High pressure CVD inside microstructured optical fibres

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Abstract *We report the fabrication of semiconductor structures within holey fibres via a pressure driven microfluidic chemical vapour deposition process, demonstrating templated growth of crystalline Group IV semiconductor structures and devices in extreme aspect ratio geometries.*

Introduction

Synthesis of materials within templates is a powerful means to fabricate integrated microdevices and nanostructures. Here we report fabrication of semiconductor structures within microstructured optical fibres (MOFs), including an in-fibre field effect transistor, via the templated growth of crystalline Group IV semiconductor wires and tubes up to a metre long and less than 100 nm in diameter, thus enabling a wide range of compositionally and structurally complex novel fibre devices for manipulating light down to nanoscale dimensions[1].

Deposition inside MOFs

Interest in fabricating and characterizing MOF metamaterials is driven by their applications in photonic devices such as sensors, amplifiers and lasers. By appropriately designing the stacked preform, the capillary holes within a single MOF can have a wide range of shapes and sizes in precisely engineered periodic or aperiodic spatial configurations that allow for guiding of light by either a modified form of internal reflection or photonic bandgap effects. Materials within MOFs can interact with waveguided electromagnetic radiation over extended length scales that are not possible with typical planar device geometries. Incorporation of hydrogen, liquid crystals and polymers, and low melting temperature metals into holes in fibres has allowed for stimulated Raman scattering[2], variable attenuation[3], and Mach-Zehnder interferometry[4], respectively. Drawing of polymer fibre preforms that contain embedded structures has also been used to fabricate microscale diameter wires and sub-micron thick layers in optical fibre devices such as photodetectors, but this approach has thus far also been limited to low melting temperature metals and/or amorphous semiconductors[5]. However, the deposition of technologically important crystalline materials into MOFs, as described here, allows for exploitation of a much wider range of phenomena, including those that form the basis for modern optoelectronics. Our silica MOF designs can be fabricated with sub-100nm diameter capillaries that are configured in densely packed arrays. Silica MOFs are thus versatile engineered nanotemplates, which have unparalleled optical transparency combined with extreme aspect ratio, scalable geometries and tensile strength much greater than that of steel.

By treating the empty pores in a MOF as micro/nanoscale reaction chambers, we can directly deposit a wide range of technologically important semiconductors and metals with exceptional control, because we can now exploit the decades-long knowledge base developed for chemical vapour deposition (CVD) onto planar substrates. Very high pressures (10 to 100 MPa) facilitate rapid mass transport through the fiber pores. In a typical experiment, a germanium precursor flows through the heated MOF along with an inert carrier gas. High pressures and toxic precursors such as germane are safe and practical because the pressure reservoir and the fiber pores have a very small volume. A smooth layer of amorphous Ge begins to deposit on the pore walls as the temperature is ramped up past 300°C. Crystalline grains then nucleate and grow as the temperature exceeds the crystallization point of 375°C. As growth proceeds, a remarkably uniform tube forms (Fig. 1A); as it fills with Ge, a 1 micron diameter pore can be narrowed by a factor of 100 down to 25 nm or smaller, tapering open gradually over a deposition length of 70 cm. Silica capillaries drawn to a 100-nm diameter were also successfully filled with germanium to form nanotubes over macroscopic lengths of up to 30 cm, with an inner diameter of less than 10 nm (Fig. 1B).

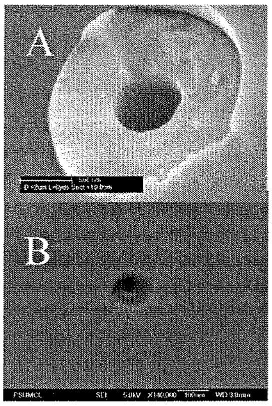

Figure 1. Field emission SEM cross section of a Ge tube inside (A) micron scale and (B) nanoscale silica capillary

