

# Step-edge like template fabrication of polyelectrolyte supported nickel nanowires

Devesh Srivastava, Troy R Hendricks and Ilsoon Lee<sup>1</sup>

Department of Chemical Engineering and Materials Science, Michigan State University,  
2527 Engineering, East Lansing, MI 48824, USA

E-mail: [leeil@egr.msu.edu](mailto:leeil@egr.msu.edu)

Received 15 March 2007, in final form 18 April 2007

Published 18 May 2007

Online at [stacks.iop.org/Nano/18/245305](http://stacks.iop.org/Nano/18/245305)

## Abstract

A method to produce novel polymer supported nickel nanowires, which are asymmetric (or anisotropic) in shape and function, using an alumina membrane as a template is presented. This paper reports a step-edge like fabrication technique using anodized alumina membranes. First the membrane is treated with fluorosilanes to make the surface completely hydrophobic. It is then cleaved to expose the freshly prepared alumina edges, which are hydrophilic. These freshly cleaved hydrophilic edges are used as templates for the deposition of polyelectrolyte multilayers and nickel. We selectively deposit polyelectrolyte multilayers on those hydrophilic edges. Then the electroless deposition of nickel is used to create nickel nanowires. After dissolving the membranes, we obtain nanostructures which are asymmetric in shape and function.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

One of the biggest challenges in the field of nanotechnology is the cost-effective fabrication of nanowires. To date there are many methods that use top-down approaches or involving elaborate equipment to form nanowires such as dip-pen [1] and electron beam lithography [2], but both are expensive and slow. Cost-effective methods such as soft-lithography [3, 4] and nanoimprint lithography [5–7] are also being developed. The bottom-up approach involves the self-assembly of molecules based on various interactions such as electrostatic, hydrogen bonding or covalent bonding. It offers a more cost-effective method for the fabrication of nanostructures. It also provides more control over the variety of nanostructures that can be fabricated. Nanowires and nanotubes of various materials have also been fabricated using template assisted techniques such as filling the membrane pores of anodized alumina [8–13], track etched polymer membranes [14, 15] and decoration of step-edges [16–19]. Most methods using membranes as a template involve electrodeposition. This is done by coating one side with a metal to make it conductive, followed by electrodeposition of the metal inside the pores. Electroless methods are slightly more difficult, especially in depositing

metal inside the pores, as the process is hindered by the slow diffusion of metal ions into pores.

There are a variety of metals that are being used to make nanowires such as gold [20, 21], copper [22, 23] and silver [24, 25]. Nickel nanowires are also finding great interest among researchers due to their unique magnetic properties. Also at the nanometre scale, quantum confinement leads to unique properties. For example, the band gap of nanowires varies as the inverse square of its diameter [26]. Biological molecules can also be attached to nanowires to form nanomachines [27]. Most fabrication methods for nickel nanowires and nanotubes involve filling pores of membranes [28], step-edge [19] and also using biomolecules such as DNA [29].

In this paper, we report a step-edge like methodology for the fabrication of polyelectrolyte supported nanowires. Polyelectrolytes provide flexible support to metallic nanowires and prevent them from falling apart. Our method is simple, can be performed on a lab-bench top and does not require any equipment for metal deposition. In our method an alumina membrane was functionalized with hydrophobic molecules and then broken to expose freshly cleaved hydrophilic edges along the broken pore walls. Then, polyelectrolyte multilayers (PEMs) were built on the hydrophilic edge of the pore membrane and an electroless nickel bath was used for the deposition of nickel onto the multilayers to form nickel

<sup>1</sup> Author to whom any correspondence should be addressed.

nanowires. After dissolving the membrane, free standing nickel nanowires were obtained.

