Supporting Online Material for

Microstructured Optical Fibers as High-Pressure Microfluidic Reactors


*To whom correspondence should be addressed. E-mail: pjas@orc.soton.ac.uk (P.J.A.S.); jbadding@chem.psu.edu (J.V.B.)

Published 17 March 2006, Science 311, 1583 (2005)
DOI: 10.1126/science.1124281

This PDF file includes:

Materials and Methods
References
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Germanium and Silicon Deposition and Physical Characterization.

Microstructured optical fibers (MOFs) were fabricated using a conventional stack and draw technique (S1) on a 5m tower. A high pressure mixture of precursor and carrier gas, typically of 2 MPa of GeH₄ in 38 MPa of argon contained in a stainless steel reservoir, was configured to flow through MOF capillaries ranging from <50 nm to 10 µm in diameter. High pressure mixtures of precursors such as GeH₄ are very toxic and explosive, so it is critical that they are handled with appropriate care. Germanium was deposited on the inner walls by heating the precursor mixture to 500 °C at a rate of 2°C/min over a length of 70 cm. The polymer cladding of the fibers was either stripped before heating or burned off during heating. Evolution of gas was monitored by placing the ends of the fibers in a hydrocarbon liquid and examining the rate of bubble formation. Scanning electron microscopy (SEM) cross-sections every centimeter along the length of the capillaries filled with germanium were collected. It was observed that deposition occurred even in sub 10 nm holes, indicating that substantive fluid flow must have occurred through centimeters long nanoscale channels. We used the Poiseuille equation to approximate the linear flow rate inside a 10 cm long, 10 nm diameter pore with a 100 MPa pressure drop to be 13 µm/sec (assuming an argon viscosity of ~1x10⁻⁴ Pa-s; the density and viscosity of the compressible argon fluid will change as the pressure drops), which is fast enough to allow for deposition over centimeters of length on a time scale of hours (S2). Cross sectioning of the 100 nm diameter capillary revealed that it was filled with germanium over a length of more than 30 cm. Similar deposition conditions and characterization methods were used for silicon, with the exceptions that a silane precursor
was used and the fibers were heated to 700 °C. A focused ion beam (FIB) instrument was used to obtain and thin cross sections from the fibers for transmission electron microscopy (TEM) analysis. Micro-Raman spectra were collected with a Renishaw inVia Raman microscope with 514.5 nm excitation.

**Electrical Characterization**

The 94 µm OD silica cladding of a 5 µm diameter germanium wire was etched with hydrofluoric acid at both ends to expose several hundred µm of the semiconductor core (Fig. 2 inset). 200 nm of aluminum was thermally evaporated onto the exposed semiconductor ends and sintered at 430°C for 30 mins to produce ohmic contacts. Aluminum forms low resistance ohmic contacts to n-type germanium (S3). Electrical connection to an external circuit, comprising a probe station and semiconductor parameter analyser, was completed using indium-gallium 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.

The capacitance of the sample is determined using a simple co-axial approximation (S4), with the germanium core being treated as the central conductor and the silica cladding as the cylindrical dielectric spacing between core and outer conductor (the In-Ga eutectic gate). The capacitance per unit length is given by $C/L \approx 2\pi\varepsilon\varepsilon_0/\ln(2h/r)$, where $\varepsilon$ is the dielectric permittivity of silica, $h$ the radial thickness of the silica cladding, $L$ the gate length (1.5 mm) and $r$ the radius of the germanium core, resulting in a capacitance per unit length of $\sim 6 \times 10^{-11}$ Fm$^{-1}$. The resistivity determined from two terminal measurements is $5.6 \times 10^{-2}$ Ω cm. As the gate bias voltage is varied from -100V to +100V (+/- 2.2x10$^6$ Vm$^{-1}$), the slope of the $I_{\text{drain}}$-$V_{\text{source}}$ curve increases
(Fig. 2), indicating that the carriers are n-type. Electron mobility can be calculated from the field effect transistor (FET) transconductance characteristics according to the following:

