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Supercritical Fluid Deposition of Nanowire Building Blocks

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The importance of the Information and Communication Technology (ICT) sector to the economy and society at large cannot be overstated, and few technologies have as far-reaching societal and economical impacts. The semiconductor industry plays a pivotal role in ICT. The 2005 Annual Report from the SIA (Semiconductor Industry Association) states that “The semiconductor industry sets the pace of global economic growth. Just as the industry’s strength provides a leading indicator of the world’s economic health, advanced semiconductor products and systems are bringing new opportunities, growth, and development to countries around the globe.” Moore’s Law is the beating heart at the centre of this industry, driving business growth, through the technological realisation of new process technologies which double the number of transistors on a chip about every two years. However, as the semiconductor industry continues to miniaturise in following Moore’s Law, there are some real challenges ahead, particularly in moving deeper and deeper into the nano length scale.¹ Sustaining the traditional logic MOSFET transistor structure, design, and materials composition will be especially difficult, particularly beyond the 22 nm technology node (9 nm physical gate length, predicted to be reached in 2016 according to the ITRS, as early as 2011 according to some company roadmaps²). There is even the question of how far silicon charge-based logic MOSFET transistor devices can be scaled. The semiconductor sector of the ICT industry is therefore actively chasing a solution for fulfilling the Moore criteria. This solution is sought in new materials. Nanowires offer two possible solutions for the given challenge. The first lies in their unique properties, the other in realising revolutionary hierarchical 3D nanoscale architectures and designs not achievable with conventional materials and techniques. At University College Cork, in collaboration with CRANN at Trinity College Dublin, supercritical fluid (SCF) solution phase methods³ have been exploited for forming arrays of semiconductor, metal and metal oxide, nanowire within the channels of porous templates for potential

nanoscale device applications.⁴ In this article we report on recent work in our laboratories which demonstrate the flexibility of SCF methods for producing a range of useful templated nanowire structures.

Recently we reported the use of SCF techniques to consistently produce high-density, ordered arrays of crystalline germanium nanowires within anodised aluminium oxide (AAO) templates.^{4,5} Conductive atomic force microscopy (C-AFM) and macro-contacting strategies have been utilised to study the electrical properties of the Ge nanowires within these arrays (figure 1). Each nanowire was found to possess similar electrical properties demonstrating the continuous and reproducible nature of SCF methods for creating high quality nanowire structures. Additionally, the optical properties of SCF-grown silicon and germanium nanowires within the pores of hexagonal mesoporous silica matrices have been investigated.⁶ A clear blue-shift in the photoluminescence (PL) of the semiconductor composite material was observed as the diameter of the nanowires decreased from 85 to 22 Å (figure 2). Powder X-ray diffraction revealed that, as the diameter of the confined nanowires decreased, the strain on the crystallographic structure increased, due to escalating lattice expansion, resulting in a shift in the PL maximum to higher energies. The ability to manipulate the optical properties in templated semiconductor nanowires, through strain engineering, has important implications for the design of future optical devices.

Dilute magnetic semiconductor (DMS) materials exhibit semiconducting properties and long-range ferromagnetic ordering. It is anticipated that these materials will play a vital role in the integration of spintronic devices with traditional semiconducting technologies.⁷ We have reported the synthesis of $\text{Ge}_{1-x}\text{Mn}_x$ ($0 \leq x \leq 0.05$) DMS nanowire arrays with diameters between 35-60 nm in AAO templates. These nanowires exhibited room temperature ferromagnetism which is surprisingly high for this class of material.^{7,8} Structural investigations showed that these wires comprised of a highly crystalline germanium host lattice containing discrete and spatially separated manganese ions. Additionally, we have realised the integration of magnetic and semiconducting materials through the synthesis of a range of high density arrays of coaxial nanocables, for example germanium nanowires surrounded by a cobalt nanotube sheath within AAO (figure 3).⁹ Structural studies on these heterostructured nanowires have clearly shown the presence of discrete core-shell phases with no evidence of alloy formation. These

materials form well-defined building blocks which may lead to new spin-based multifunctional devices.

In conclusion, the adaptability of SCF deposition techniques combined with versatile templating materials offers the opportunity to synthesise and assemble ordered arrays of orientated nanowire structures with specific dimensions and controllable electronic, optical and magnetic properties. Identifying the synthetic parameters to 'dial-up' nanowires with specific properties, in robust and hierarchical templates, could lead to many new and exciting applications of these materials in future devices.