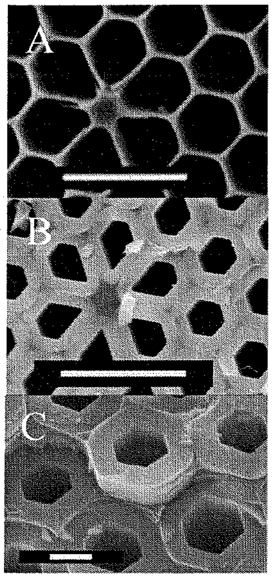

Figure 2. Unfilled silica "honeycomb" MOF template (A). Honeycomb after Ge deposition (B; scale bar 5 microns) and after Silicon deposition (C; scale bar 1 micron)

Deposition within a "honeycomb" large air fraction fibre with 2 micron cells (Fig. 2A) forms smooth hexagonal germanium (Fig. 2B) and silicon (Fig 2C) tubes. An unexpected feature of the filling process is that the interior vertices of the semiconductor tube, initially conformal to the rounded silica honeycomb template, become sharp as growth proceeds. The resulting faceted tubes resemble lithographically patterned micro and nanostructures, yet are formed in a simple deposition process. This faceting arises due to uniform inward motion of the surface along the local normal during deposition; the rounded corners of a polygon become sharp as the thickness of the deposited layer exceeds the radius of curvature of the corner.

Processing and device characterisation

To demonstrate the integration of continuous, electrically active semiconductor into optical fibres over macroscopic length scales, an 11mm long, 5 micron diameter Ge tube inside a single silica capillary (94 micron OD) was configured as a 3-terminal field effect transistor (FET) for standard electron transport measurements at 300K. Electrical connection to an external circuit was completed using In-Ga eutectic electrodes applied to the Al-Ge alloyed contacts, with an additional capacitatively coupled coaxial In-Ga eutectic gate placed on top of the silica cladding. Transconductance measurements of the unintentionally doped samples show the carriers to be n-type with a carrier mobility of 1.05 cm^2/Vs at room temperature. Figure 3 shows how the drain current varies as a function of gate voltage for a similar device; the conduction channel is "pinched-off" at approx. -100V, emphasising the operation of this

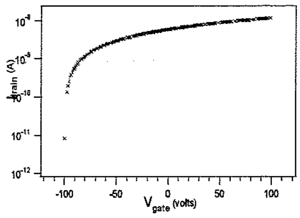

Figure 3. Drain current of *in-fibre* Ge FET, plotted logarithmically as a function of gate bias, showing channel pinch-off at V_g = -100V

sample as a fibre based FET switch. Whilst the available range of applied gate voltages limits characterisation of the "off" regime, we can estimate a FET on/off ratio of 10^4 or better. We also fabricated a 5 micron diameter silicon tube inside a capillary fibre, with a silica wall thickness of several hundred nm. 3-terminal measurements again indicated n-type carriers, with a sample resistivity of 0.21 Ohm cm and carrier mobility of 0.014 cm^2/Vs at 300K. By extrapolating the effect of gate bias on the transconductance, the channel pinch-off was estimated to be -320V, corresponding to a free carrier concentration of 6.6×10^{15} cm^{-3}. We expect mobility values will approach values more typical of bulk n-type polycrystalline Ge and Si upon further optimisation of the deposition conditions (e.g. precursor and carrier gas purity, thermal tratment for grain growth, etc.)

Conclusions

Hierarchical bottom-up organisation of nanomaterials into device configurations remains a central challenge in nanotechnology. High pressure CVD growth within the ordered arrays of capillary holes in MOFs provides an elegant and powerful method to spatially organise functional materials at nanoscale dimensions and allow for cooperative photonic and electronic processes between them over highly extended EM interaction lengths. Crystalline semiconductors grown within MOFs could serve as direct bandgap gain media for fibre lasers that operate over a range of wavelengths not previously possible. Such devices could be robust, inexpensive and seamlessly integrated into the existing fibre infrastructure. More generally, the ability to engineer radial, longitudinal and compositional complexity within optical fibres, whose own microstructure can be engineered independently thus allowing fabrication and materials synthesis inside the fibre to be orthogonal, heralds an opportunity to fabricate 3D optoelectronic devices of unprecedented sophistication within the fibre geometry.

References

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