Metallic and Semiconducting Nanowires: Properties and Architectures

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ABSTRACT

Nanowires are expected to play an important role in future electronic, optical devices and nanoelectromechanical devices. Measuring the electrical and mechanical properties of nanowires is however a difficult task due to their small dimensions. Here we report the use of an in-situ microscopy technique, which combines transmission electron microscopy (TEM) with scanning probe microscopy (SPM), to investigate the electrical and mechanical properties of metallic and semiconductor nanowires. Additionally, in this paper we describe a novel approach for synthesizing mesoporous silicas with tunable pore diameters, wall thickness and pore spacings that can be used as templates for the assembly of semiconductor nanowire arrays. Silicon and germanium nanowires, with size monodisperse diameters, can readily be formed within the mesoporous silica matrix using a supercritical fluid inclusion technique. These nano-composite materials display unique optical properties such as intense room temperature ultraviolet and visible photoluminescence. The implication of these mesoporous nanowire materials for future electronic and opto-electronic devices is discussed.

Keywords: TEM-SPM, Scanning Probe Microscopy, nanowires, conductivity, mechanical properties, nanowire arrays, mesoporous materials

1. INTRODUCTION

Many technologies, including electronics, separation science and coatings will be enhanced by the ability to control the structure of materials on a nanometer-length scale. The ability to pack high densities of memory storage and processing circuitry into specific nanoscale arrays, and utilise the unique transport properties associated with these architectures, is expected to lead to future generations of (nano)-computer processors with device sizes many times smaller and faster than current silicon based processors1. However, both physical constraints and economics are expected to limit continued miniaturization of electronic and optical devices using current ‘top-down’ lithography based methods2. Consequently, alternative non-lithographic methodologies for constructing the smallest mesoscopic features of an integrated circuit will soon be needed. One promising non-lithographic strategy for creating mesoscopic architectures is the use of solution phase chemistry to assemble materials from precursor ‘building block’ into structurally complex mesoscopic architectures3.

One dimensional (1D) structures, or nanowires, have great potential as building-blocks for the ‘bottom-up’ assembly of nanoscale structures as they can function as both devices and as the conducting wires that access them. Several groups have demonstrated that carrier type (electrons, n-type; holes, p-type) and carrier concentrations in single crystal silicon nanowires can be controlled during growth using phosphorous and boron dopants4,5. Additionally for low-dimensional semiconductors, quantum effects due to spatial confinement may give rise to novel and unusual properties such as tunable photoluminescence (PL). In particular, the discovery of visible luminescence from nanocrystalline silicon has led to an explosion of interest in this material for potential opto-electronic applications6. A number of techniques for preparing pseudo- 1D semiconductor wires have been reported including laser ablation of silicon and germanium targets7, liquid crystal templating methods and vapour-liquid-solid growth mechanisms8. We have been instrumental in developing a novel supercritical fluid (SCF) solution–phase technique for producing silicon nanowires with tunable crystal orientation and hence controllable optical properties9. In the first section of this paper we describe the use of a combined transmission electron microscopy (TEM) and scanning probe microscopy (SPM) technique to investigate the electrical and mechanical
properties of isolated silicon and gold nanowires \textit{in situ}^{10-17}. In particular, we report the quantization of conductance through gold using the \textit{in situ} TEM-SPM technique\textsuperscript{11,13}. Even though the preparation of semiconductor nanowires in bulk quantities is now possible, unanswered questions relating to their processibility remain. 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. Investigations in our laboratories have also focused on preparing ultra high-density 3-D arrays of metal and semiconductor nanowires within the pores of mesoporous silica hosts\textsuperscript{18-22}. The SCF inclusion-phase technique developed has proved successful not only in allowing a range of stable nanowire-matrix composites to be reproducibly synthesised but is extremely fast, efficient and cost effective. Typically, reactions are completed within 15-30 minutes compared to other techniques which may require days. In addition, using simple liquid phase precursors offers a relatively safer preparation method to many CVD approaches. Additionally in this paper, we describe in detail the use of non-ionic triblock copolymer surfactants to template the formation of ordered hexagonal mesoporous silica materials and the use of SCF methods to reproducibly form a range of tailor-made high quality silica-nanowire composites with unique optical properties.

