Conductive films of ordered nanowire arrays

Kirk J. Ziegler\textsuperscript{a}, Boris Polyakov\textsuperscript{b}, Jaideep S. Kulkarni\textsuperscript{a}, Timothy A. Crowley\textsuperscript{a}, Kevin M. Ryan\textsuperscript{a}, Michael A. Morris\textsuperscript{a}, Donats Erts\textsuperscript{b} and Justin D. Holmes*\textsuperscript{a}\textsuperscript{a}\textsuperscript{a} Department of Chemistry, Materials Section and Supercritical Fluid Centre, University College Cork, Cork, Ireland. E-mail: j.holmes@ucc.ie; Fax: +353 (0)21 4274097; Tel: +353 (0)21 4903608

\textsuperscript{b}Institute of Chemical Physics, University of Latvia, LV-1586, Riga, Latvia

Received 22nd September 2003, Accepted 24th October 2003
First published on the web 24th November 2003

High-density, ordered arrays of germanium nanowires have been synthesised within the pores of mesoporous thin films (MTFs) and anodized aluminium oxide (AAO) matrices using a supercritical fluid solution-phase inclusion technique. Conductive atomic force microscopy (C-AFM) was utilised to study the electrical properties of the nanowires within these arrays. Nearly all of the semiconductor nanowires contained within the AAO substrates were found to be conducting. Additionally, each individual nanowire within the substrate possessed similar electrical properties demonstrating that the nanowires are continuous and reproducible within each pore. C-AFM was also able to probe the conductance of individual nanowires, 3–4 nm in diameter, within the MTF templates. The ability to synthesise ordered arrays of semiconducting nanowires is a key step in future ‘bottom-up’ fabrication of multi-layered device architectures for potential nanoelectronic and optoelectronic devices.

Introduction

The ability to pack high densities of memory storage and processing circuitry into specific nanoscale arrays, and utilize the unique transport properties associated with these architectures, is expected to lead to future generations of computer processors with device sizes many times smaller and faster than current silicon based processors. However, both physical and economic constraints are expected to limit continued miniaturization of electronic and optical devices using current ‘top-down’ lithography based methods.\textsuperscript{1,2} Consequently, alternative non-lithographic methodologies for
constructing the smallest mesoscopic features of an integrated circuit will soon be required.

One dimensional (1D) structures, or nanowires, are expected to play a role in future integrated circuits as both devices and interconnects. One of the most successful approaches for producing nanowires is based on the vapour–liquid–solid (VLS) growth process described nearly 40 years ago by Wagner and Ellis. Several researchers have used adaptations of this method to generate nanowires. One inherent problem with these approaches however, is the formation of entangled meshes of nanowires. While Lieber and co-workers have made significant progress in manipulating these nanowire meshes into useful configurations for potential electronic devices, other researchers have focused on forming nanowires in predefined architectures to allow easier processing and integration of the nanostructures into functioning devices.

Encapsulation of nanowires within an ordered template offers the possibility of manipulating nanowires into useful configurations and allows their aspect ratios and, hence, their physical properties to be tailored. Nanometer-wide channels of ordered anodic aluminium oxide films, polycarbonate track etched membranes, orientated steps at single crystal surfaces and nanochannel array glasses have previously been used as templates for nanowires. While these templating methods are useful, the formation of ordered arrays of nanoscale channels within these templates is difficult and the channel dimensions are often too large to exhibit useful quantum confinement effects.

Mesoporous solids that contain uni-directional arrays of pores, typically 2–15 nm in diameter, running throughout the material have been successfully exploited as templates for nanomaterials synthesised from chemical vapour deposition (CVD), electrodeposition, and incipient wetness techniques. These methods have yielded nanomaterials within the pores but the high temperatures or extensive reaction times often required for successful nucleation and growth of the materials within the mesopores makes these techniques costly and time-consuming. Furthermore, these approaches often have significant problems with complete pore inclusion due to pore plugging where the surface tension of the liquid solvent prevents precursor penetration into the pores. CVD approaches are less prone to pore plugging but can undergo capillary condensation resulting in liquid phases within the pores.

