Template assisted electrodeposition of germanium and silicon nanowires in an ionic liquid

R. Al-Salman,[a] J. Mallet,*[b] M. Molinari,[b] P. Fricoteaux,[b] F. Martineau,[b] M. Troyon,[b] S. Zein El Abedin†[a] and F. Endres*[a]

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In this paper we report for the first time on the room temperature template synthesis of germanium and silicon nanowires by potentiostatic electrochemical deposition from the air- and water stable ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[Py_{1,4}]Tf_2N$) containing $GeCl_4$ and $SiCl_4$ as a Ge and Si source, respectively. Commercially-available track-etched polycarbonate membranes (PC) with an average nominal pore diameter of 90–400 nm were used as templates. Ge and Si nanowires with an average diameter corresponding to the nanopores' diameter and lengths of a few micrometres were reproducibly obtained. Structural characterization of the nanowires was performed by EDX, TEM, HR-SEM and Raman spectroscopy. Despite the rough surface of the nanowires, governed mostly by the original shape of the nanopore's wall of the commercially-available PC membrane, preliminary structural characterizations demonstrate the promising prospective of this innovative elaboration process compared to constraining high vacuum and high temperature methods.

1. Introduction

Due to their particular importance in future electronic and optoelectronic devices, semiconductor nanowires are of great interest.[1] Semiconductor nanowires exhibit quantum confinement effects and are expected to play a key role in future nanosized electronic and optical devices. Their quasi-one-dimensional structures give them tunable features depending on their size and structural characteristics. Bruno *et al.* reported in ref. 2 on the quantum confinement effects of silicon and germanium nanowires, showing a dependence of the electronic band gap on both wire's diameter and orientation.

Both silicon and germanium nanowires (SiNWs, GeNWs) exhibit a high carrier mobility compared to the bulk materials which gives them promising potential in the fabrication of nanowire field effect transistors,[3] solar cells and nanomagnets.[4] A significant new application of GeNWs and SiNWs was recently reported by Chan *et al.*,[5,6] which describes the use of these materials as higher-capacity anodes for Li-ion batteries. In particular, the results showed that a battery with GeNWs has an initial discharge capacity of 1141 mA h g^{-1}, which was stable over 20 cycles at a charge rate of C/20, while the traditionally used graphite anodes have a maximum theoretical specific capacity of only 372 mA h g^{-1}.

A variety of techniques have been used hitherto for the synthesis of GeNWs and SiNWs such as employing metal nanoclusters as catalyst *via* a vapor–liquid–solid (VLS) process, pulsed laser deposition and molecular beam epitaxy.[7–9] For all these approaches, high vacuum and high temperature processes are required. In this paper we demonstrate an innovative elaboration method which does not necessitate such constraining conditions. Electrodeposition through nanoporous templates is an elegant and versatile method for the fabrication of nanowires;[10] it is low cost, simple and allows a controllable production and quality of the nanowires by just changing the electrodeposition parameters like deposition potential, electrolyte concentration and temperature. Two types of commercially available templates are commonly used for the fabrication: track-etched polycarbonate (PC) and anodic aluminum oxide (AAO) membranes. A conductive metal is sputtered on one side of the membrane which acts as electrode during electrodeposition. The nanowire arrays grow by filling the cylindrical pores of the membrane.

The PC membrane has the advantage of choosing the density of pores from 10^9 cm^{-2} down to a single pore per membrane. In addition, they are easily dissolved in dichloromethane or chloroform without harming the nanowires. A lot of research has been done on the template fabrication of a variety of metal- and alloy nanowires like Cu, Ni, Au, Zn, Co–Gd, CoPt[11–15] and semiconductors like ZnO and CdSe[16–18] from aqueous solutions. Most recently and for the first time the synthesis of silver nanowires from the nonaqueous ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) was reported.[19] The fascinating properties of ionic liquids like negligible vapor pressure, in most cases high thermal stability and, more interestingly, their significantly large electrochemical windows,[20] make it possible