## 2. Experimental details

Anodized alumina membranes of 200 nm pore size were purchased from Whatman. The fluorosilanes ((tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-methyldichlorosilane) were purchased from United Chemical Technologies Inc. 16-mercaptohexadecanoic acid, positively charged polyelectrolyte, poly(diallyldimethylammonium chloride) (PDAC) ( $M_w \sim 100\,000 - 200\,000$ ), and negatively charged polyelectrolyte, poly(styrene)sulfonate (SPS) ( $M_w \sim 70\,000\text{ g mol}^{-1}$ ), were purchased from Sigma Aldrich. The bath for electroless deposition was prepared using nickel sulfate, sodium hydroxide, sodium citrate, lactic acid and dimethylamine borane (DMAB), which were all purchased from Sigma Aldrich. The palladium catalyst ( $\text{Na}_2[\text{PdCl}_4]$ ) was purchased from Strem Chemicals. More details on electroless nickel deposition can be found in our previous work in which selective nickel plating was made on the particle arrays deposited on patterned polyelectrolyte templates [30].

In this work, alumina membranes were first treated with fluorosilanes by chemical vapour deposition. Both the fluorosilanes and the membranes were placed under vacuum for 30 min. This was followed by 2 h of heating at 120 °C which allows the silanes to cross-link with the alumina membrane both inside the pores and on the outer surface. The fluorosilane treated surfaces are extremely hydrophobic [31]. This was followed by breaking the membrane which exposes the freshly cleaved alumina surface that is hydrophilic [32], unlike the other surfaces of the membrane.

These fresh hydrophilic edges now act as templates for deposition of PEMs and nickel. The alumina membrane is positively charged at a pH of 7 because the isoelectric point of alumina is around pH 8–9 [32]. Polyelectrolyte multilayers were selectively built on the hydrophilic edges by dipping broken membrane in (1) SPS and (2) PDAC solutions for 30 min each. Intermediate washing steps were carried out using de-ionized (DI) water. Two bilayers of (SPS/PDAC)<sub>2</sub> were built leaving a positively charged polyelectrolyte (PDAC) at the top.

The PEM coated membranes were then immersed in a negatively charged palladium catalyst for 15 s and rinsed with DI water at pH of 3.0. The palladium catalyst is necessary to reduce  $\text{Ni}^{2+}$  to metallic Ni. Without the catalyst, nickel will not plate on any surface. The Pd catalyst was adsorbed onto the PEM surface through electrostatic interactions and is the location where the reduction of Ni ions to Ni metal occurs. This gives rise to the nanowires structure supported by polyelectrolytes. The nickel reduction occurred when samples were placed in a 100 ml nickel bath whose composition is summarized in table 1. Before use, the pH of the nickel bath was adjusted to  $6.5 \pm 0.1$  by adding small amounts of 1.0 M NaOH. Electroless deposition times of up to 10 min were used.

Once nickel was deposited, the membrane was dissolved in 3 M NaOH to extract the nickel nanowires. Nickel nanowires were filtered and washed in DI water using a centrifuge. Nickel nanowires were imaged using a scanning electron microscope (SEM, JEOL 6300F) by drop coating

**Table 1.** Chemical composition of a 100 ml nickel bath used for electroless deposition.

Nickel sulfate	4.0 g
Sodium citrate	2.0 g
Lactic acid	1.0 g
DMAB	0.2 g

a glass slide with a suspension containing nickel nanowires which were sputter coated with 7 nm of gold before imaging. Energy dispersive spectroscopy (EDS) was also done to analyse the composition of the nanowires.

Quartz crystal microbalance (QCM) crystals (5 MHz, Maxtek, Inc., Santa Fe Springs, CA) with gold electrodes were cleaned in piranha solution (seven parts concentrated sulfuric acid and three parts 30% hydrogen peroxide) for 30 s followed by rinsing with an excess of DI water and drying by a stream of nitrogen. A self-assembled monolayer (SAM) of 16-mercaptohexadecanoic acid was formed on the surface of the QCM crystals by immersion in a 5 mM ethanol solution for 1 h followed by rinsing with ethanol and drying with nitrogen. Then ten and a half bilayers of (PDAC/SPS)<sub>10</sub>PDAC were formed on the –COOH terminated SAM. The QCM crystals were then immersed in a palladium catalyst solution for 30 s, rinsed with DI water and dried with nitrogen.