2. PROPERTIES OF INDIVIDUAL NANOWIRES AND NANOCONTACTS

2.1. Experimental

A schematic representation of the TEM-SPM probe with stepper motor is shown below in figure 1. A detailed description of the TEM-SPM probe is reported elsewhere\textsuperscript{15,16}. In our system the SPM tip can be replaced by an AFM tip for mechanical measurements. AFM tip displacement is measured by directly observing the tip move within the TEM.

![Figure 1. Stepper motor based TEM-SPM (Not to scale): 1-stepper motor with gearbox, 2 - shifting rod, 3-spring, 4-micrometer screw, 5 - piezo tube, 6-electron beam.](image)

The TEM-SPM probe was inserted into a field emission TEM (Philips CM200 Super TWIN FEG microscope). The vacuum inside the microscope is $10^{-5}$ mbar. The electron irradiation density during the observation was $2.8 \times 10^5$ A/m$^2$. The samples were electrochemically etched gold tips, made from a 0.25 mm diameter wire (99.99 % Au). Argon milling was used to clean the gold tips prior to each experiment. The AFM cantilever tips were a standard silicon nitride contact mode type with a force constant of 0.4 N/m. The tip and the cantilever were coated with 5 nm Cr adhesive layer and 15 nm of Au. Inside the TEM we prepared the sample locally by pressing the tip hard into the sample, breaking the contamination layer or by pulling wire and breaking a mechanically created neck. The bias was applied between two electrodes. Current was monitored on a digital oscilloscope simultaneously with the video TEM images.

2.2. Conductivity of Au nanowires

The conductance of gold nanowires were measured as function of nanowire radius. Nanowire diameters varied from between one atom size to 15 nm (Fig. 2). Nanowire diameters within the size range permitted quantized conductance, ballistic and quasiballistic (sum of diffusive and ballistic) electron transport regimes to be investigated.

![Figure 2. One atom (a) and 0.9 nm (b) wide gold nanowires between electrodes.](image)
When the diameter of the contact approaches the Fermi wavelength, quantized conductance $G_0$ is observed according to equation 1 below:\(^23\):

$$G_0 = \frac{2e^2}{h},$$  \hspace{1cm} (1)

where $e$ is electron charge and $h$ is Plank constant.

In our experiments the resistance of Au nanowires with a radius less than 0.4 nm displayed quantized conductance\(^13\) in agreement with theory\(^23\) and experiment\(^11\).

When $\ell > > \alpha$, the conductance $G_\ell$ could be characterized by Sharvin equation\(^24\) below:

$$G_\ell = \frac{3\pi\alpha\ell}{4\rho\ell},$$  \hspace{1cm} (2)

where $\alpha$ is contact radius, $\ell$ – electron mean free path, $\rho$ - resistivity which is given by:

$$\rho = \frac{m\nu_F}{ne^2\ell},$$  \hspace{1cm} (3)

$m$ is electron mass, $\nu_F$ – the Fermi velocity, $n$ is the electron density. Since $\rho$ is inversely proportional to $\ell$, the Sharvin conductance does not depend on electron mean free path and electron transport is ballistic. In figure 3 the solid line corresponds to the Sharvin conductance. Ballistic conductance was observed in short contact radiiuses range, around 1 nm (Fig. 3).

In the quasiballistic regime conductance $G_{W}$ is expected to be sum of diffusive and ballistic conductances and may be describes by Wexler interpolation formulae\(^25\):

$$G_{W} = G_0 \left[ 1 + \frac{3\pi}{8} \frac{\Gamma(K)\alpha}{\ell} \right]^{-1},$$  \hspace{1cm} (4)

Experimental data for a contact radius greater than 1 nm were fitted with Wexler interpolation formulae (Fig. 3, thin line). From the fitting we found the electron mean free path in the gold nanowires to be 4 nm, which is 10 times less than what has previously been reported for bulk gold. The low mean free path values can be explained by the presence of electron scattering centers in the nanowires\(^13\).