[a] *Institute of Particle Technology, Chair of Interface Processes, Clausthal University of Technology, D-38678 Clausthal-Zellerfeld, Germany. E-mail: frank.endres@tu-clausthal.de; Fax: (+49)5323-722460*
[b] *Laboratoire de Microscopies et d'Etudes des Nanostructures (LMEN), UFR des Sciences, Université de Reims Champagne-Ardenne, 21 rue Clément Ader, 51685 Reims Cedex 2, France. E-mail: jeremy.mallet@univ-reims.fr*
† Permanent address: Electrochemistry and Corrosion Laboratory, National Research Centre, Dokki, Cairo, Egypt.

to electrodeposit metals and semicoductors like Al, Ta, Ge and Si that can not be otherwise electrodeposited from aqueous solutions due to hydrogen evolution instead of deposition.[21] For details we would like to refer to the Wiley VCH book "*Electrodeposition from Ionic Liquids*",[22] edited by one of us (F.E.).

Here we report for the first time on the potentiostatic electrochemical deposition of germanium and of silicon nanowires from the air- and water stable ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[Py_{1,4}]Tf_2N$), containing $GeCl_4$ or $SiCl_4$ as solutes, by using commercially available track-etched polycarbonate membranes (average nominal pore diameter: 90 or 400 nm) as templates. For detailed information about the electrochemistry of this system, we refer the reader to ref. 23 and 24. The main aim of the present paper is to show how easily Ge and Si nanowires can be made.

2. Experimental

$[Py_{1,4}]Tf_2N$ was purchased in the highest quality from Io-li-tec (Germany) or from Solvionic (France) and used after drying under vacuum at 100 °C to water contents below 2 ppm. $GeCl_4$ (99.9999%) and $SiCl_4$ (99.998%) were purchased from Alfa Aesar. The M90 and M400 types of track-etched PC membranes were supplied by Whatman (USA). The thickness of the membranes is 16 μm with an average pore diameter of 90 nm in the case of M90 type and of 400 nm for the M400 PC membrane with pore density of 10^9 cm^{-2}. One side of the membrane was sputtered with a 120 nm thick gold film to act as a working electrode during the electrochemical deposition. A copper sheet was put in contact with the working electrode to provide a better connection to the potentiostat. Ag and Pt wires were used as a quasi-reference and counter electrodes, respectively.

The electrochemical experiments were performed in an argon-filled glove box with water and oxygen content below 1 ppm (OMNI–LAB from Vacuum-Atmospheres). The electrochemical cell was made of Teflon and clamped over a Teflon–covered Viton O-ring onto the membrane yielding a geometric surface area of 0.3 cm^2. The electrochemical measurements were performed using a VersaStat™ II (Princeton Applied Research) potentiostat/galvanostat controlled by powerCV software.

3. Results and discussion

3.1 Germanium nanowires

In order to understand the electrochemical process of Ge (and Si) deposition inside the PC membrane, cyclic voltammograms have been performed. Fig. 1 shows the cyclic voltammogram of 0.1 M $GeCl_4$ (in $[Py_{1,4}]Tf_2N$) inside the M90 polycarbonate membrane acquired at a scan rate of 10 mV s^{-1} at 25 °C. The first reduction peak at −1.4 V *vs.* Ag quasi reference electrode is correlated with the reduction of Ge(IV) to Ge(II). The shoulder at −1.65 V was not observed in the case of Ge electrodeposition on Au(111) electrode (without the membrane) and might be due to transport limitations in the

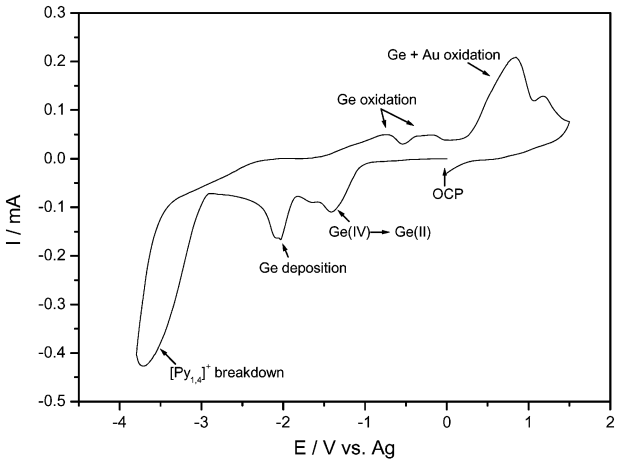

Fig. 1 CV of 0.1 M $GeCl_4$ in $[Py_{1,4}]Tf_2N$ inside the M90 PC membrane with an Au sputtered film on one side of the membrane as working electrode. Scan rate: 10 mV s^{-1}, at 25 °C.