## 3. Results and discussion

Figure 1 illustrates the scheme for the formation of the nickel nanowires. Here the fabricated nanowires have two different materials interwoven along their length. The side of the nanotubes that was in contact with the alumina membrane is polyelectrolyte whereas the other side is metal. Hence this simple technique can impart two different functionalities on the same wire. The thickness of each side can be controlled by changing the number of PEM bilayers and the electroless deposition time.

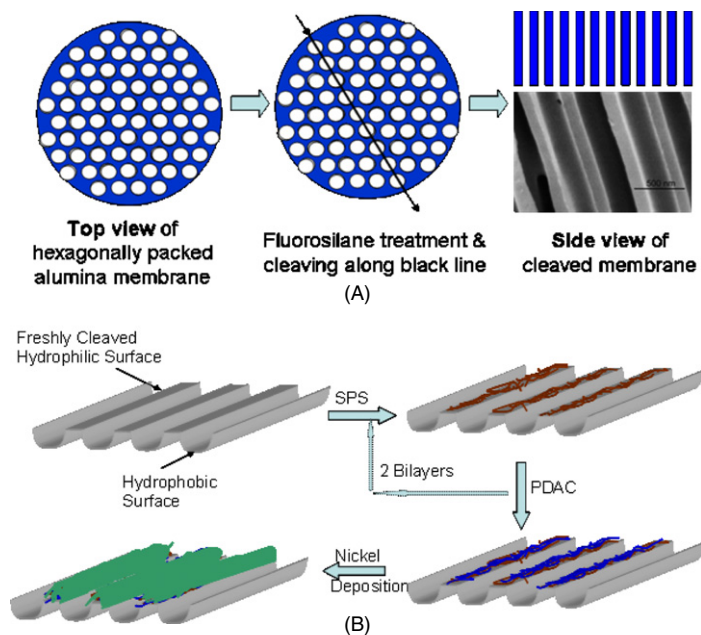
The initial width of the edges can be estimated theoretically from the data given by the manufacturer. The surface density of the 200 nm diameter pores in the membrane is approximately  $10^9$  pores  $\text{cm}^{-2}$ . The linear pore density can be approximated to  $3.1 \times 10^4$  pores  $\text{cm}^{-1}$ . Hence, the theoretical average spacing between the pores can be estimated as:

$$d_{\text{avg}} = \frac{(1 - 31\,000 \times 200 \times 10^{-7})}{31\,000} \text{ cm} = 125 \text{ nm}. \quad (1)$$

We also observed the cross-sectional of the alumina membrane using a SEM. From these images, we estimated edge size to be approximately  $101.5 \pm 32.4$  nm. This observed value is consistent with the theoretical value.

The PEMs act as adhesion layers between the membrane and the metal. Without the PEM layers the nickel would not grow. The polyelectrolytes are hydrophilic molecules so after treating membranes with fluorosilanes, the treated part repels the adsorption of polyelectrolytes. Hence, once the membrane is broken, the polyelectrolytes are selectively deposited on the new exposed region which is hydrophilic.

The purpose of the polyelectrolytes is two fold. First they provide a surface adhesion layer for the negatively charged catalyst to deposit followed by the growth of metal.



**Figure 1.** (A) Schematic representation of the template formation process including top and side views of alumina membranes before and after cleavage. A side view SEM image after the fluorosilane treatment showing cleavage. The actual membranes have quasi-hexagonally packed nanopores, but hexagonally packed nanopores were assumed for the determination of the cleaved edges in which nickel nanowires grow. (B) Schematic illustration of each step of the nanowire formation process, deposition of PEM layers selectively on the freshly cleaved hydrophilic edge area and then selective nickel deposition followed.

They also help to form a continuous support on the edge of the membrane. Since polyelectrolytes are fuzzy structures (i.e., layers of polymer which are intertwined), they can compensate for the irregularities on the edges, hence providing a smoother support for metal wire. In addition, the electrostatic interactions among the polyelectrolyte layers provide a strong adhesion layer for metal growth. The polyelectrolytes used were strong polyelectrolytes hence the charge on them is independent of the surrounding pH environment. So these bilayers maintain their structure and strength in the low pH condition, while washing off catalyst, which it encounters during the growth of the metal.