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Figures

Figure 1: {Holmesfig1.JPEG} Conductive atomic force microscopy (C-AFM) of Ge nanowires embedded within AAO. (a) Representation of the C-AFM, (b) AFM topography of Ge-nanowires-AAO surface, (b) C-AFM current map at 20 V and (d) current map at 40 V.⁵

Figure 2: {Holmesfig2.JPEG} (a) Electron Microscopy image of free-standing Ge nanowires. (b) Solid state PL spectra at room temperature for silicon nanowires with diameters (from left to right) 73 Å, 50 Å, 45 Å and 30 Å respectively.⁶

Figure 3: {Holmesfig2.JPEG} Electron Microscopy images of Co-Ge coaxial nanocables. (a) SEM image of nanocables partially liberated from AAO matrix and (b) TEM image of a Co nanotube formed within AAO, showing nanotube wall thickness of 7 nm.⁹

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Figures

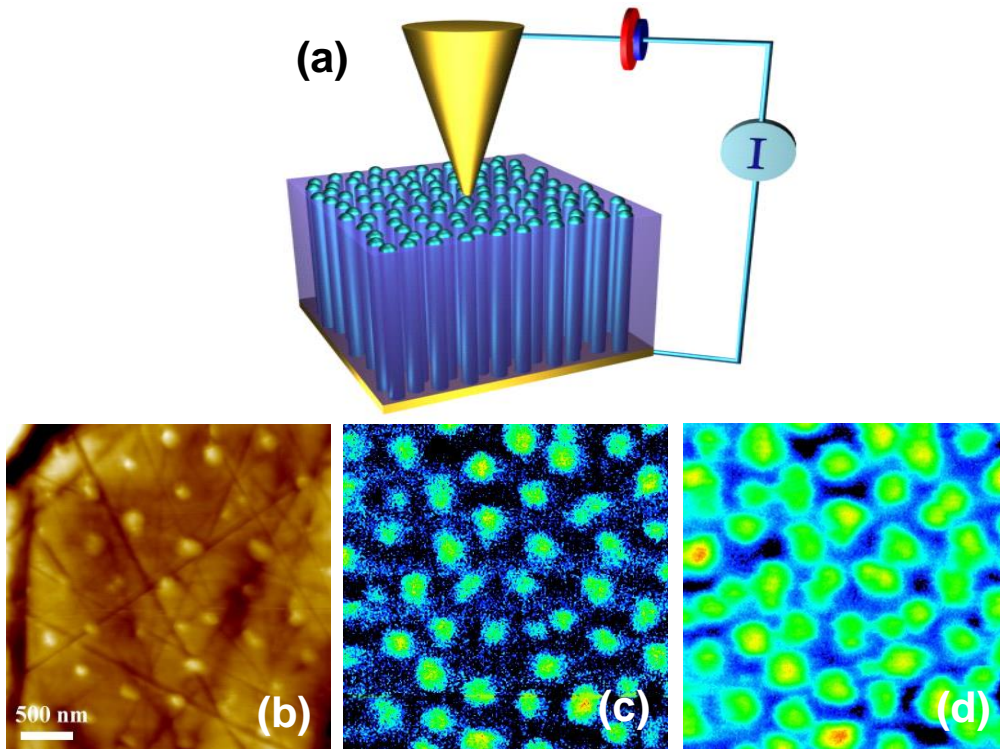


Figure 1: {Holmesfig1.JPEG} Conductive atomic force microscopy (C-AFM) of Ge nanowires embedded within an AAO membrane. (a) Representation of the C-AFM setup used to measure conductivities in individual wires, (b) AFM topography of a polished GeNW-AAO surface, (b) C-AFM current map of (b) at 20 V and (d) current map of (b) at 40 V.¹¹