membrane. At −1.86 V the bulk deposition of Ge takes place and the rising current at −2.9 V is corresponding to the decomposition of the organic cation. The oxidation peaks in the back scan are attributed to germanium and gold oxidation.

In order to deposit Ge nanowires with a length of approximately 2 μm, the potential was held at −2.1 V for 1 h. It was quite interesting that after about 30 min of the potentiostatic electrodeposition the whole of the membrane appeared black, which is a strong sign of a very high density of Ge nanowires. The membrane with the nanowires embedded inside was removed under potential control and washed quickly with isopropanol in order to avoid any attack of the solute on the nanowires.[25] Prior to the characterization of the Ge nanowires by transmission electron microscopy (TEM), high resolution scanning electron microscopy (HR-SEM) and electron diffraction X-ray analysis (EDX), the membrane was carefully dissolved by dichloromethane (CH_2Cl_2) and the free nanowires were then harvested.

Fig. 2 shows a HR-SEM image of Ge nanowires prepared in the commercially available M90 PC membrane. The diameter of the nanowires is ranging from about 80 to 130 nm and the

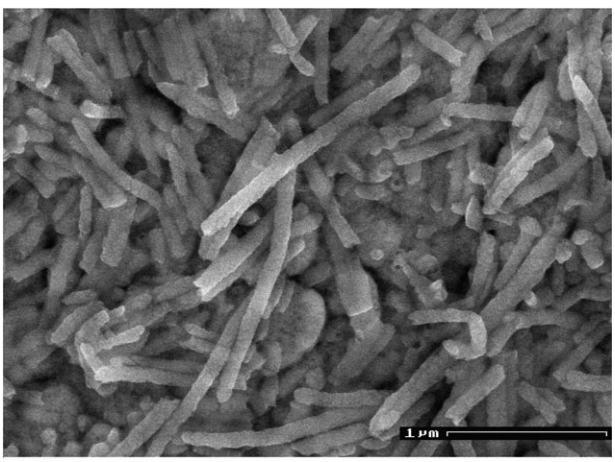

Fig. 2 HR-SEM image of Ge nanowires after the dissolution of the M90 PC membrane.

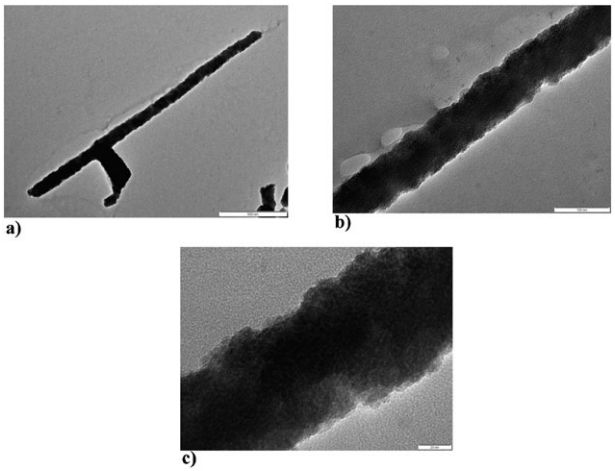

Fig. 3 TEM images of a Ge nanowire with high magnifications. Scale bars are: (a) 500 nm, (b) 100 nm and (c) 20 nm.