We did not deposit more than two bilayers since a larger number of bilayers may cause multilayers on adjacent edges to merge as the diameter of nanowires for two bilayers of polyelectrolytes was  $\sim 200$  nm. The thickness of the multilayers grows with the number of bilayers and in this case the polyelectrolytes are growing on an edge. Our previous work on this system shows that each bilayer of PDAC/SPS is 3.4 nm thick [33].

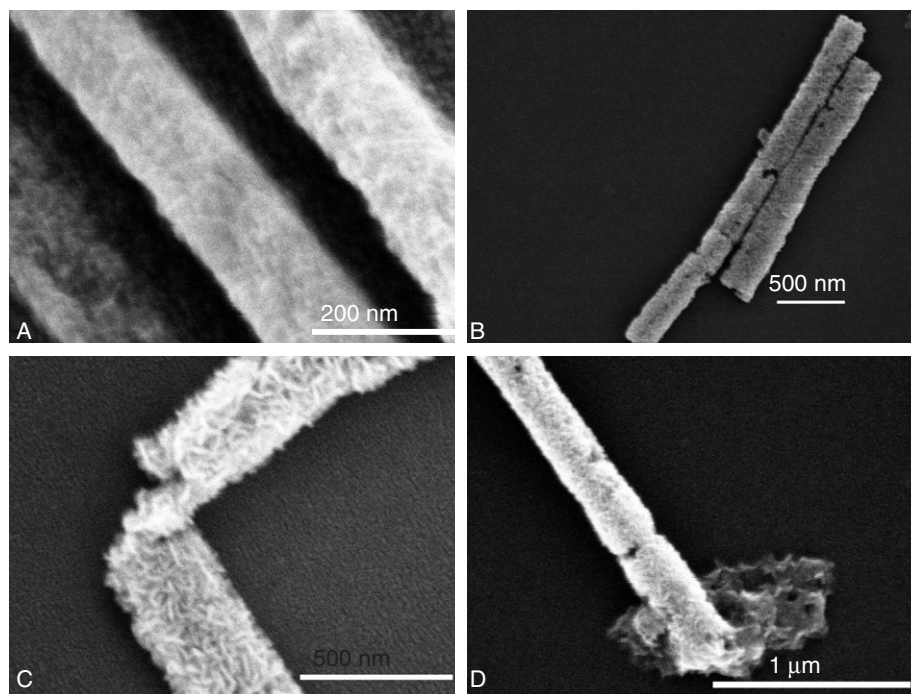
We investigated whether the PEMs were required to form nanowires. The role of the polyelectrolytes was confirmed by a control experiment. As before the alumina membrane was treated with fluorosilanes and then broken. However, the PEMs were not deposited. The membrane was then dipped into the negative catalyst solution and nickel was electrolessly deposited directly on the edges of the alumina membrane. This was followed by filtering and washing. This resulted in no nanowire structures being formed. A second control experiment was performed where the membrane was not treated with fluorosilanes and broken. This time nickel growth occurred at the top and bottom surfaces as well and

not exclusively on the pore edge of the membrane. Again no nanowires were obtained.

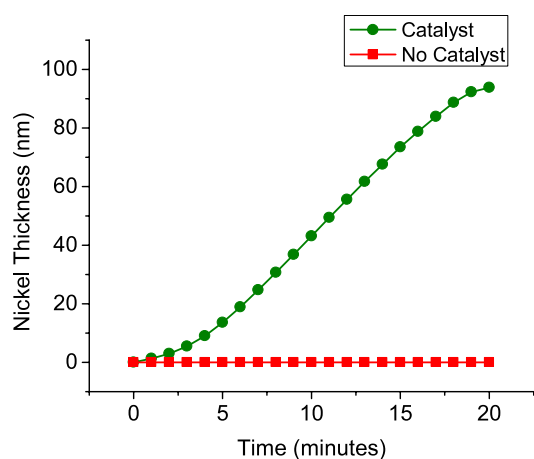
Nickel nanowires were obtained by the dissolution of the alumina membrane and further purified by repeated washing and filtering using a centrifuge and DI water. The samples were imaged using SEM. The images obtained are shown in figure 2. The length of the resulting nanowires was 2–4  $\mu\text{m}$  though the membranes are 60  $\mu\text{m}$  thick. The shorter than expected length could be due to wires breaking during the repeated filtering process. Figure 2(A) shows nickel nanowires growing on the pore edges in an alumina membrane. Figure 2(B) shows a collection of nickel nanowires.