In our laboratories, we have developed a supercritical fluid (SCF) solution-phase method for forming metal, metal oxide, and semiconductor nanowires within mesoporous materials. The high-diffusivity, high precursor solubility, and reduced surface tension of the SCF results in rapid nucleation and growth of the nanowires within the pores reducing the reaction time for pore inclusion by at least an order of magnitude compared to chemical vapour deposition (CVD). Additionally, SCFs cannot be condensed to a liquid phase reducing the problems of pore plugging and incomplete inclusion seen with CVD, electrodeposition, and incipient wetness techniques. Silicon and germanium nanowires were the first materials synthesised within mesoporous silica powders using the SCF method. These studies showed that nearly complete inclusion of the mesopores was achieved, as characterised by magic angle spinning nuclear magnetic resonance (MAS-NMR) and X-ray fluorescence (XRF).

More recently, metal (copper and cobalt) and metal oxide (iron oxide) nanowires have also been synthesised within mesoporous silica powders using our SCF method. In these studies, we showed that under the appropriate reaction conditions nanotubes could be synthesised where the thickness of the tube wall could be
controlled by the precursor concentration. Furthermore, different crystal phase mixtures of Co nanowires could be synthesised by changing the pressure and temperature conditions during synthesis. This result is significant as the magnetic properties of Co can be correlated to its crystal structure. To our knowledge, this was the first report of the pressure-sensitive synthesis of different crystal phases at low pressures (250–400 bar).

Although mesoporous powders are ideally suited for nanowire synthesis, these mesoporous solids need to be cast as well-ordered silicate or aluminosilicate mesoporous thin films (MTFs) for future applications such as nanowire devices and interconnects. Recently, we have prepared germanium nanowire arrays within MTFs (GeNW-MTFs) on silicon and quartz substrates using our SCF method. High-resolution TEM and X-ray diffraction showed that nanowires formed within the ordered matrix were aligned at slight angles from the perpendicular axis. Packing densities of $10^{12}$ nanowires per cm$^2$ were achievable. In this paper, we describe the preparation of GeNW-MTFs and germanium nanowire arrays within anodized aluminium oxide membranes (GeNW-AAO). Conductive atomic force microscopy (C-AFM) was utilized to investigate the electrical properties of GeNW-MTFs and GeNW-AAO. The conductance through individual Ge nanowires, 3–4 nm in diameter, was demonstrated within the mesoporous templates. Additionally, the nanowires formed within each pore of the AAO membranes were observed to have similar electrical characteristics. These results suggest that each nanowire is continuous throughout the length of the substrate demonstrating the reproducibility of nanowire synthesis within the pores. Furthermore, nearly all of the nanowires formed within the AAO membranes are conducting suggesting nearly complete inclusion of nanowires within the matrix.

**Experimental**

**Preparation of mesoporous thin films**

Mesoporous thin films (MTFs) were produced by mixing tetraethoxy silane (TEOS, 25 g), ethanol (13 ml), and HCl (2.5 ml, 0.12 M) together in the presence of a surfactant (7 g), i.e., poly(ethylene oxide)–poly(propylene oxide) triblock copolymer surfactant P85 (PEO$_{26}$PPO$_{39}$PEO$_{26}$) or P123 (PEO$_{20}$PPO$_{69}$PEO$_{20}$) (Uniquema, Belgium). The resultant solution was stirred at 310 K for 10 min to prehydrolyse the silica precursor. H$_2$O was then added and the solution was allowed to condense for 20 h prior to film casting. KCl crystals were cut and scraped with a blade to obtain a rough flat surface. The crystals were then placed on an optically flat glass block and polished with various grades of carborundum using figure eight motions. The crystals were rotated often and methanol or ethanol (anhydrous) was used as a lubricant. The sol was placed on the substrates by spin coating (2000–4000 rpm) for 30 s. The cast films were dried at 373 K for 40 min to complete the condensation process and were subsequently calcined at 723 K for 1 h for template removal. Residual surfactant was removed with a 5% ozone stream (Yanco Ozone Generator GE60/MF 5000) flowing over the silica substrate for 30 min.

**Nanowire inclusion into mesoporous thin films (MTFs) and porous anodised aluminium oxide (AAO) membranes**

Germanium nanowires were synthesized within the pores of MTFs (GeNW-MTFs) and AAO membranes (GeNW-AAO) (Anodisc filters, SPI Supplies, West Chester,
Briefly, the ordered porous films were placed inside a 25 mL high-pressure reaction cell with diphenylgermane placed inside an open top quartz glass boat adjacent to the membranes under an inert atmosphere. The reaction cell was attached via a three-way valve to a stainless steel reservoir (~48 mL). A high-pressure ISCO pump (Lincoln, NE) was used to pump CO₂ through the reservoir into the reaction cell. The reaction cell was placed in a tube furnace and heated to 873 K using a platinum resistance thermometer and temperature controller. The pressure was simultaneously ramped to 37.5 MPa and the reaction proceeded at these conditions for 30 min. **Caution:** the high pressures and temperatures used in these experiments and the volatile nature of the chemicals could potentially lead to fire or explosion. Suitable safety precautions should be taken into consideration including the use of a blast screen.