length is 2–2.5 μm. Due to a mechanical stress caused by dissolving the membrane (16 μm thick) with dichloromethane, some nanowires have a bent shape and most of them are shortened. The Ge nanowires do not have a perfect cylindrical shape and they have a rather rough surface as indicated by the TEM images in Fig. 3. This morphology is mainly controlled by the original shape of the pores of the PC membrane, since the deposited material acquires, more or less, the same shape as the pores. Ferain and Legras[26] have reported that the shape of pores in commercially available track-etched PC membranes is, in general, not cylindrical with a constant cross-section but is rather toothpick- or cigar-like. Similar observation was also found by Motoyama *et al.*,[11] who reported that Cu and Ni nanowires prepared in commercially available PC membranes do not have a perfectly uniform diameter along the axis of the nanowires, thus our results are in agreement with the mentioned literature data. One has to bear in mind that most of the commercially available PC membranes are rather manufactured as filters for analytical use like, for example, the analysis of airborne contaminants and other particles using optical or electron microscopy. Thus they are not optimized for the production of metal or semiconductor nanowires. However, some improvement of track-etched PC membranes to be used as templates with perfect cylindrical pore-shape has been reported.[12,26]

There are no ordered electron diffraction patterns of the nanowire, indicating that the Ge nanowires are amorphous. The EDX spectrum (Fig. 4) of one of the nanowires shown in Fig. 2 shows that the wire is elemental Ge with quite a small amount of germanium oxide which is due to the exposure of the sample to air. Au and Cu are from the gold film (working electrode) and the supporting copper sheet, respectively. As seen from the EDX spectrum, no detectable amounts of chlorine or sulfur (from ionic liquid) were observed. These results agree quite nicely with earlier results from the group on nanoscale electrodeposition of germanium, proving that elemental (amorphous) germanium nanowires, presented here, have been formed.

3.2 Silicon nanowires

Fig. 5 shows the CV of 0.5 M $SiCl_4$ (in $[Py_{1,4}]Tf_2N$) inside the M90 polycarbonate membrane acquired at a scan rate of 10 mV s^{-1} at 25 °C. Two main reduction peaks appear in the forward scan: the first one at −2.5 V *vs.* Ag quasi reference is due to the bulk deposition of Si. Deposition at −2.5 V on Au(111) without the membrane gives clearly a Si deposit.[24] The second reduction peak at −2.9 V was not observed in the case of 0.1 M $SiCl_4$ in $[Py_{1,4}]Tf_2N$, thus it is concentration dependent and can be attributed further to the over potential deposition (OPD) of Si. The rising current at −3.1 V is correlated with the decomposition of the organic cation. The PC membrane was removed and dissolved with dichloromethane as described above.

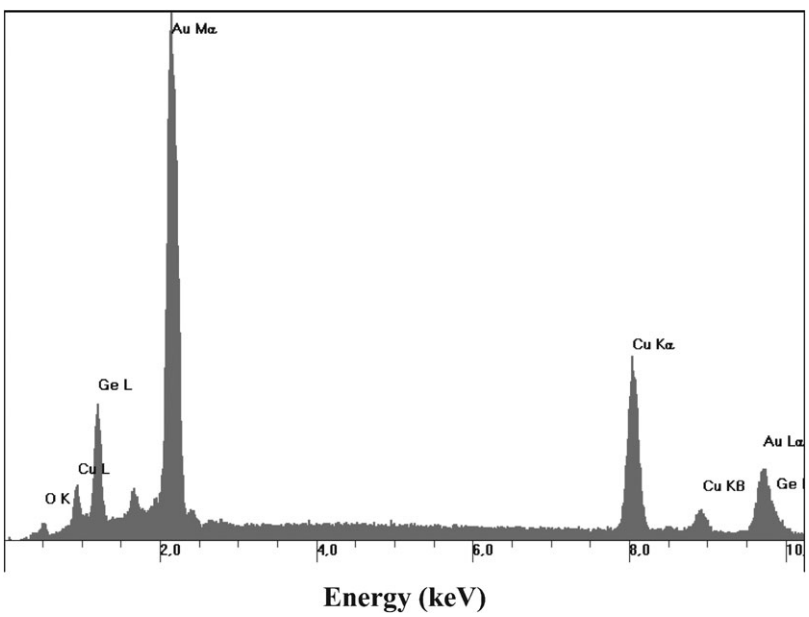

Fig. 4 EDX spectrum of one of the Ge nanowires shown in Fig. 1.

