) and then the experiment was carried out under the same conditions as used for the GaN nanowires on the surface of AAM. Figure 8 displays the SEM images of the GaN nanowire microarrays embedded in a honeycomb structure of AAM.

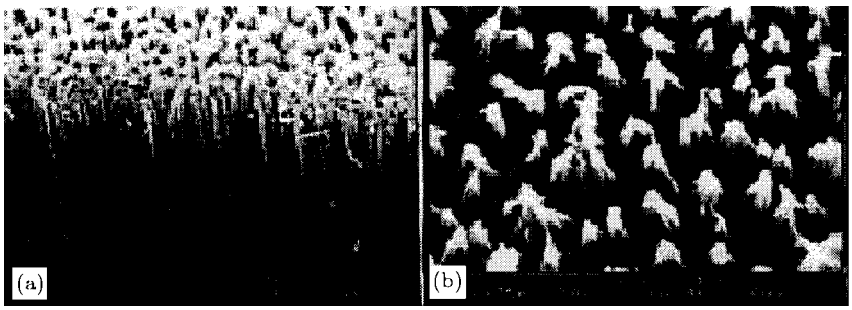


Fig.8. Low-magnification SEM images of GaN microarrays embedded in AAM (a) cross sectional image (b) top-view image.

Carbon nanotube arrays with densities up to $10^{12}/cm^2$ were successfully synthesized by pyrolysis of acetylene within highly ordered nanochannel arrays in AAMs.[45] Au was deposited as an electrode on one side of the AAMs using an ion sputtering apparatus. A small amount of Co particles was electrodeposited into the bottom of the holes by a DC method from the following solution: 150g/l $CoSO_4 \cdot 7H_2O$, 50g/l H_3BO_3; pH 4.2. The temperature of the bath was maintained at 30°C. The ordered arrays of carbon nanotubes were grown by first reducing the catalysts by heating the catalyst-loaded AAMs in a tube furnace at 600°C for 1h in a flow of 9% H_2 in N_2 ($100cm^3/min$). Subsequently, a mixture of 10% acetylene in nitrogen was introduced at a flow rate of $80cm^3/min$. Carbon nanotubes were formed on the Co/Au substrate within the porous AAMs at 700°C. Figure 9 shows the SEM image of the carbon nanotube microarrays. Figure 10 represents a lattice-resolved image of a carbon nanotube.

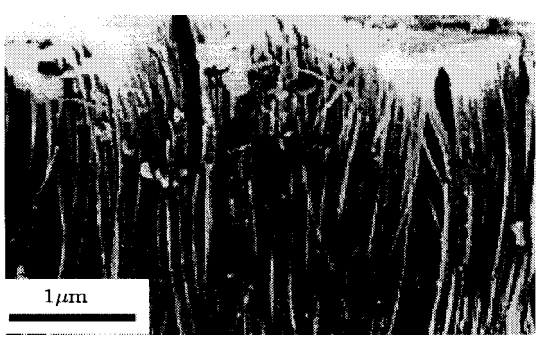


Fig.9. SEM image of the cross-sectional view of carbon nanotube arrays after cleaning in an ultrasonic bath followed by etching off the aluminum oxide using a mixture of phosphoric acid and chromic acid.

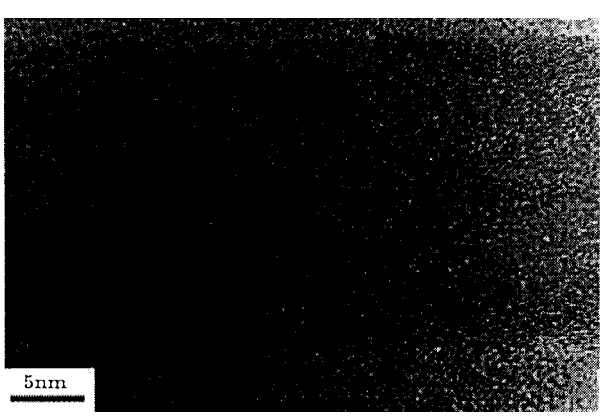


Fig.10. HRTEM image of a carbon nanotube.

B. Sol-gel method to produce microarrays in AAMs

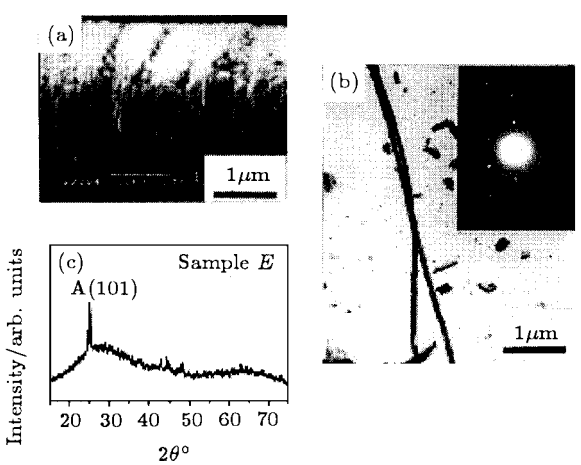


Fig.11. (a) SEM image of TiO_2 nanowire arrays, (b) TEM image of TiO_2 nanowires (insert is the SAED), and (c) XRD pattern of sample.