**Film and nanowire characterization**

Scanning electron microscopy (SEM) images were obtained on a JEOL20. The preparation of GeNW-MTFs for conductive atomic force microscopy (C-AFM) is illustrated in Fig. 1. To remove contaminants and possible oxides present at the end of the nanowires within the MTFs and AAO membranes, the film surface was cleaned by RF Ar plasma at 100 W for 5 min with a flow rate of 30 sccm and a pressure of 13 mbar. This plasma cleaning removed approximately 30 nm of the surface layer. The AAO membranes were also mechanically polished to remove any bundles of nanowires. GeNW-MTFs and GeNW-AAOs were placed inside the chamber of a Balzers PLS550 sputter coater at a pressure of 5.6 × 10⁻⁸ mbar. A gold film was then deposited onto the film surface at a rate of 0.73 nm s⁻¹ (DC sputtering at 40 W) resulting in a film approximately 200 nm thick. GeNW-MTF samples prepared on KCl substrates were then inverted so that the gold film was placed directly onto a conductive substrate and glued with conductive epoxy. The KCl substrate was then dissolved with de-ionized water to expose the GeNW-MTF. A custom-built conductive atomic force microscope was utilized for simultaneous measurement of the surface topography and conductance mapping as shown in Fig. 2. The AFM tips, having a radius of curvature less than 35 nm, were Pt-coated ultrasharp silicon cantilevers (Micromasch CSC12/Pt/50). Special programmes to deconvolute the effect of tip shape have not been used; hence convolution may take place in topographic images. In C-AFM mode conductivity conditions are difficult to control but by changing the conductivity regime from direct contact to tunnelling, where the tunnelling current exponentially depends on distance, the resolution can be improved. In some cases, a gold electrode 2 mm in diameter was deposited onto the top surface of the GeNW-AAO membranes to determine the quality of the contacts. The MTFs and AAO membranes, without nanowires, were found to be non conductive using our C-AFM set-up (current amplifier was 1 pA).
Fig. 1 Schematic of the preparation of germanium nanowires embedded within mesoporous thin films (GeNW-MTF) prepared on KCl substrates. (1) GeNW-MTF prepared using the supercritical fluid inclusion technique. (2) The substrate is cleaned with Ar plasma and a gold film approximately 200 nm thick is sputter coated onto the top surface. (3) The sample is inverted and placed on a conductive substrate. The KCl is removed with de-ionized water. (4) The sample is loaded in the conductive atomic force microscope for measurements.

Fig. 2 Conductivity experiments with (a) conductive atomic force microscopy
experiments (C-AFM) and (b) with a gold contact deposited on top surface by sputter coating.

**Results and discussion**

The electrical properties of individual semiconductor nanowires\(^{48-52}\) have been investigated by a number of research groups. To date, there are few studies on the electrical properties of organized arrays of nanowires.\(^{53}\) The lack of electrical characterisation of nanowire arrays stems from the difficulties in placing nanowires into organized structures. However, the inclusion of nanowires in MTFs or AAO membranes combined with conductive atomic force microscopy (C-AFM) has the potential to yield the electrical properties of thousands of individual nanowires that are aligned in ordered architectures. Due to the poor conductivity of the silicon substrates used in our prior preparations,\(^{47}\) GeNW-MTFs were prepared on KCl substrates which could later be dissolved and replaced with a conductive gold layer. C-AFM measurements on GeNW-MTFs prepared on KCl substrates are shown in Fig. 3. As seen in the figure, there are regions of significant conductivity through the substrate. However, large portions of the substrate appear to be non-conductive. Some of the regions are quite large stretching for several hundred nanometres while some are quite small. Ideally, we would like to have observed very small conductivity regions corresponding to the diameter of the nanowires evenly distributed throughout the substrate in a hexagonally ordered array. The smallest conductivity regions in Figs. 3e and 3f are approximately 3–4 nm which correlates to the diameter of an individual Ge nanowire within a P85 or P123 MTF.\(^{47,54}\) In addition, Fig. 3e shows that some of these conductivity regions appear to be separated by the expected pore centre-to-pore centre separation distance for P123 (6–8 nm). Therefore, these results suggest that a portion of the pores in the MTF are orientated with the hexagonal mesoporous structure stretching towards the surface and that these pores are successfully filled with conducting nanowires. A typical I-V curve for an isolated Ge nanowire is shown in Fig. 3g.
Fig. 3 Conductive atomic force microscopy (C-AFM) images of Ge nanowires embedded within a P85 and P123 mesoporous thin film (GeNW-MTF): (a–b) surface topography, (c–d) conductivity map, and (e–f) selected area of conductivity map showing the conductivity of individual nanowires within the MTF. Note (e) which shows conductivity through individual nanowires with diameters approx. 3–4 nm and
separated by the mesoporous structure by 6–8 nm corresponding to the expected pore diameter and pore centre-to-pore centre distances for P123 MTFs; (g) shows a typical I/V curve obtained from an isolated Ge nanowire within the MTF matrix.