The close up image (figure 2(C)) of a nanowire shows the fuzzy surface structure of the nanowire. This fuzzy surface structure is caused by the presence of the supporting polyelectrolyte layers. Hence the fabricated nanostructures can be considered more like metal nanocactuses (desert plants) supported by a nanofilm of polyelectrolytes. Figure 2(D) shows the end of a nanowire where the metal end is spreading out. This is probably due to the metal film forming at the end of a pore where polyelectrolytes might have deposited at the top surface of the membrane and not in the pore of the membrane.

We estimated the thickness of the nickel film growing on the polyelectrolytes by using QCM. This was done by adsorbing a  $-\text{COOH}$  terminated SAM onto gold coated QCM crystals. Next polyelectrolytes were deposited onto the SAM followed by the deposition of nickel. The weight of nickel deposited caused a shift in the resonance frequency of the quartz crystal. Hence the rate of nickel deposition was calculated by measuring the change in frequency of the quartz crystal. The thickness of the nickel is plotted as a function of time and is shown in figure 3. We have



**Figure 2.** (A) Nickel nanowires growing on the edge of the alumina membrane pore wall. (B) A group of nickel nanowires after dissolution of the alumina membrane. (C) Fuzzy nanostructure showing the polyelectrolyte base as a support for nickel growth. (D) A nickel nanowire with spreading ends showing possible deposition of polyelectrolytes on the top surface of the alumina membranes.



**Figure 3.** Rate of nickel deposition determined from quartz crystal microbalance.

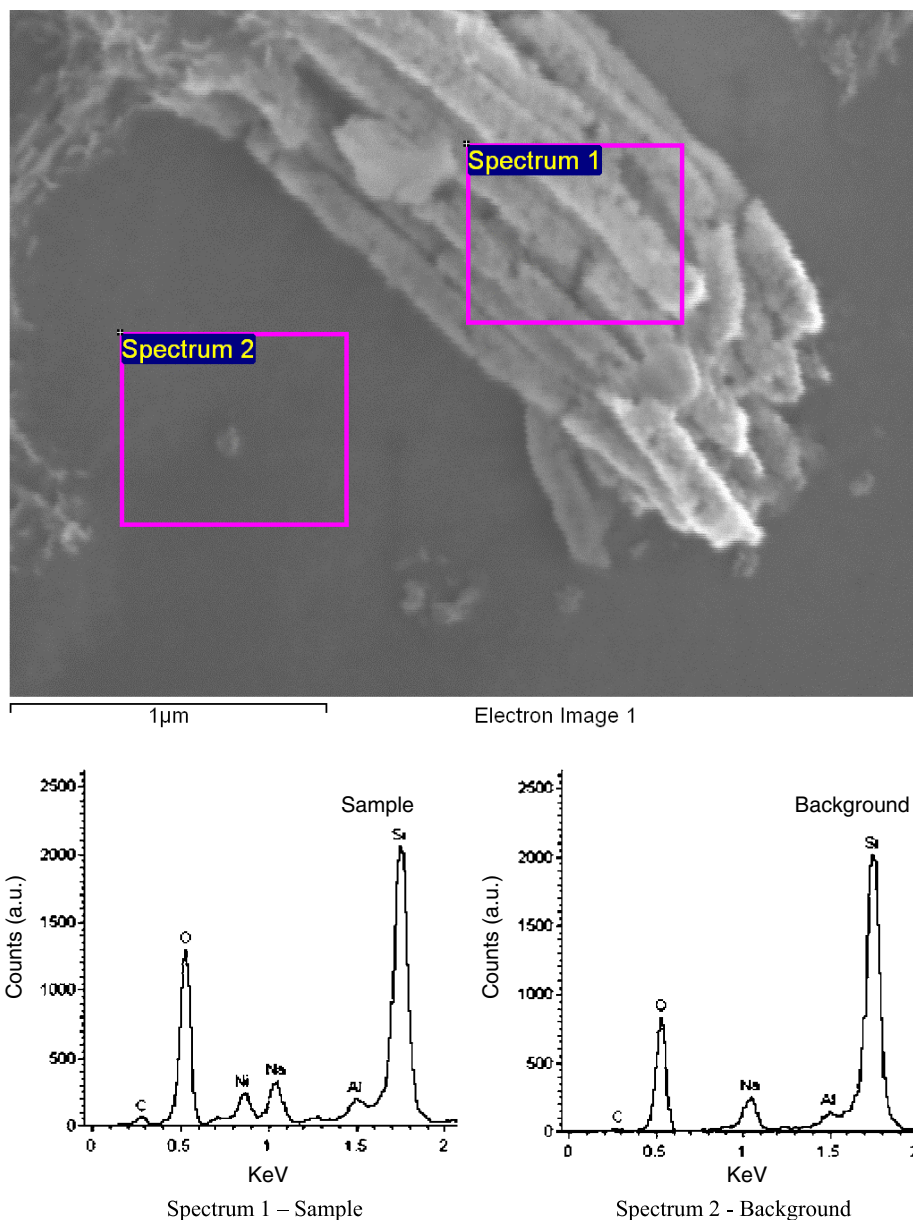
also created homogeneous nickel films on planar substrates. Measurement of these thin metal films shows that they are conductive. However, we have not independently measured the conductivity of the nickel nanowires. Samples with no catalyst showed no controlled nickel deposition. Samples with the palladium catalyst showed initial non-linear growth as the nickel agglomerated on the surface and as time passed coalesced into a uniform coating. Once the surface was uniform the deposition became linear at a rate of  $5.9 \text{ nm min}^{-1}$  for plating times between 5 and 15 min. At about 20 min the plating rate slowed and became non-linear before the nickel started to delaminate and peel off due to the build-up of internal stresses.