Highly ordered TiO_2 nanowire arrays were prepared in the nanochannels of AAMs by a sol-gel method.[46] First, 8.5ml of tetrabutyl titanate were added to 25ml of ethanol. Then, 4.5ml of CH_3COOH were mixed with 1.8ml of water and 12.5ml of ethanol. The latter solution was added in drops to the former solution under continuous stirring. The resultant alkoxide solution was kept standing at room temperature for 30min, resulting in a TiO_2 sol. AAMs were

immersed into the sol. The sol-gel transition took place gradually at 30°C for 10h. The samples were heated in a tube furnace in air. The temperature was first ramped to 400°C, then ramped to 650°C, and held at this temperature for 2h. The results are shown in Fig.11(a) SEM image of TiO_2 nanowire arrays, (b) TEM image of TiO_2 nanowires (the SAED is inserted), and (c) XRD pattern of the sample.

C. Electrodeposition

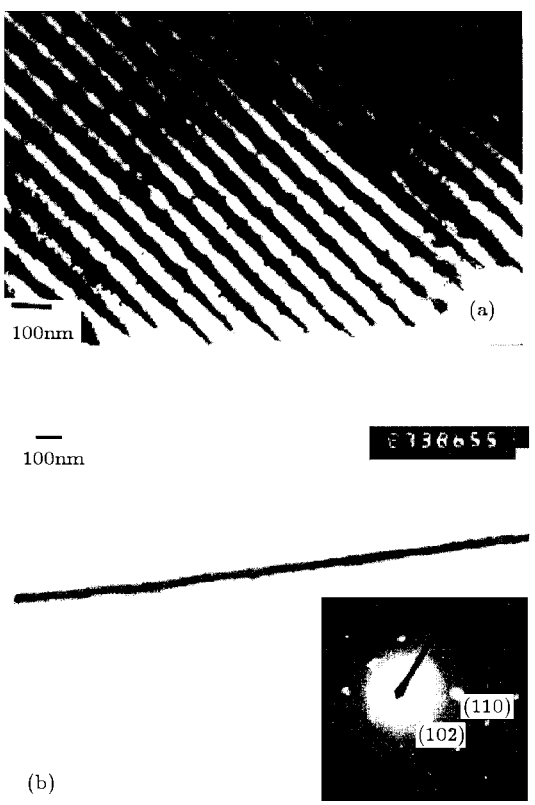


Fig.12. (a) TEM image of a row of Bi nanowires with 50nm in diameters; (b) TEM image of a single Bi nanowire with 50nm in diameter. The inset shows selected area electron diffraction pattern.

Single-crystalline Bi nanowire arrays were successfully assembled into the nanochannels of AAMs by electrodeposition.[47] A layer of Au was sputtered onto one side of the AAM to serve as the working electrode in a standard three-electrode electrochemical cell. The electrolyte contained 75g/l bismuth nitrate pentahydrate, 65g/l potassium hydroxide, 125g/l glycerol, and 50g/l tartaric acid. The deposition solution was buffered to pH=0.9 with nitric acid. The electrodeposition was performed relative to the Ag+/AgCl reference electrode with carbonate serving as the counter electrode. The Bi nanowires are essentially single crystalline and highly oriented. TEM results are shown in Fig.12. Furthermore Fe_xAg_{1-x} nanowire arrays were also electrodeposited into the nanochannels of AAMs.[48] Additionally, ordered semiconductor ZnO nanowire arrays embedded in AAMs were synthesized by electrodeposition and oxidization.[49]

IV. CONCLUSION

In summary, several methods were exploited to prepare nanowires and microarrays in our Lab. Silicon based compound nanowires were synthesized by carbothermal reduction of the sol-gel-derived xerogels containing carbon nanoparticles. Carbide nanowires were prepared by CVD on mesoporous active carbon embedded with transition metal nanoparticles inside the pores. SiC-cored nanowires were produced by carbothermal reduction with the help of VLS crystal growth mechanism. For microarrays, AAMs were used as templates, microarrays embedded in AAMs were fabricated using several methods, such as, chemical vapor reaction, sol-gel technique, electrodeposition and electrodeposition with subsequent oxidation.

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