The large conducting and non-conducting regions of the GeNW–MTFs on KCl substrates suggests that there are some problems with the preparation of ordered arrays of conducting nanowires within the mesoporous films. These problems can be summarized as arising due to (a) problems with the ordered MTF or (b) problems with the SCF inclusion technique of embedding nanowires within the MTF. The potential problems with the film preparation and inclusion process are outlined in Fig. 4. Film preparation problems can arise from several factors such as: i. MTF grain boundaries, ii. surface roughness or film adhesion problems, iii. MTF cracking and iv. film-to-electrode contact problems. The problems associated with the SCF inclusion technique could be expected to derive from two major sources: i. pore collapse during nanowire inclusion and ii. insufficient filling of the pores or multiple clusters within a single pore.

![Fig. 4 Schematic of the mesoporous thin film (MTF) prepared on KCl substrates. Each region highlights potential problems with the film preparation or inclusion process.](image)

Previous work on the inclusion of Ge nanowires in MTFs on silicon substrates has shown that a portion of the pores are aligned at slight angles from the vertical axis. However, the formation of MTFs on KCl substrates could have significantly different pore alignment characteristics than MTFs prepared on silicon or quartz substrates. The C-AFM images in Figs. 3e and 3f suggest that there is some amount of upward pore structure within the MTF. However, the overall structure throughout the
substrate could be divided into domains with some pores orientated parallel to the surface inaccessible to the C-AFM tip while some domains may have little long range order. The topography of the GeNW-MTFs in Fig. 3a and 3b shows that the surface of the film appears to have some grain boundaries or surface roughness characterised by sphere-like domains. These domains could have implications on the long range order of the mesoporous hexagonal arrangement and could be the cause of some of the ordering problems described above. In addition, surface roughness or film adhesion problems could also cause large conducting regions. Little is known about the adhesion properties of the MTFs on these substrates and it is plausible that there could be some separation of the film from the substrate surface prior to inclusion. Surface roughness or film separation would result in small pockets that would be filled during the inclusion process resulting in a surface layer that stretches across multiple nanowires resulting in one large conductivity region. However, the conductive regions do not appear to have a thick surface layer that accounts for the large regions of conductivity. Therefore, a surface layer cannot be ruled out but if present it must be a very thin layer (i.e. less than 20 nm). Previous work on the inclusion of Ge nanowires in mesoporous powders and MTFs on silicon substrates has shown that the Ge nanowires do not cause pore collapse of the silica substrate and further show that a significant portion of the mesopores are filled. Furthermore, the use of SCFs in the inclusion process should significantly reduce surface tension which is the main cause of pore collapse.

