Microstructured Optical Fibers as New Nanotemplates for High Pressure CVD

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ABSTRACT

Solid state chemists have long been interested in templated growth of materials using many approaches. The resulting materials have been useful in areas as diverse as photonics and catalysis. Microstructured optical fibers (MOFs) form a new class of nanotemplates that can have sub 20 nm pores that are meters to kilometers long. We have developed a high-pressure microfluidic chemical process that allows for conformal deposition of materials within MOFs to form the most extreme aspect ratio semiconductor nanowires known. The wires can be spatially organized with respect to each other at dimensions down to the nanoscale because the MOF templates can be designed with almost any desired periodic or aperiodic pattern. Many if not most of the chemistries used for conventional chemical vapor deposition (CVD) can be adapted for this process. The resulting materials should enable a large range of scientific and technological applications.

INTRODUCTION

Advanced devices and materials are enabled by hierarchal organization at length scales less than 10 to 100 nm. Nanoparticle superlattices, for example, may open the door to a wide range of new materials properties [1]. Chemists have long employed templates such as anodic alumina [2], mesoporous silica [3], and polycarbonate membranes [4] for growth of materials organized down to nanoscale dimensions. Here we report on our progress in using microstructured optical fibers (MOFs) as templates for the synthesis of new photonic and electronic materials. MOFs are drawn from silica performs in a manner similar to that used for conventional optical fibers. However, MOF preforms can be designed to have patterns of holes of arbitrary geometry that are scalably reproducible upon drawing down to dimensions of 10 nm [5]. They are thus versatile new nanotemplates that have a number of attractive features beyond the design flexibility in the patterns of holes. They are typically produced from silica giving them exceptional optical transparency, high strength, and the potential for 10% elastic deformation. Such elasticity should enable strain-tuning materials deposited within the MOFs. The walls of the capillaries within MOFs have a roughness of 1 angstrom RMS providing an ideal surface for the deposition [6].
EXPERIMENTAL

We have developed a technique for infiltrating the capillaries of MOFs with semiconductor materials [7]. High-pressure gases carry chemical vapor deposition (CVD) precursors through the capillaries of the MOFs. The fibers are then heated to temperatures suitable for the CVD chemistries being employed depositing the semiconductor materials onto the walls of the capillaries. Next the deposited semiconductors are annealed producing polycrystalline materials. Silane and germane are used as precursors for the deposition of silicon and germanium with helium serving as an inert carrier gas. Pressures of 20-35 MPa are used to achieve sufficient mass transport of the precursor-carrier gas mixture into the extreme aspect ratio dimensions of the MOF templates. Without such high pressures, there would be insufficient mass transport through the MOF templates. The fibers are heated to 550 degrees Celsius for the deposition of silicon and 425 degrees Celsius for germanium.

Scanning electron microscopy (SEM) images were collected using a JEOL XL20 SEM, and field emission SEM images were collected with a JEOL 6700F FESEM. Silver paint is used to secure cross-sections of the fibers to SEM pins. The tubes and wires are freed from the silica by etching with a buffered HF solution (33% HF in 10% NH$_4$F solution) to observe the silica-semiconductor interface. Raman spectra to characterize the crystallinity and materials quality are collected with a Renishaw invia microRaman. Samples are prepared for transmission electron microscopy (TEM) by sectioning and thinning with a focused ion beam (FIB).

DISCUSSION

A cross-sectional SEM image of a large air fraction MOF displaying a honeycomb scaffolding of silica within the fiber cladding is in figure 1a. The cells of the honeycomb structure are approximately 2 microns across and the silica walls separating the cells are 30nm at the thinnest point. As the deposition proceeds remarkably well formed tubes of silicon are deposited onto the walls of the capillaries (figure 2b).

Figure 1. SEM images of an empty honeycomb structured MOF template (a), and a honeycomb structured MOF with silicon tubes deposited.
An SEM image of a 6-micron diameter silicon tube (figure 2a) that has been etched free from the silica with a hydrofluoric acid solution is shown below. The smooth surface generated by the deposition is seen inside the tube as well as the smooth outer surface produced by deposition onto the smooth capillary walls of the MOF. The ability to deposit over extreme aspect ratios, centimeters to meters in length at the nano to microscale, is a result of both the highly conformal deposition and the ultra-smooth surface from which the deposition begins. Nanoscale capillaries have also been infiltrated with semiconductor materials. Below is a FESEM image of germanium deposited with in a 100nm diameter capillary (figure 2b).

![Figure 2](image2.png)

**Figure 2.** SEM image of a silicon tube that has been etched free from the silica and sliced using a FIB (a), and an FESEM image of a 100nm capillary with germanium deposition.

Below is an SEM image (figure 3a) of a silicon wire deposited within a 1.6-micron diameter capillary. In this image the deposition has continued down to a hole 25nm across. The hole is still well formed at nanoscale dimensions. A second section of this fiber several mm further down was also imaged (figure 3b). The hole is no longer visible indicating that it is less than 10nm in diameter. This indicates the potential of this high-pressure technique to operate at nanoscale dimensions, as nanofluidic flow of the high-pressure gas mixture continues the deposition.

![Figure 3](image3.png)

**Figure 3.** SEM image of a 1.6-micron diameter capillary filled to 25nm (a) and to sub 10nm (b) dimensions with germanium.
By exploiting to decades long knowledge base of CVD we are able to introduce complexity into the capillaries. Sequential deposition of precursors allows the fabrication of radial hetero-junctions within individual capillaries (figure 4a). The deposition is not limited to Silicon and germanium within silica MOFs. The MOFs can be constructed from a variety of glasses[8], we are continuing to introduce new materials into the capillaries by adapting CVD chemistries to this high-pressure technique. We have introduced Si, Ge, GeS2, Au, Pt, Cr, and TiO2, and presently we are working on the chemistries to introduce direct gap materials.

![Figure 4](image)

**Figure 4.** SEM image of a radial hetero-junction in a 6-micron diameter capillary produced by sequential deposition of germane followed by silane.

**CONCLUSIONS**

MOFs display potential as templates for the organization materials at dimensions down to the nanoscale. The highly conformal deposition within nanoscale pores, coupled with the design flexibility of the MOFs is evident when studying the profiles of the micro and nanoscale tubes and wires fabricated by this high-pressure technique. Fabrication of junctions and incorporation of crystalline materials which can enable the production of functional electronic and optoelectronic materials has been demonstrated.

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**REFERENCES**