![Figure 3](image-url) Measured point contact conductance ($\Omega^{-1}$) vs. radius squared ($\alpha^2$), at bias 10 mV. The Wexler interpolation formula is plotted using a mean free path value of 3.8 nm and $\Gamma$=0.7. Sharvin conductance (straight thick line) is added for comparison. Reproduced with permission from *Phys. Rev. B* 2000, 61, 12725, Copyright 2000 American Physical Society.
2.2. Force in gold nanocontacts and nanowires

Figure 4 shows a typical sequence of TEM images where the gold tip is moved towards and away from an AFM tip. The corresponding force curve is found in figure 5. In figure 4 the AFM tip had a radius of 30 nm and the sample surface had a protrusion with a radius of 8 nm. When the gradient of the attractive tip-sample force exceeds the spring constant $k$ of the cantilever, the sudden jump-to-contact occurs (Fig. 4b, Fig. 5b). The extra neck was organized in the gap between two contacts (inset in Fig. 4b). The neck formation (shown in figure 4b) is due to the high mobility of the gold atoms at room temperature in the van der Waals field gradient

![Figure 4](image)

Figure 4. A set of TEM images of a gold tip and gold coated AFM tip. a) No contact. b) Jump-to-contact. (Inset: neck formed in the gap in connection during the jump-in-contact event) c) Moving further in. d) Withdrawal of the sample. e) By lateral motion of the sample a small nanowire is formed between the sample and tip. Just before breaking, the diameter of the wire is about 1 nm, which corresponds to about 10 atoms. f) After jump-off-contact. (Inset: nanowire area magnified 3 times). Reproduced with permission from Appl. Surf. Sci. 2002, 188, 460, Copyright 2002 Elsevier North-Holland.

![Figure 5](image)

Figure 5. Experimental force-distance curve where the labels a-f corresponds to the TEM images in figure 4a-f. Reproduced with permission from Appl. Surf. Sci. 2002, 188, 460, Copyright 2002 Elsevier North-Holland.

We applied a shear force by a lateral motion of the sample during the withdrawal to reduce the contact radius (Fig. 4d,e; Fig. 5d,e). During this process, a nanowire with a diameter of less than 1 nm and length of 2 nm was created (Fig. 4e and inset). The nanowire broke at a retraction of 22 nm (Fig. 4e,f) which corresponds to an attractive force of about 9 nN (Fig. 5). The area of the neck just before rupture was 0.6 nm$^2$, which is about 8-10 atoms (area per atom 0.08 nm$^2$). This gives a cohesion force of about 1 nN per atom, in agreement with gold nanowire force experiments (1.6 nN for the last atom)$^{26}$ as well as by theoretical calculations (from 1 to 2.2 nN)$^{27-29}$. 

2.3. Au-Au contact size: comparison between contact theories

The contact radius at zero applied load for different contacts load was measured to compare between different contact theories. At zero load, the cantilever spring constant is not necessary to know, and uncertainties in the cantilever force constant is not important.

There are two well-known adhesion theories that describe two limiting cases. The Johnson-Kendall-Roberts (JKR) 30 theory is suitable for soft materials with strong adhesion forces and large tip radii. The Derjaguin-Müller-Toporov (DMT) theory 31 is covering the opposite limit, with stiff material, weak forces, and small tip radii. These theories are for elastic contacts, but we can still use them for cases with limited plastic deformation, as in the present case.

These limiting cases, and the transition between them, can be described by a dimension less transition parameters called Tabor parameter $\mu$ 32 and Maugis parameter $\lambda$. 33 Both parameters are related and for contact between identical materials can be expressed as:

$$\lambda = 1.157 \mu = \left( \frac{64 R \gamma^2}{9 K^2 z_0^3} \right)^{\frac{1}{3}},$$

where $z_0$ is a typical atomic dimension, $\gamma$ is surface energy and the reduced Young modulus $K$ is given by

$$K = 4/3 \left( \frac{(1 - V_1) / E_1 + (1 - V_2) / E_2}{1 - V_1} \right)^{-1},$$

where $V_1$ and $V_2$ are Poissons ratio and $E_1$ and $E_2$ are Young modulus for two contacting spheres.