$$\frac{dI_{\text{drain}}}{dV_{\text{gate}}} = \mu \frac{V_{\text{source-drain}}}{C/L^2}$$

where $\mu$ is the carrier mobility, calculated to be 1.05 cm$^2$/Vs at room temperature. An estimate of the carrier density can be obtained by calculating the total charge in the germanium wire as $Q = CV_{\text{threshold}}$, where $C$ is the semiconductor wire capacitance and $V_{\text{threshold}}$ the voltage necessary to completely deplete the device. The total charge density is thus given by:

$$N_e = \frac{Q}{e\pi r^2 L}.$$  

Thus, taking $V_{\text{threshold}}$ (pinch-off) as $-100$ V and $C = 9 \times 10^{-14}$ F, $N_e \approx 2 \times 10^{21}$ m$^{-3}$ (or $2 \times 10^{15}$ cm$^{-3}$).

**Optical characterization**

A continuous wave (CW) laser diode was used to launch up to 100 mW of 1.55 µm radiation through free space into the cleaved end of a 5 cm long, 2 µm ID silicon filled capillary. The fiber axis was aligned with piezoelectrically controlled xyz stages. A 0.65 numerical aperture (NA) 3.1mm focal length aspheric lens was used to focus the beam waist to 2µm at the core. The etched-out silicon core was imaged both parallel and perpendicular to the fiber axis using a IR vidicon camera. Measurement of output power from the isolated silicon core was performed using a IR power meter. For a 100 mW launch, we observed an output of 0.03mW.
Germanium sulfide and gold MOF structures.

GeS$_2$ was deposited by heating a 1:3:9 molar ratio mixture of GeH$_4$, H$_2$S, and He at a pressure of 20 MPa flowing through a 1.6 $\mu$m capillary to 300 °C for 10 hours. Gold structures were deposited inside silicon tubes using a flowing precursor mixture (S5) consisting of 20 mg of dimethyl(trifluoroacetylacetonate)gold (III) dissolved in 2 mL of carbon dioxide at 8.6 MPa. The MOFs were heated to temperatures in the range of 100 to 300 °C.

Direct writing of gold and silicon particles.

Gold particles were direct written within MOF capillaries using 514.5 nm light focused with a 1.25 NA 100X oil immersion objective into a 1.6 $\mu$m diameter capillary surrounded by index matching fluid. We used the same precursor and pressure employed for the deposition of the gold tubes. Silicon particles approximately 1 micron long were also deposited at precise locations using a SiH$_4$ precursor mixture similar to the one used for deposition of silicon tubes.

Single crystal wire growth and physical characterization.

A high pressure SiH$_4$ precursor mixture similar to the one used for deposition of the silicon tubes was configured to flow into both ends of a 1.6 $\mu$m diameter capillary 10 cm long that had a single laser written gold plug. Next the capillary was heated over a length of 3 cm to 370°C, causing catalytic decomposition of the precursor at the gold plug and seeded growth of a single crystal silicon wire. The wire was etched out of the silica matrix and cross-sectioned and thinned for TEM analysis with a FIB. Selected area diffraction patterns collected along the entire length of the wire revealed it to be a single crystal.
Calculation of Raman modes under tensile strain

To investigate the Raman spectra of silicon under tensile strain, we performed ab initio density functional calculations in the generalized gradient approximation as implemented by the Perdew-Burke-Ernzerhof functional, employing a plane wave basis set with the projector augmented-wave method (S6, S7). Structural coordinates were relaxed until residual forces were less than 0.01 eV/Å. Both hydrostatic and uniaxial tensions were investigated, with free transverse relaxation in the uniaxial case. Assuming linear response, these two cases bracket reasonably well the possible stress boundary conditions in the actual fiber geometry. The dynamical matrix for phonon calculations was obtained by central finite differences with a step length of 0.03 Å.