Semiconducting Nanowires: Properties and Architectures

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Abstract. The paper describes 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 individual silicon and germanium nanowires. Additionally, the formation of ordered arrays of size-monodisperse silicon and germanium nanowires within mesoporous silica powders and thin films using a supercritical fluid inclusion phase technique is described. In particular, we demonstrate ultra high-density arrays of germanium nanowires, up to 2 x 10¹² wires per square centimetre. These matric embedded nano-composite materials display unique optical properties such as intense room temperature ultraviolet and visible photoluminescence.

Introduction

In the near future physical and economic constraints are expected to limit the continued miniaturisation of electronic and optical devices using current ‘top-down’ lithography-based methods. Consequently, non-lithographic methods for synthesising and organising materials on the nanometre-scale are required. One dimensional (1D) structures, or nanowires, are expected to play a role in future integrated circuits as both devices and interconnects. Indeed, some researchers have begun to demonstrate that these building blocks can function as simple devices [1-3]. Additionally, a key aspect of nanotechnology is that quantum confinement effects evident in low-dimensional materials can give rise to unique and unusual optical, electronic and catalytic properties [4-5]. In particular, with many semiconductor materials there is a strong correlation between their optical properties and their size. As the size of a semiconductor is reduced the electronic excitations in the material shift to higher energies and the oscillator strength is concentrated into just a few discrete transitions. These unique size-dependent properties may afford innovative electronic, optical, and sensor applications. For example, the discovery of visible luminescence from nanocrystalline silicon has led to an explosion of interest in this material for potential opto-electronic applications [6,7].

A number of techniques for preparing pseudo-1D semiconductor wires have been reported in the literature including the laser ablation of silicon and germanium targets [8], liquid crystal templating methods and vapour-liquid-solid growth mechanisms [9]. We have been instrumental in developing a supercritical fluid (SCF) solution–phase techniques for producing silicon and germanium nanowires with tunable crystal orientation and hence controllable optical properties [10]. The first section of the paper describes the use of a combined transmission electron microscopy (TEM) and scanning probe microscopy (SPM) technique [11-17] to investigate the electrical properties of isolated silicon and germanium nanowires in situ.
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. Recently we have adapted our supercritical fluid (SCF) solution-phase technique for producing arrays of semiconductor (Si, Ge), metallic (Co, Cu) and metal oxide ($\text{Fe}_3\text{O}_4$) between 2 and 8 nm in diameter, within the pores of mesoporous silica powders and thin films [19-23]. Such a comprehensive filling of the mesopores with nanowires effectively formed the first three dimensional array of nanowires insulated at a finite distance of separation. Discrete transitions observed in the uv-visible absorption and photoluminescence emission (PL) spectra of the silicon nanowires constrained within the mesoporous silica matrices suggested that they possess unusual optical properties that could be exploited in a number of applications [21,23]. In the second section of this paper we describe the combination of mesoporous thin-film science with SCF technology to produce ordered high density arrays of quantum-confined germanium nanowires that could be utilized in future optical and electronic devices [21].

**Individual nanowires.**

**Experimental.** A schematic representation of the TEM-SPM probe with stepper motor is shown below in Fig. 1. A detailed description of the TEM-SPM probe is reported elsewhere [14-17]. 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](image)

**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.

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 $2.8 \times 10^8 \text{A/m}^2$. The samples were electrochemically etched gold tips, made from a 0.25 mm diameter wire (99.99 % Au). The bias was applied between two electrodes. Current was monitored on a digital oscilloscope simultaneously with the video TEM images.

**Properties of nanowires.** Si and Ge nanowires were grown on Au SPM tips using a SCF technique as described previously [10]. In this process the precursors diphenylsilane and diphenygermane are degraded at elevated temperatures and pressures to form crystalline Si and Ge nanowires respectively. Figure 2 shows one Si nanowire grown on a Au SPM tip. Using the SCF technique Si and Ge nanowires with diameters between 40-90 nm and lengths up to 10 µm can readily be produced. EDX data (Fig. 3a) on the middle of nanowire (Fig. 2a) 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 (Fig. 3b) is composed of gold (Fig. 3b).
Figure 2. Si nanowire grown on Au tip. Gold nanoparticle on the end is clearly visible (b).

Figure 3. EDX analysis on Si nanowire shown in Fig. 2: a- middle on nanowire; b – Au particle at end of the nanowire.