To help understand the discrepancy between the expected and measured conductivity map results, Ge nanowires were also prepared within AAO membranes (GeNW-AAO). As seen in Fig. 5a, the SEM of the AAO membranes typically have larger pore diameters than mesoporous matrices and the pores are typically not as well-ordered as with hexagonal mesoporous materials but the pores run vertically through the substrate. Therefore, all nanowires formed within these AAO substrates were aligned perpendicular to the substrate eliminating MTF preparation problems and allowing the investigation of the SCF inclusion process and contact formation. This ordering is further supported by the topography map of the GeNW-AAO membrane shown in Fig. 5b which reveals nanowires are protruding vertically up from the surface. The C-AFM results in Fig. 5c show that a large portion of the substrate is conductive. Furthermore, the areas of conductivity correlate strongly with the pore diameter seen in the SEM and the nanowire diameter seen in the topography map. The uniformity of the conductance (i.e. green colour) suggests that there is little difference between the nanowires within each pore. This is an important result and suggests that the substrate consists of highly reproducible continuous nanowires within each pore that are uniform single crystals running throughout the substrate. If the pores were filled with clusters as suggested in the inset of Fig. 4, the gaps of varying length between the clusters would result in a wide variance of the conductivity of each nanowire. However, the uniformity of the conductance through each pore contained within the substrate clearly suggests complete pore inclusion of continuous nanowires from end-to-end. Comparison of the average density of pores within the AAO substrate to the average density of conducting GeNWs within the AAO substrate shows that approximately 85–90% of the pores contain conducting nanowires. Previous results have shown that approximately 85–90% of the pores are filled through the SCF inclusion process in mesoporous silica powders. Therefore, nearly all of the nanowires synthesised in the substrates are conducting.
**Fig. 5** Conductive atomic force microscopy (C-AFM) of Ge nanowires embedded within an anodized aluminium oxide membrane (GeNW-AAO). (a) Scanning electron microscopy image, (b) Surface topography, (c) Conductivity map. Note that the conductive regions in (c) are the same diameter as the pore diameters in (a) and the nanowire diameters in (b). Furthermore, the consistency in the conductivity from pore to pore (i.e. green colour) suggests that the nanowires are continuous single crystals within each pore.

To obtain a measure of the quality of the contact between the gold coating and the AAO membrane, a gold electrode 2 mm in diameter was deposited onto the top surface of the GeNW-AAO membranes in a similar approach to the bottom contact and is shown in Fig. 2b. The resistance of an individual GeNW measured above through C-AFM was approximately $R_i = 450 \, \text{G}\Omega$. The number of GeNWs contained within the gold contact area was determined to be approx. $1.9 \times 10^7$ nanowires ($N$). The expected resistance between the electrodes would be $R_{\text{calc}} = R_i/N = 0.02 \, \text{M}\Omega$; however, the measured resistance between the two contacts is often close to 5 M$\Omega$. The high measured resistance suggests that the top contact of the GeNW-AAO film is
quite poor and similarly the bottom contact would be expected to be a poor contact as well.

**Conclusions**

Metal and semiconductor nanowires have potential applications in nanodevices and as interconnects. While the electrical properties of individual nanowires have been intensely investigated, there are few studies of the electrical properties of organized arrays of nanowires due to the difficulties in placing nanowires into organized structures. Mesoporous thin films and anodic aluminium oxide membranes, however, have been utilised as templates for the synthesis of high-density, ordered arrays of nanowires. C-AFM was shown to be a useful probe for studying the conductivity of nanowire arrays within these substrates that are oriented towards the surface.

The conductivity of GeNW-MTFs prepared on KCl substrates suggests that there is a limited amount of upward hexagonal pore orientation resulting in large non-conducting regions. However, it is clear that some ordered porosity is achieved and that the conductivity of individual Ge nanowires can be obtained in some domains. The large conducting regions on these GeNW-MTFs appear to indicate that there is some surface layer that connects multiple nanowires likely due to film adhesion or surface roughness problems. The preparation of GeNW-AAO substrates shows that a significant portion of the pores are filled with nanowires and that nearly all of the nanowires formed are conducting. Furthermore, the consistency of the conductivity of the nanowires within these GeNW-AAO substrates suggests that the nanowires are continuous throughout the length of the substrate and do not vary from pore to pore. The high resistances measured suggest that the film-to-electrode contact formation is problematic. Although these results have outlined multiple engineering problems to be resolved, it appears the preparation of ordered arrays of Ge nanowires within MTFs using our SCF inclusion technique has promise in the future development of electronic devices since high inclusion rates and reproducibility can be achieved within each pore of the AAO substrate. Further work in our laboratories will be investigating the formation of MTFs on conductive substrates which will yield highly ordered pores with good mechanical properties. The preparation of better contacts will also be required before the electrical properties of individual nanowires within the arrays can be studied.

**Acknowledgements**

JDH is grateful to the editors of the *Journal of Materials Chemistry* for the invitation to write this article. The authors acknowledge financial support for their work from Enterprise Ireland, the Higher Education Authority (HEA) in Ireland, Intel (Ireland) Ltd, the Council of Science of Latvia, and the University of Latvia.

**References**

33 Y.-J. Han, J. M. Kim and G. D. Stucky, Chem. Mater., 2000, 12, 2068 [Links].
The diameters of the pores and the pore centre-to-pore centre distances within MTFs are typically smaller than that achieved in mesoporous powders.


This journal is © The Royal Society of Chemistry 2003