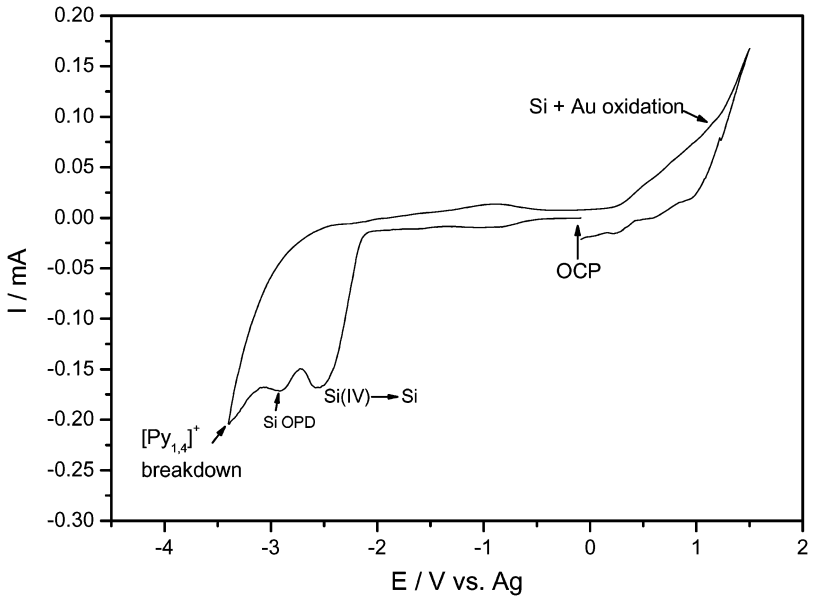

Fig. 5 CV of 0.5 M $SiCl_4$ in $[Py_{1,4}]Tf_2N$ inside the M90 PC membrane with an Au sputtered film on one side of the membrane as working electrode. Scan rate: 10 mV s^{-1}, at 25 °C.

Fig. 6 represents SEM images of Si nanowires obtained from 0.5 M $SiCl_4$ in $[Py_{1,4}]Tf_2N$ after polarization at −2.8 V *vs.* Ag quasi reference electrode for one hour in the M400 and M90 PC membranes, Fig. 6a and b, respectively. The average diameter of the Si wires is around 400 nm in the case of (a) and around 100 nm in the case of (b). The length is in the range of 4 to 6 μm.

An SEM picture of a single Si nanowire and an associated EDX line profile are shown in Fig. 7. The same quantitative analysis profile was obtained for all tested nanowires. A certain amount of gold is revealed at one end of the wire. This gold concentration is certainly correlated to the Au coating of the membrane and not to a diffusion process. This gold quantity rapidly decreases as the probe sweeps over the wire.

Quite a simple experiment has been done to verify that the presence of oxygen in the Si deposit is mainly due to an *ex situ* oxidation after synthesis. EDX analysis of SiNWs just after their immersion for a few seconds in 10% HF solution has revealed a huge drop of the oxygen concentration from 66 to only 10%. It confirms that indeed elemental Si has been electrodeposited initially as we know independently from an XPS study of nanoscale silicon.[27]

A Raman spectrum of a bunch of Si nanowires is shown in Fig. 8. The Raman effect is an efficient way to determine the presence of pure silicon in its crystalline or amorphous form. Bulk crystalline silicon exhibits a very thin band with a Raman shift at 520 cm^{-1},[28] while in amorphous silicon,[29] the selection rules are broken and the Raman spectrum is characterized by the density of phonon states, which presents two broad bands at 150 and 480 cm^{-1}. When silicon nanocrystals are present, a thin band usually appears between 480 and 520 cm^{-1}. Its position is directly linked to the cluster sizes and a growth of the crystallites provokes a blueshift of this band. In Fig. 8, the two bands at 150 and 480 cm^{-1} are clearly visible which indicates the presence of a pure amorphous silicon phase.

