THREE DIMENSIONAL ARCHITECTURES OF ULTRA-HIGH DENSITY SEMICONDUCTING NANOWIRES DEPOSITED ON CHIP USING SUPERCRITICAL FLUIDS

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ABSTRACT

We report a 'clean' supercritical method for producing ultra high densities, up to 10^{12} nanowires per square centimetre, of ordered semiconductor nanowires on silicon and quartz substrates. Uniform mesoporous thin films, with pores orientated perpendicular to the substrate surface are used as templates for unidirectional nanowire growth. The process steps involved in creating these nanowire arrays are reproducible, fast and compatible with current CMOS technology. The ability to synthesise ultra high-density arrays of semiconducting wires on-chip is a key development towards future 'bottom up' fabrication of multi-layered device architectures. Additionally, the photoluminescence properties of the nanowire arrays, was found to be dependent on the diameters of the confined wires. We believe that these constrained nanowires, within a transparent matrix, have enormous potential for use in future, nanoelectronic and optoelectronic devices.

INTRODUCTION

Continued advances in technologies such as nanoelectronics and optoelectronics will rely on the ability to control the structure of materials on a nanometre-length scale. Packing high densities of memory storage and processing circuitry into specific nanoscale arrays, and utilising the unique transport properties associated with these architectures, is expected to lead to the next generation of integrated circuits thousands of times smaller and faster than current silicon based processors [1-3]. However, physical and economical restraints to further minaturisation, particularly in conventional 'top-down' lithographic generated features, limits the ability of current processing techniques to fabricate devices on the nanoscale [4,5]. Alternative, non-lithographic, techniques are required to generate these critical device dimensions [6]. One potential strategy suggested is the use of solution phase chemistry to promote the self assembly of materials from precursor 'building blocks' into complex mesoscopic architectures [7].

One dimensional (1D) structures, such as nanowires and carbon nanotubes, have enormous potential as building blocks for nanoscale structures as they can function both as devices and as the wires that access them [8-13]. Recently we demonstrated a supercritical fluid (SCF) inclusion technique for producing silicon and germanium nanowire arrays, 4.5–7.3 nm in

diameter, within the pores of mesoporous silica 'powders' [14-17]. Such a comprehensive filling of the mesopores with semiconductor nanowires effectively formed the first three dimensional nanowire array insulated at a finite distance of separation. Discrete transitions observed in the uv-visible absorption and photoluminescent (PL) spectra of the constrained nanowire arrays suggest that they possess quantum confinement effects that could be exploited in a number of applications [17]. However, even though mesoporous powders are ideally suited for many purposes, *e.g.* as solid phase catalysts, for other uses, such as nanowire templates for devices and interconnects, these mesoporous solids need to be cast as mesoporous thin-films (MTFs). For example, semiconducting nanowires of silicon and germanium constrained within transparent MTFs could be used as LED arrays or in the formation of very high resolution screen displays, a key component in the expansion of information based technologies.

EXPERIMENTAL

Preparation of Aluminosilicate Mesoporous Thin-Films (Al-MTFs). The synthesis of mesoporous aluminosilicate thin-films (Al-MTFs) is based on a modification of the method described by Yoldas *et al.* [18] for the production of non-porous films. In a typical synthesis tetraethoxysilane (TEOS, 25 g), ethanol (13 ml) and HCl (2.5 ml, 0.12 M) were mixed together in the presence of a surfactant (6-7 g), *i.e.* poly(ethylene oxide) (PEO) – poly(propylene oxide) (PPO) triblock copolymer surfactants, P85 ($PEO_{26}PPO_{39}PEO_{26}$) and P123 ($PEO_{20}PPO_{69}PEO_{20}$) (Uniquema, Belgium) or Brij 35 ($C_{12}EO_{23}$) (Sigma-Aldrich, Ireland). The resultant solution was stirred at $40^{o}C$ for 10 min to prehydrolyse the silica precursor. The solution was rapidly cooled in an ice bath prior to the addition of aluminium butoxide ($Al(Obu)_3$), 1g). Finally, H_2O (2.5 ml) was added and the solution which was then allowed to condense for 20 hr prior to film casting. .

Preparation of Germanium Nanowire Arrays within Al-MTFs. Germanium nanowires were grown within the pores of Al-MTFs using a supercritical fluid inclusion-phase technique. Ordered AL-MTFs deposited on silicon wafers were coated with diphenylgermane and placed in a 100 ml high pressure cell under an inert atmosphere. The cell was attached via a three-way valve, to a stainless steel reservoir (~21 ml). A high-pressure pump (Isco Instruments, PA) was used to pump CO_2 through the reservoir in to the reaction cell. The cell was placed in a furnace and heated to 873 K and pressurised to 375 bar simultaneously using a platinum resistance thermometer and temperature controller. The reaction proceeded at these conditions for 30 min.