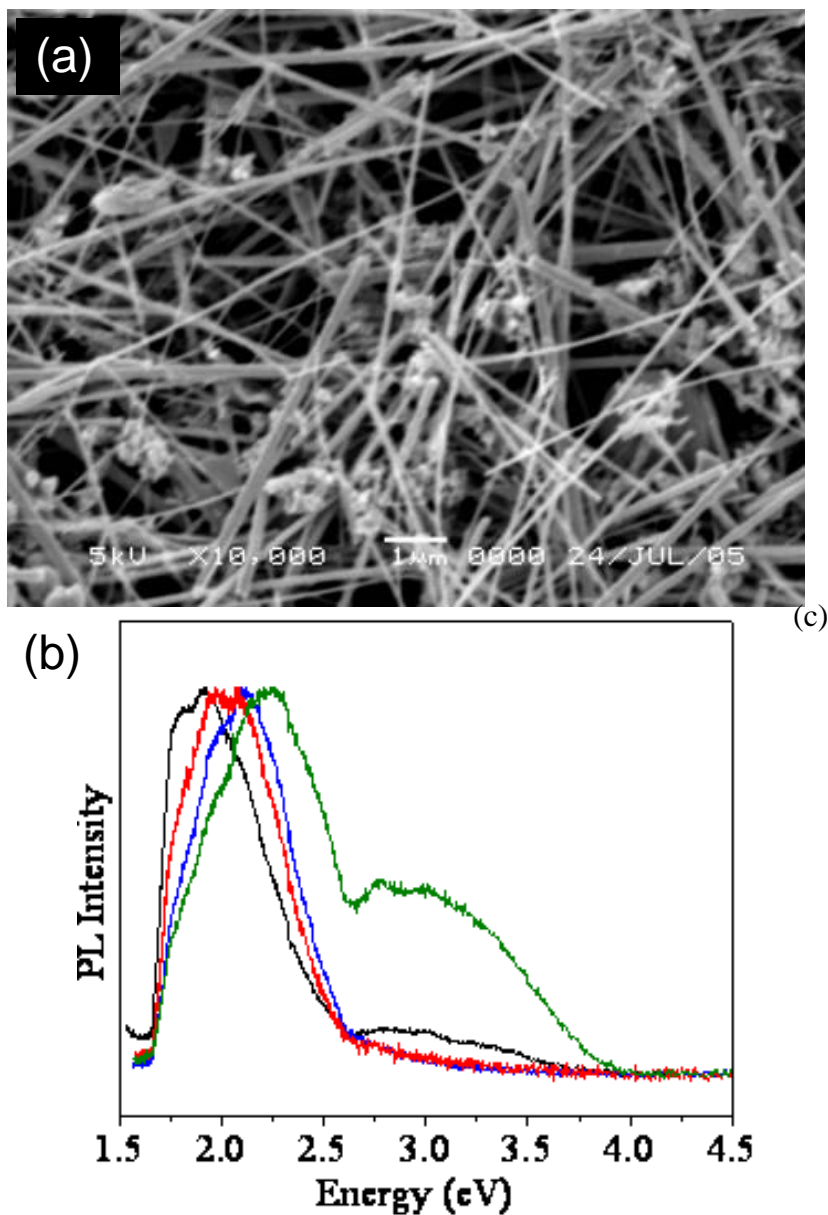


Figure 2: {Holmesfig2.JPEG} (a) Electron microscopy image of free-standing nanowires synthesised under the same conditions as the Ge nanocomposites (mean diameter approximately 140 nm and length of several microns), (b) Solid state PL spectra at room temperature for silicon nanowires with diameters (from left to right) 73 Å, 50 Å, 45 Å and 30 Å respectively.⁶

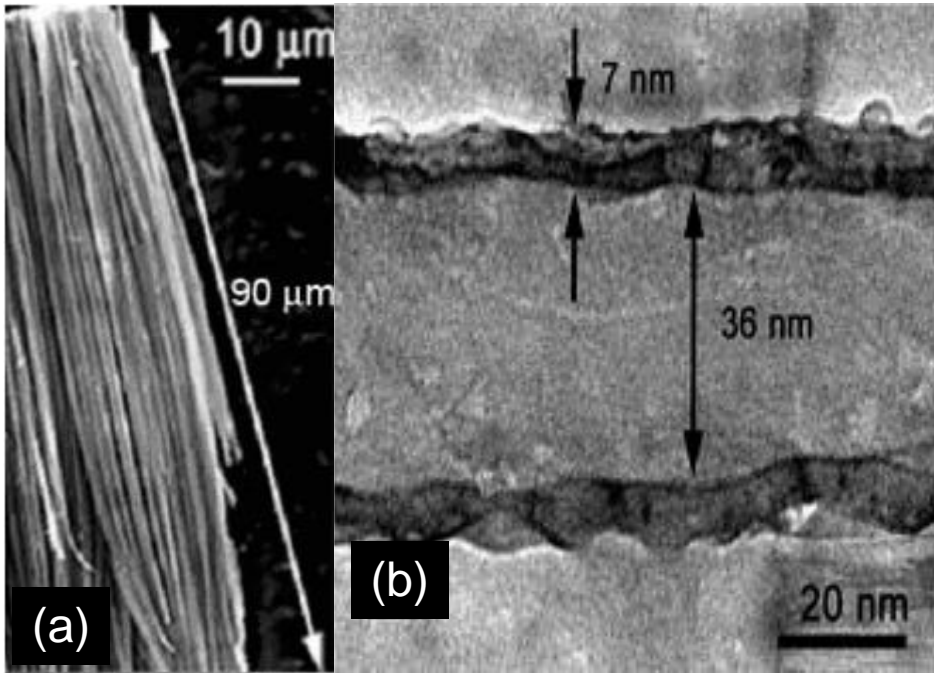


Figure 3: {Holmesfig2.JPEG} Electron microscopy images of Co-Ge coaxial nanocables. (a) SEM image of nanocables partially liberated from AAO matrix and (b) TEM image of a Co nanotube formed within an AAO membrane (mean pore diameter of 50 nm) showing nanotube wall thickness of 7 nm.⁹