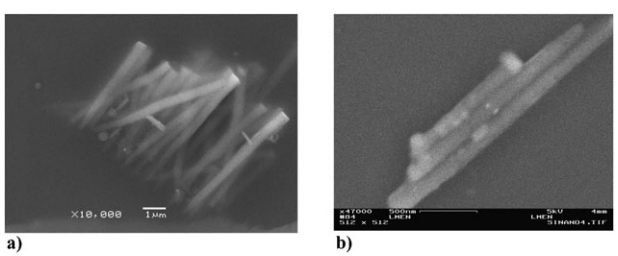

Fig. 6 SEM images of Si nanowires after the dissolution of: (a) M400 PC membrane and (b) M90 PC membrane.

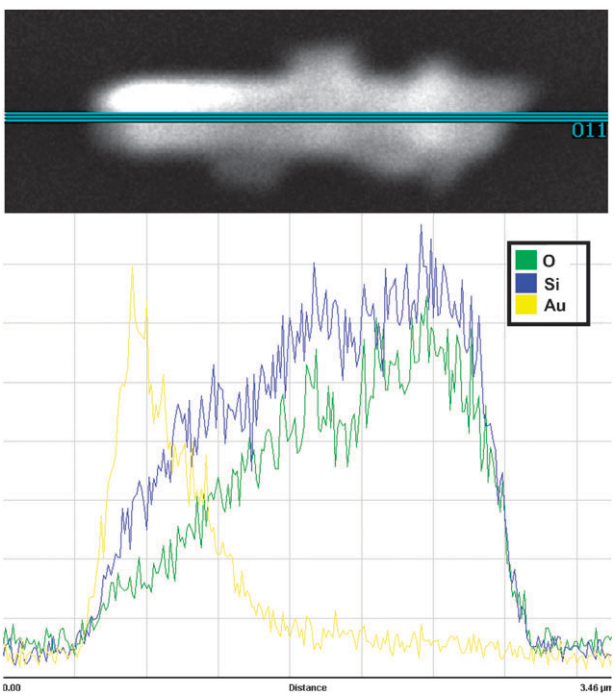

Fig. 7 SEM picture of a single Si nanowire with the associated EDX line profile.

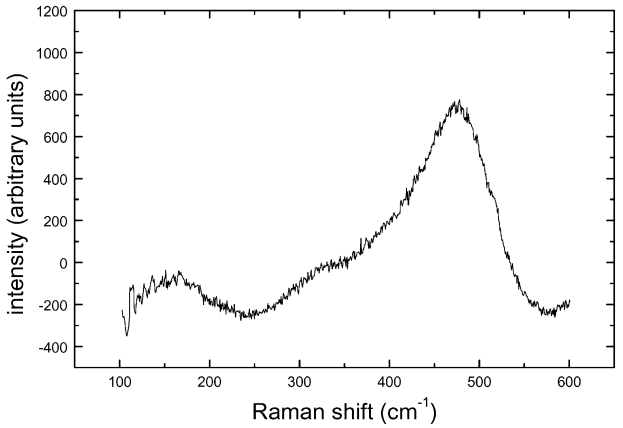

Fig. 8 Raman spectrum of a bunch of Si nanowires. The two broad bands at 150 and 480 cm^{-1} are indicative of pure amorphous silicon.

4. Conclusion

We have shown in this paper for the first time that Ge and Si nanowires with diameters of 90–400 nm can be made by a simple electrochemical template synthesis in an ionic liquid. The simplicity and the mild reaction conditions of the synthesis process, compared to the traditionally used ultra-high vacuum techniques, make it an attractive method for the manufacture of such materials. The only restriction in this method is the need to perform the synthesis under inert gas conditions because of the hygroscopic nature of the precursors $GeCl_4$ and $SiCl_4$. There is a variety of commercially available PC membranes, with different pore diameters and membrane-thickness, which makes it possible together with electrochemistry to control the length and diameter of deposited nanowires. PC membranes with a very small pore diameter close to 10 nm are commercially available, which would enable the synthesis of Ge, Si and Si_xGe_{1-x} nanowires in the quantum-confinement size regime.