Film and Nanowire Characterization. High resolution transmission electron microscopy (HRTEM) data were collected on a (JEOL2010F field emission TEM), courtesy of Intel Oregon, with EDX attachment. Typically films were thinned using a focused ion beam such that some gallium ion damage is expected. Scanning electron microscopy (SEM) data were collected with a JOEL JSM-35 electron microscope. Samples were either gold or carbon coated to reduce sample charging and cleaved for cross-sectional analysis. Photoluminescence (PL) emission experiments were performed using a deuterium continuous discharge source and a spark discharge source of 6 ns duration in a helium-hydrogen gas mixture. Powder X-ray diffraction (PXRD) data was collected on PANalytical XPERT PRO MPD diffractometer. CuK_a radiation from an anode run at 40 kV and 40 mA was used in all experiments. An incident Soller slit of 0.02 radians was used resulting in a 240 mm incident beam radius.

RESULTS AND DISCUSSION

Unidirectionally ordered MTFs have previously been formed by slow epitaxial-like growth from dilute solutions [19] or by using electrical or magnetic fields to direct ordering [20]. Films formed using these methods however typically lack the mechanical and thermal stability necessary to survive the high temperature (800 K) and high pressure (400 bar) required for SCF nanowire inclusion. In our work, aluminium containing MTFs (AL-MTFs), templated from neutral surfactants, were used. Aluminium incorporation into the silica matrix was used to promote the hydrothermal and mechanical stability of the films suitable for SCF processing.

Figure 1a shows a SEM image of an Al-MTF templated from the surfactant P123 and spin-coated onto a silicon wafer. The mesopores within the film are orientated perpendicular the substrate surface as confirmed by powder X-ray diffraction (PXRD) and as depicted in figure 1b.
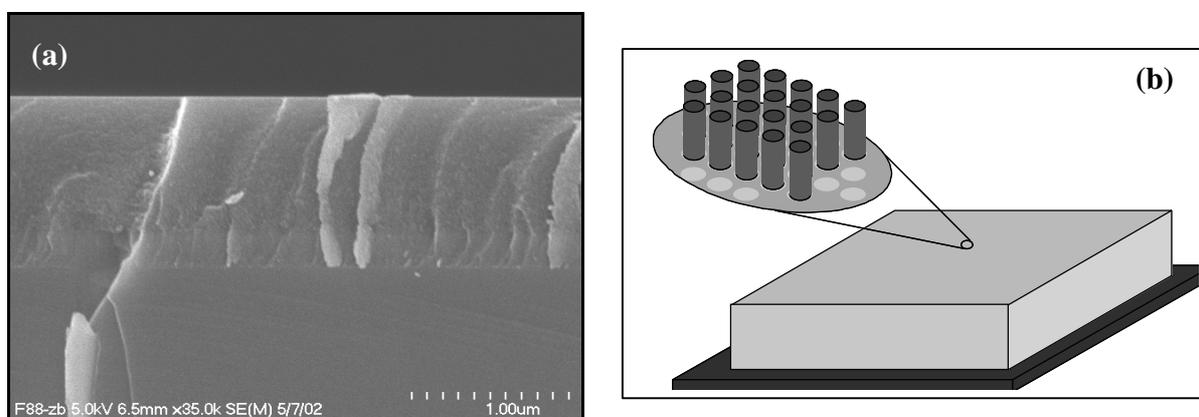

Figure 1: (a) Scanning electron micrograph (SEM) image of a cross-section from an ordered P123 templated Al-MTF deposited on a silicon wafer and (b) a graphic illustrating pore orientation with the Al-MTF.

The P123 templated Al-MTF is extremely uniform and well adhered to the substrate. Effective control over film thickness can be facilitated, between 100 nm to 1 μm, by controlling the spinning rate during film casting. Similar results were also found with Al-MTFs templated from the surfactants P85 and Brij 35.