The DMT theory is valid when $\mu < 0.1$ and the JKR theory is valid when $\mu > 5$. Maugis 33 provides a more general theory suitable for the full range, with $\lambda$ as a transition parameter. A dimensionless contact radius at zero applied load, $\tilde{a}_0$ is described by:

$$\tilde{a}_0(\lambda) = a_0 \left( \frac{K}{2\pi \gamma R^2} \right)^{\frac{1}{3}},$$

where $a_0$ is the real contact radius. Maugis solution is analytical, but here we used a simplified fitting version given by Carpick et al. 34:

$$\tilde{a}_0(\lambda) = 1.54 + 0.279 \left( \frac{2.28 \lambda^{1.3} - 1}{2.28 \lambda^{1.3} + 1} \right),$$

To calculate $\lambda$, the following values for gold were used: $\gamma=1.37 \text{ J/m}^2$, $E=117 \text{ GPa}$, $V=0.42$, $z_0=0.28$ nm. The theoretical and experimental values of the contact radius at zero applied load are shown in figure 6. Our experimental results were in the transition region between the DMT and JKR models (Fig. 6a,b,c). So far, very few experimental verification on the Maugis theory is reported, we found the one by Lantz et al. 37.

![Figure 6](image-url)
2.4. Magnetic nanoparticles

Pulling notched Ni wire resulted in creating of nanosize Ni particles in the gap between electrodes. We find position of nanoparticle between two Ni contacts where adhesion forces on both nanoparticle ends were equal (Fig. 7) and switch the nanoparticle from one position to another by the change in electrode positions. Presence of nanoparticles in the gap between 2 electrodes explains observed particularities in tunnelling current - distance dependencies (see more detailed in 18).

![Figure 7. 50 nm long Ni nanoparticle between Ni electrodes created by breaking Ni wire. Rotation of nanoparticle was realised by changing left electrode position in plane.](image)

2.5. Free standing Si nanowires

Silicon nanowires were grown using a novel SCF technique on gold SPM tips by the degrading the silicon precursor, diphenylsilane, at elevated temperatures and pressures 14. Figure 8 shows one Si nanowire grown on a Au SPM tip. Using this SCF technique Si nanowires with diameters between 40-90 nm and lengths up to 10 µm can readily be produced.

![Figure 8. Si nanowire grown on Au tip. Gold nanoparticle on the end is clearly visible.](image)

EDX data (Fig. 9a) on the middle of nanowire shows that the nanowire is predominantly composed from Si. Some traces of gold material is also observed. Gold diffusion may take place during nanowire growing process. The nanoparticle on end of nanowire is composed of gold (Fig. 9b).

![Figure 9. EDX analysis on Si nanowire: a- middle on nanowire; b – Au particle at end of the nanowire.](image)
The conductivity of nanowires was measured by contacting end of nanowire to a second gold electrode (Fig. 10). The Si nanowires were all conductive with high resistivity between 20-150 MΩ. The resistance of nanowires did not change significantly when the contact width was changed from 4 to 55 nm. This result suggests that the conductivity measured is not a property of the contacts but of the Si nanowires. The conductivity observed in the Si nanowires at low bias may be due to the doping of the nanowires with gold atoms.

![Figure 10. Different size contact area between the end of Si nanowire and gold contact during conductance measurements.](image)

### 3. NANOWIRE ARCHITECTURES

#### 3.1. Mesoporous Materials as Templating Agents

Nanometre-wide channels of anodic aluminium oxide films, polycarbonate track etched membranes, and nanochannel array glasses have previously been used as templates for nanowires of conductive polymers, metals, and semiconductors. While these templating methods are useful, forming an ordered array of nanoscale channels is difficult and the channel dimensions are usually too large to engineer nanowires that exhibit quantum confinement effects. Mesoporous materials, however, have unidirectional pores with diameters in the range 2-15 nm and offer a convenient route to forming ordered arrays of nanowires.

Mesoporous solids have previously exploited as templates for semiconductor materials formed from the gas phase with moderate success. In particular, Leon et al. reported the partial filling of MCM-41 mesoporous silica with germanium wires using vapour-phase epitaxy. In a similar approach, Dag et al. employed chemical vapour deposition to deposit silicon nanocrystals within the pores of hexagonal mesoporous films. These gas phase methods have met with some success but the high temperatures, ca. 800 °C, or extensive reaction times, ca. 48 h, required for successful nucleation and growth of nanowire arrays makes these techniques both costly and time-consuming. Furthermore, these methods have been unable to achieve complete filling of the pores with nanowires or nanoparticles. The relatively high diffusion coefficients, higher precursor solubility, and reduced surface tension of high-temperature SCFs however, results in almost complete inclusion of the mesoporous materials with nanowires.