Based on the QCM data shown in figure 3 and our previous work on the PEMs [30], the PEM–nickel nanowire has a thickness of around 47 nm, 7 nm from the PEMs and 40 nm from the nickel. Each thickness can be adjusted by changing the number of PEM bilayers and the metal deposition time. In addition, the width of the nanowires can be changed by using membranes with different sized pores.

Elemental analysis of the wires was done using energy dispersive spectroscopy (EDS). The EDS spectra, in figure 4, showed a strong nickel peak, along with other elements from the background. There was also a small carbon peak showing the presence of the polyelectrolytes. For comparison a background spectrum was also taken where both the nickel and copper peaks were absent. In addition, the control experiments gave indirect evidence for the presence of carbon, in the form of polyelectrolytes that support the nickel nanowires, since no nanowires were observed without the polyelectrolyte bilayer deposition step.

#### 4. Conclusion

Here we have demonstrated the step-edge like fabrication of nickel nanowires. This is an easy technique to produce nanowires that does not require an elaborate set-up or a large amount of equipment. It can readily be extended to different metals which can be electrolessly deposited. These nanowires are supported by polyelectrolyte bilayers as the base which makes these wires flexible as they have polyelectrolyte multilayers as support. These nanowires can possibly be printed on polymeric substrates to achieve a printed nanowire array structure. In addition, it imparts functional anisotropy to the composition of the wires where one side is metal and



**Figure 4.** SEM image showing the two regions where EDS spectra were obtained, on the sample and on the background. The sample spectrum has nickel and carbon peaks, showing the presence of nickel from electroless deposition and carbon as polyelectrolytes, which were absent in the background spectrum.

the other side is polymer. This has the added advantage of the ability to have two different molecules adsorbed on single nanowires by functionalizing different sides of the nanowires. In addition, bimetallic nanowires can easily be created by depositing a second metal on top of the first.

### Acknowledgments

We would like to thank the National Science Foundation (CTS-0609164), the AFOSR, the Michigan Economic Development Corporation, and the MSU Foundation for funding our project.