The degradation of germanium, from diphenylgermane, into the ordered channels of the Al-MTFs was undertaken using supercritical carbon dioxide as the fluid medium instead of supercritical hexane as previously used for silicon and germanium nanowire inclusion into mesoporous silica powders [15,16]. CO_2 is a highly recyclable, cost effective solvent and is less likely to contain potential dopant impurities present in organic solvents. By careful selection of the surfactant template it is possible to control the pore size within Al-MTFs and hence the diameters of the nanowires formed within the pores [21]. Direct visual evidence for nanowire formation within the Al-MTF was provided by high-resolution transmission electron microscopy (TEM). Figure 2a shows a high resolution TEM image of directionally ordered germanium nanowires constrained within an Al-MTF templated from the surfactant Brij35. Focused ion beam etching was used to reduce the film thickness to facilitate 200 KV TEM imaging. The constrained nanowires are approximately 2 nm in diameter, with a wall thickness of about 1 nm

and have a packing density greater than 2×10^{12} nanowires per cm^2. Close analysis of the wires reveals the clear presence of atomic rows, which are not due to the amorphous aluminosilicate framework. A cubic cell geometry can be isolated from the Ge nanowires with a unit cell lattice of 0.568 nm which agrees with that of bulk crystalline germanium (0.5657 nm). The wires appear to be orientated along the length of the mesopores in the <100> direction as which agrees with that previously reported for Ge nanowires embedded within mesoporous powders [16]. Elemental analysis of the crystallites, by energy dispersive X-ray analysis (EDXA), confirmed that nanowires of metallic germanium are hosted within the aluminosilicate matrix (figure 2b). Both Si and Ge peaks are evident in the EDXA spectrum in addition to Cu from the microscopy grid.
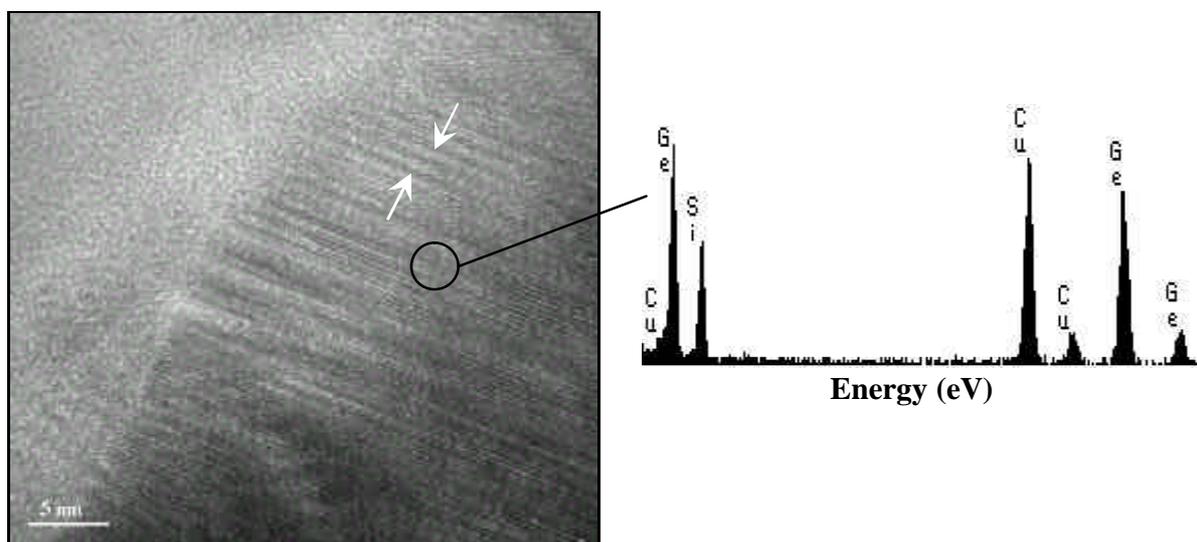

Energy (eV)

Figure 2: (a) High-resolution TEM image of germanium nanowires, 2 nm in diameter, constrained within an Al-MTF templated from the surfactant Brij35. Arrows show the confined nanowires and (b) EDX analysis of wires in (a)

Our previous work on silicon nanowires constrained within tailored mesoporous silica powders showed that these nanocomposite materials display intense room temperature UV and visible photoluminescence (PL) where the UV emission wavelength maximum is dependent on the diameter of the encased nanowires [17]. Similarly, a shift in the PL emission maximum of the Ge nanocomposite films to higher energies as the diameter of the germanium nanowires decreased was observed. PL is detected in the blue region, 2.64 eV, for 5 nm germanium nanowires encased in Al-MTFs which shifts to 2.75 eV and 3.01 eV for nanowires with diameters of 4 and 2 nm respectively. The observed peak positions fit favourably to the energy of the lowest direct $1s_e \rightarrow 1s_h$ transition calculated from theoretical data of quantum confinement in nanocrystals and nanowires [22-24].