#### 3.2. Supercritical Fluid Solution Phase Inclusion of Mesoporous Materials

Investigations in our laboratories have focused on preparing ultra high-density 3-D arrays of metal and semiconductor nanowires within the pores of mesoporous silica hosts. The SCF inclusion-phase technique developed has proved successful not only in allowing a range of stable nanowire-matrix composites to be reproducibly synthesised but is extremely fast, efficient and cost effective. Typically, reactions are completed within 15-30 minutes compared to other techniques, which may require days. In addition, using simple liquid phase precursors offers a relatively safer preparation method to many CVD approaches.

Characterisation of these nanowire-silica host matrix composites has shown that the SCF inclusion-phase method is an efficient alternative to gas or liquid phase inclusion techniques. Prior to nanowire guest inclusion, TEM of the mesoporous silica matrix reveals an open hexagonal open-pore framework (Fig. 11a). After nanowire inclusion, crystalline nanowires are easily witnessed within the mesopores by TEM (Fig. 11b). Further evidence of inclusion can be seen by low angle X-ray diffraction (XRD), adsorption techniques, and solid-state nuclear magnetic resonance. All of these investigative techniques have provided a clear indication of the success of the SCF inclusion-phase technique as a method for creating hierarchical materials on the nanoscale.
Furthermore, we have discovered that silicon nanowires prepared within mesoporous matrices have exhibited high intensity ultraviolet (UV) and visible PL. Bulk silicon is an indirect band-gap semiconductor that traditionally exhibits very weak PL. However, as the size and dimensionality of silicon is decreased, quantum confinement effects become pronounced resulting in electronic characteristics that are different from the bulk material \(^{51,52}\). We have recently discovered an ability to manipulate the UV PL \(^{21}\) of these encased silicon nanowires (Fig. 12) by controlling the pore size of the silica matrix and hence diameter of the silicon nanowires grown within them \(^{53}\).

UV PL in silicon has previously been ascribed to electron excitation followed by electron-hole pair recombination at oxygen defect centres in silica. However, simple electron-hole recombination in silica can not explain the variation in the UV PL emission wavelength of the silica-silicon composite materials as the silicon nanowire diameter changes. We have argued that this UV PL arises due to the intrinsic strain and have suggested that as the curvature or strain of nanowires increases, the UV PL emission maximum is shifted to higher energies. This control over the UV PL demonstrates the ability to manipulate optical properties in semiconductor nanowires through strain-induced effects which could be a new parameter in the design of 3-D optical devices.

The great advantage of this SCF inclusion technique is that it may be easily applied to a range of other semiconductor and metallic nanowires including germanium, copper, cobalt, iron oxide, and nickel \(^{18-22,50}\). In addition, not only can elemental nanowires be synthesised within porous materials but also doped or alloyed nanowires may be formed and is the source of further investigation within our laboratories. The ability to create elemental, doped, and alloyed nanowires within porous materials will make supercritical methodologies one of the techniques of choice in emerging fabrication technologies.

5. SUMMARY

While electronic functionality has previously been demonstrated in metal and semiconductor nanowires, no comprehensive structural and electronic characterisation of these novel nanostructures has been undertaken to date. For example, transport mechanisms in semiconductor nanowires have not been rigorously investigated \(\text{viz.}, \ e.g., \ \text{influence of wire structure and morphology on measured nanowire device electrical parameters.} \) Using the combined TEM-SPM technique we are
currently investigating the electrical and mechanical properties of free-standing metallic and semiconductor nanowires, as a function of wire structure etc., with the aim of developing future nanowire devices.

Additionally, we have developed a unique SCF inclusion technique to fill the pores of a series of tailored hexagonal mesoporous silica, prepared using a contemporary surfactant templating method, with quantum confined semiconductor nanowires. Unlike chemical vapour deposition techniques where the deposited material extends in almost all directions, promoting the growth of solid material across the tops of the pores and subsequent blocking of the pores, with our SCF method this is not observed. Furthermore the results presented in this chapter demonstrates the ability to manipulate quantum confinement properties in 1-D semiconductor nanowires offering experimental insight into a mechanism of light emission from nanocrystalline silicon that has not been widely investigated to date.

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