References

1 W. Lu and C. M. Lieber, *J. Phys. D: Appl. Phys.*, 2006, **39**, R387.
2 M. Bruno, M. Palummo, S. Ossicini and R. Del Sole, *Surf. Sci.*, 2007, **601**, 2707.
3 D. Wang, Q. Wang, A. Javey, R. Tu, H. Dai, H. Kim, P. C. Mclntyre, T. Krishnamohan and K. C. Saraswat, *Appl. Phys. Lett.*, 2003, **83**, 2432.
4 A. Alguno, N. Usami, T. Ujihara, K. Fujiwara, G. Sazaki, K. Nakajima and Y. Shiraki, *Appl. Phys. Lett.*, 2003, **83**, 1258.
5 C. K. Chan, X. F. Zhang and Y. Cui, *Nano Lett.*, 2008, **8**, 307.
6 C. K. Chan, H. Peng, G. Liu, K. Mcllwrath, X. F. Zhang, R. A. Huggins and Y. Cui, *Nat. Nanotechnol.*, 2008, **3**, 31.
7 R. S. Wagner, *Whisker Technology*, Wiley, New York, 1970.
8 H. J. Fan, P. Werner and M. Zacharias, *Small*, 2006, **2**, 700.
9 L. J. Lauhon, M. S. Gudiksen, C. L. Wang and C. M. Lieber, *Nature*, 2002, **420**, 57.
10 L. Piraux, S. Dubois and S. Demoustier-Champagne, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1997, **131**, 357.
11 M. Motoyama, Y. Fukunaka, T. Sakka, Y. H. Ogata and S. Kikuchi, *J. Electroanal. Chem.*, 2005, **584**, 84.
12 S. Karim, M. E. Toimil-Molares, F. Maurer, G. Miehe, W. Ensinger, J. Liu, T. W. Cornelius and R. Neumann, *Appl. Phys. A*, 2006, **84**, 403.
13 J.-G. Wang, M.-L. Tian, N. Kumar and T. E. Mallouk, *Nano Lett.*, 2005, **5**, 1247.
14 R. Mishra and E. J. Podlaha, *Electrochem. Solid-State Lett.*, 2006, **9**, C199.
15 J. Mallet, K. Yu-Zhang, S. Mátéfi-Tempfli, M. Mátéfi-Tempfli and L. Piraux, *J. Phys. D: Appl. Phys.*, 2005, **38**, 909.
16 L. E. Greene, M. Law, D. H. Tan, M. Montano, J. Goldberger, G. Somorjai and P. Yang, *Nano Lett.*, 2005, **5**, 1231.
17 S. Kumar, S. Kumar, N. K. Verma and S. K. Chakavartib, *J. Optoelectron. Adv. Mater.*, 2007, **9**, 3191.
18 K. Yu-Zhang, D. Z. Guo, J. Mallet, M. Molinari, A. Loualiche and M. Troyon, *J. Nanosci. Nanotechnol.*, 2008, **8**, 2022.
19 I. Kazeminezhad, A. C. Barnes, J. D. Holbrey, K. R. Seddon and W. Schwarzacher, *Appl. Phys. A*, 2007, **86**, 373.
20 F. Endres and S. Z. El Abedin, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2101.
21 S. Zein El Abedin and F. Endres, *ChemPhysChem*, 2006, **7**, 58.
22 *Electrodeposition from Ionic Liquids*, ed. F. Endres, D. R. MacFarlane and A. P. Abbott, Wiley-VCH, Weinheim, 2008.
23 N. Borisenko, S. Zein El Abedin and F. Endres, *J. Phys. Chem. B*, 2006, **110**, 6250.
24 R. Al-Salman, S. Zein El Abedin and F. Endres, *Phys. Chem. Chem. Phys.*, 2008, **10**, 4650.
25 F. Endres and S. Zein El Abedin, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1649.
26 E. Ferain and R. Legras, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2001, **174**, 116.
27 F. Bebensee, N. Borissenko, M. Frerichs, O. Höfft, W. M. Friedrichs, S. Zein El Abedin and F. Endres, *Z. Phys. Chem.*, 2008, **222**, 671.
28 J. Puigdollers, J. Cifre, M. C. Polo, J. M. Asensi, J. Bertomeu, J. Andreu and A. Lloret, *Appl. Surf. Sci.*, 1995, **86**, 600.
29 M. Marinov and N. Zotov, *Phys. Rev. B*, 1997, **55**, 2938.