CONCLUSION

Ultra high density arrays of high purity germanium nanowires can be synthesised perpendicularly orientated onto silicon substrates using supercritical carbon dioxide as an inclusion medium. The high-diffusivity of the fluid enables rapid transport of the germanium precursor into the mesopores of the silica thereby allowing 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 2×10^{12} wires per cm^2, which will facilitate Moore's law extension for the next century [4]. These nanowire arrays potentially allow multilayered device formation using semiconducting nanowires as opposed to single level devices [12,13]. Furthermore, the ability to control the optical properties of semiconductor wires in a transparent matrix at one thousandth the width of a human hair will allow for extremely high resolution intelligent image displays with almost real resolution.

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REFERENCES

[1] COMPANO, R., *Technology Roadmap for Nanoelectronics*; European Communities: Brussels, **2000**.

[2] TIMP, G., *Nanotechnology*; 1st ed.; Springer-Verlag: New York, **1999**.

[3] HEATH, J. R., KUEKES, P. J., SNIDER, G. S., WILLIAMS, R. S., Science, Vol. 280, **1998**, p. 1716.

[4] MOORE, G. E., Electronics, Vol. 38, **1965**, p. 1.

[5] MAYDAN, D., Materials Science and Engineering, Vol. A302, **2001**, p. 1.

[6] TRINDADE, T., O'BRIEN, P., PICKETT, N. L., Chem. Mater., Vol. 13, **2001**, p. 3843.

[7] HUCK, W. T. S., TIEN, J., WHITESIDES, G. M., J. Am. Chem. Soc., Vol. 120, **1998**, p. 8267.

[8] TANS, S. J., VERSCHUEREN, A. R. M., DEKKER, C., Nature, Vol. 393, **1998**, p. 49.

[9] HU, J., OUYANG, M., YANG, P., LEIBER, C. M., Nature, Vol. 399, **1999**, p. 48.

[10] HOLMES, J. D., JOHNSTON, K. P., DOTY, R. C., KORGEL, B. A., Science, Vol. 287, **2000**, p. 1471.

[11] YU, J.-Y., CHUNG, S.-W., HEATH, J. R., J. Phys. Chem. B, Vol. 104, **2000**, p. 11864.

[12] CUI, Y., DUAN, X., HU, J., LIEBER, C. M., J. Phys. Chem. B, Vol. 104, **2000**, p. 5213.

[13] CUI, Y., LIEBER, C. M., Science, Vol. 291, **2001**, p. 851.

[14] COLEMAN, N. R. B., MORRIS, M. A., SPALDING, T. R., HOLMES, J. D., J. Am. Chem. Soc, Vol. 123, **2001**, p. 187.

[15] COLEMAN, N. R. B., O'SULLIVAN, N., RYAN, K. M., CROWLEY, T. A., MORRIS, M. A., SPALDING, T. R., STEYTLER, D. C., HOLMES, J. D., J. Am. Chem. Soc, Vol. 123, **2001**, p. 7010.

[16] COLEMAN, N. R. B., RYAN, K. M., SPALDING, T. R., HOLMES, J. D., MORRIS, M. A., Chem. Phys. Lett., Vol. 343, **2001**, p. 1.

[17] LYONS, D. M., RYAN, K. M., MORRIS, M. A., HOLMES, J. D., Nano Lett., Vol. 2, **2002**, p. 811.

[18] YOLDAS, B., J. Non-Cryst. Solids, Vol. 63, **1984**, p. 150.

[19] YANG, K., KUPERMAN, A., COOMBS, N., MAMICHE-AFARA, S., OZIN, G. A., Nature, Vol. 379, **1996**, p. 703.

[20] TOLBERT, S. H., FIROUZI, A., STUCKY, G. D., CHMELKA, B. F., Science, Vol. 278, **1997**, p. 264.

[21] RYAN, K. M., COLEMAN, N. R. B., LYONS, D. M., HANRAHAN, J. P., SPALDING, T. R., MORRIS, M. A., STEYTLER, D. C., HEENAN, R. K., HOLMES, J. D., Langmuir, Vol. 18, **2002**, p. 4996.

[22] KAYANUMA, Y., Phys. Rev. B, Vol. 38, **1988**, p. 9797.

[23] ZACHARIAS, M., FAUCHET, P. M., Appl. Phys. Lett., Vol. 71, **1997**, p. 380.

[24] BRUS, L. E., J. Chem. Phys., Vol. 80, **1984**, p. 4403.