### References

- [1] Piner R D, Zhu J, Xu F, Hong S H and Mirkin C A 1999 *Science* **283** 661
- [2] Hersee S D, Sun X Y and Wang X 2006 *Nano Lett.* **6** 1808
- [3] Bruinink C M, Peter M, de Boer M, Kuipers L, Huskens J and Reinhoudt D N 2004 *Adv. Mater.* **16** 1086
- [4] Helt J M, Drain C M and Batteas J D 2004 *J. Am. Chem. Soc.* **126** 628
- [5] Zhang F X and Low H Y 2006 *Nanotechnology* **17** 1884
- [6] Luo G *et al* 2006 *Nanotechnology* **17** 1906
- [7] Maury P, Escalante M, Reinhoudt D N and Huskens J 2005 *Adv. Mater.* **17** 2718
- [8] Wang J G, Tian M L, Mallouk T E and Chan M H W 2004 *Nano Lett.* **4** 1313
- [9] Steinhart M, Wendorff J H, Greiner A, Wehrspohn R B, Nielsch K, Schilling J, Choi J and Gosele U 2002 *Science* **296** 1997
- [10] Song G J, She X L, Fu Z F and Li J J 2004 *J. Mater. Res.* **19** 3324
- [11] Kohli P, Wharton J E, Braide O and Martin C R 2004 *J. Nanosci. Nanotechnol.* **4** 605

- [12] Ai S F, Lu G, He Q and Li J B 2003 *J. Am. Chem. Soc.* **125** 11140
- [13] Srivastava D and Lee I 2006 *Adv. Mater.* **18** 2471
- [14] Liang Z J, Susha A S, Yu A M and Caruso F 2003 *Adv. Mater.* **15** 1849
- [15] Li N C, Yu S F, Harrell C C and Martin C R 2004 *Anal. Chem.* **76** 2025
- [16] Tokuda N, Watanabe H, Hojo D, Yamasaki S, Miki K and Yamabe K 2004 *Appl. Surf. Sci.* **237** 528
- [17] Li Q G, Olson J B and Penner R M 2004 *Chem. Mater.* **16** 3402
- [18] Xiao Y K, Weng B C, Yu G, Wang J Y, Hu B N and Chen Z Z 2006 *J. Appl. Electrochem.* **36** 807
- [19] Walter E C, Murray B J, Favier F, Kaltenpoth G, Grunze M and Penner R M 2002 *J. Phys. Chem. B* **106** 11407
- [20] Liu J *et al* 2006 *Nanotechnology* **17** 1922
- [21] Young N P, Palfreyman J and Li Z Y 2006 *Small* **2** 71
- [22] Gelves G A, Murakami Z T M, Krantz M J and Haber J A 2006 *J. Mater. Chem.* **16** 3075
- [23] Gerein N J and Haber J A 2005 *J. Phys. Chem. B* **109** 17372
- [24] Riveros G, Green S, Cortes A, Gomez H, Marotti R E and Dalchiale E A 2006 *Nanotechnology* **17** 561
- [25] Bhattacharyya S, Saha S K and Chakravorty D 2000 *Appl. Phys. Lett.* **77** 3770
- [26] Hangarter C M and Myung N V 2005 *Chem. Mater.* **17** 1320
- [27] Ren Q, Zhao Y P, Yue J C and Cui Y B 2006 *Biomed. Microdevices* **8** 201
- [28] Bao J C, Tie C Y, Xu Z, Zhou Q F, Shen D and Ma Q 2001 *Adv. Mater.* **13** 1631
- [29] Gu Q, Cheng C D, Suryanarayanan S, Dai K and Haynie D T 2006 *Physica E* **33** 92
- [30] Lee I, Hammond P T and Rubner M F 2003 *Chem. Mater.* **15** 4583
- [31] Zhai L, Berg M C, Cebeci F C, Kim Y, Milwid J M, Rubner M F and Cohen R E 2006 *Nano Lett.* **6** 1213
- [32] Parks G A 1965 *Chem. Rev.* **65** 177
- [33] Kidambi S, Chan C and Lee I 2004 *J. Am. Chem. Soc.* **126** 4697