The conductivity of nanowires was measured by connecting the nanowire to a second gold electrode (Fig. 4). The Si nanowires were conductive with a 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 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 4. Different size contact area between the end of Si nanowire and gold contact during conductance measurements.
Nanowire Architectures

Mesoporous materials [24] with unidirectional pores with diameters in the range 2-15 nm offer a convenient route to forming ordered arrays of nanowires. 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 [18-23]. 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.

Films containing high density arrays of Si and Ge nanowires were grown on glass and silicon surfaces. Fig. 5 shows AFM image of film surface on glass substrate. Protrusions observed in the AFM images are due to the ends of the nanowires (Fig. 5a,c). The contrast in-phase AFM images (Fig. 5b) result from the different interaction of the tip with the nanowires compared to the surrounding silica matrix. From the AFM images we can conclude that there is some ordering of the nanowires within small domain regions, with some of these nanowires orientated perpendicular and parallel to the substrate surface. Cracks with different depth from 400 nm to a few nm were observed with films cast onto glass substrate (Fig. 5a).

![Figure 5](image)

**Figure 5.** Tapping mode AFM image of mesoporous films on glass containing Ge nanowire arrays: a,c) height image; b) phase response.

The orientation of nanowire inside mesoporous films was analyzed by TEM and X-ray diffraction [21]. Figure 6a shows a TEM profile from a mesoporous thin film templated using the triblock copolymer P123. The film is extremely uniform and well adhered to the substrate (film thickness, 400 nm). Control of film thickness between 100 nm and 1 µm can be facilitated by controlling the spinning rate during film casting.

The degradation of germanium, from diphenylgermane, into the ordered channels of the film was undertaken using supercritical carbon dioxide. CO₂ is a highly recyclable, cost effective solvent and is less likely to contain potential dopant impurities present in organic solvents. Prior to Ge nanowire inclusion the mesoporous thin film showed a type (IV) adsorption isotherm, typical for mesoporous solids. After nanowire inclusion, the surface area of the mesoporous silica film decreased typically from 700-600 m² g⁻¹ to 10-50 m² g⁻¹. Further evidence for nanowire inclusion was provided by high angle X-ray diffraction characterisation of the germanium nanowires within the pores of the Al-MTFs (Fig. 6b). Although, single crystal nanowires isolated within ordered mesoporous films are highly unlikely to be aligned at the correct angle for diffraction, rotation of the film through the phi
angle (0-360°) resulted in a low intensity reflection from the <111> lattice plane of metallic germanium at 2θ = 27.26 reflecting a d spacing of 3.27 Å.

Figure 6. (a) Ge nanowires within a mesoporous thin film, (b) high angle PXRD, of the Ge nanowires within the film. Reproduced with permission from J. Am. Chem. Soc. 2003, 125, 6284. Copyright 2003 American Chemical Society.

The high-diffusivity of the SCF enables rapid transport of the germanium precursor into the mesopores of the silica which allows swift nucleation and growth. Control over pore geometry allows the aspect ratio and optical properties of the included wires to be controlled with excellent precision. Ultimately, perpendicular arrays of 2 nm wires, insulated by 1 nm walls, allow for packing densities of up to 2 × 10¹² wires per cm², which will facilitate Moore’s law extension for the next century [21].

Luminescence of Nanowire Arrays

We have discovered that silicon nanowires prepared within mesoporous matrices exhibit 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 Si is decreased, quantum confinement effects become pronounced resulting in different electronic characteristics to the bulk material [25,26]. We have recently found an ability to manipulate the UV PL [23] of these encased silicon nanowires (Fig. 7) by controlling the pore size of the silica matrix and hence diameter of the silicon nanowires grown within them.

Figure 7. PL spectra for silicon nanowires embedded in amesoporous silica matrix (excitation energy of 4.92 eV). UV PL emission maxima were observed at 2.93 eV, 3.3 eV and 3.49 eV for nanowires with 73 Å (Si73), 50 Å (Si50) and 45 Å (Si45) diameters respectively. Reproduced with permission from Nano Lett. 2002, 2, 811. Copyright 2002 American Chemical Society.
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 photoluminescent properties of the nanowire arrays were observed to be dependent on the diameters of Ge nanowires encased in aluminium containing mesoporous thin-films [21].

Conclusions

While electronic functionality in metal and semiconductor nanowires has been demonstrated, 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 viz., e.g., 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. Ultra high density parallel arrays of high purity silicon and germanium nanowires were synthesized on glass and silicon wafer surfaces. AFM and TEM data provide that in some regions of the film the nanowires are oriented perpendicular to the substrate surface.

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References