Self-Assembly Technique Enables Fabrication of Large-Area, Periodic Arrays of Aligned Carbon Nanotubes

Heretofore, carbon nanotubes (CNTs) could not be made into photonic crystals because prevailing synthetic techniques did not produce two-dimensional (2D) arrays that were simultaneously well aligned and periodic, and covered a large-enough area. Plasma-enhanced chemical vapor deposition (PECVD) is typically employed in conjunction with a catalyst (Ni, Fe, or Co) deposited as either a thin film formed by magnetron sputtering or as dots, which can be made by electron-beam lithography or by electrochemical deposition. Although large areas of aligned CNT arrays can be inexpensively grown from thin films or from electrochemically deposited dots, they are not periodic. CNT arrays grown from e-beam lithography are periodic but are expensive to produce and are limited to small areas. A team of researchers from Boston College; Natick Soldier Center in Natick, Mass.; the Hahn-Meitner Institute in Berlin; Nanolab, Inc. in Brighton, Mass.; and the University of Massachusetts at Boston has developed a self-assembly technique that produces large, 2D, periodic arrays of CNTs.

In the January issue of *Nano Letters*, Boston College researchers K. Kempa and Z.F. Ren, Natick Army researchers

B. Kimball and M. Sennett, and co-workers report on the development of nanosphere lithography, which utilizes commercially available suspensions of monodisperse polystyrene (PS) nanospheres (1 μm, 0.5 μm, 0.25 μm, and 0.125 μm in diameter). The researchers applied several μL of suspension to a clean silicon wafer. After immersion in de-ionized water and modification of the surface tension with a dodecylsodiumsulfate solution, a large, highly ordered monolayer of nanospheres formed on the water surface. Draining the water deposited the monolayer onto the silicon surface—or onto the surface of virtually any sufficiently flat substrate. Both the uniform diffraction color and a fast Fourier transform analysis confirmed that the monolayer was essentially free of defects.

The researchers subsequently employed the nanosphere monolayer as a template for catalyst deposition—electron-beam evaporation of Ni—after which the PS nanospheres were chemically removed. Images made by atomic force microscopy and scanning electron microscopy (SEM) showed that the Ni dots formed a honeycomb pattern. The Ni dots can be annealed first or used directly to grow CNT arrays by hot-filament PECVD. In this work, aligned CNTs were grown using acetylene gas as the carbon source and ammonia gas as both the plasma enhancer and growth promoter.

The researchers note that SEM images show that the CNTs are not as straight as those synthesized previously, but feel confident that the quality will improve with better nanosphere removal and with more control of the CNT growth. The colorful appearance of CNT arrays due to diffraction demonstrates their high metallicity (low dielectric loss) and the high degree of ordering, said the researchers.

The researchers employed a general theory of light diffraction to demonstrate that their honeycomb arrays of CNTs should lead to a diffraction pattern with triangular symmetry. Triangular symmetry was observed in the diffraction patterns obtained by shining green and blue laser light perpendicular to the plane of the lattice. The research team said that the rotational symmetry of the patterns shows that the scattering nanotubes are circularly symmetric in the plane and that the small hexatic pattern distortion points to the possibility of misaligned crystalline macro regions. The researchers also demonstrated that the specific dependency of the spot intensity on their order is consistent with theory.

Citing previous work demonstrating 2D hexagonal bandgap structures, the researchers reasoned that they could employ previously published theoretical results after proper dielectric-constant scaling, which implied that their honeycomb array of nanotubes should act as a 2D photonic-bandgap crystal with a bandgap of about 0.5 μm. While demonstration of the photonic bandgap in their nanotube arrays is in progress, the researchers believe they can obtain photonic bandgaps in the visible range. They also said that the nanotubes can be coated for better control of the photonic-crystal parameters or can be used as structural templates for nonmetallic photonic arrays.

STEVEN TROHALAKI

Controlled Growth of GaN Single-Crystal Nanowires Demonstrated

Gallium nitride (GaN) has been shown, over the past several years, to be an important optoelectronic material. Success in the growth of high-quality GaN thin films has led to the development of various devices including blue light-emitting diodes and laser diodes. Recently, efforts have also been directed toward producing nanowires of GaN, which could be important for nanoscale optoelectronic applications. However, it has been difficult to control the size and location of the nanowires. Now, a group from the University of Southern California including Chongwu Zhou, Song Han, and co-workers has demonstrated control of nanowire diameters, nanowire growth locations on a substrate, and nanowire orientation with respect to a substrate. This was achieved through the use of monodispersed gold clusters as catalysts, as reported in the February issue of the *Journal of Materials Research*.

The researchers first demonstrated the use of e-beam evaporated Au nanoparticle clusters as a catalyst for the growth of GaN nanowires. They used a chemical vapor deposition (CVD) technique using a pure Ga source and flowing NH_3 gas to grow the nanowires. The synthesis was found to be based on the vapor-liquid-solid (VLS) growth mechanism wherein the Ga vapor diffuses into the gold catalytic particles, grows out, and reacts with the NH_3 forming GaN after the Ga/Au alloy achieves supersaturation. The nanowires were found to be single crystals growing in the [100] direction with a wurtzite structure, with the diameter approximating the diameter of the catalytic gold particles.

The researchers then used gold nanoclusters with specific diameters of 10 nm, 20 nm , and 30 nm. In each case, the nanowire diameters were uniform. Measurements of a number of nanowires yielded Gaussian distributions of diameters with average diameters of 11.9 nm, 18.5 nm, and 28.1 nm, respectively. In a separate experiment, gold nanoclusters were deposited at desired sites on a Si/SiO_2 substrate using standard e-beam lithography, which yielded islands of the catalyst as dictated by the pattern. GaN nanowires were observed to grow only on these islands. In addition, it was possible to control the yield of nanowires by controlling the concentration of the gold nanoparticles.

An a-plane sapphire substrate, which also has a wurtzite structure, was used to grow the nanowires in an attempt to grow vertical nanowires. There is a 13% lattice mismatch between the sapphire and the GaN nanowires. Au nanoclusters were deposited using a transmission electron microscope grid as the shadow mask. CVD growth yielded GaN nanowires on the areas with the Au nanoclusters, mostly growing in a vertical orientation with respect to the substrate. Some nanowires were found to grow in other directions as well, which was attributed to the 13% lattice mismatch.

This ability to grow GaN nanowires with well-defined diameters, at desired and specified sites, and by achieving a high degree of orientation control, is crucial if the nanowires are to be used for nanoscale electronic and optoelectronic devices.

GOPAL R. RAO

Ordered Sol-Gel Composites with Submicrometer Periodicity Obtained

The preparation of mesostructured materials with high orientation order is emerging as a new area of technological and scientific interest, in particular, due to their possible use in such fields as catalysis, chromatography, filtration, photonics, and lithography of mesostructured films. Kalaichelvi Saravanamuttu and Mark P. Andrews of McGill University, Canada, have found an approach for the synthesis of macroscopically aligned mesostructured materials by using a template-free, room-temperature sol-gel route. As reported in the January issue of *Chemistry of Materials*, the researchers performed the sol-gel processing of simple silicon and transition-metal alkoxides with acrylate substituents (e.g., commercially available alkoxysilane: 3-methacryloxypropyltrimethoxysilane), which forms networks with long-range, microstructural organization with 250 nm periodicity. The suggested approach involves photoinitiated free-radical polymerization of the olefin groups, which "locks" this organization into mechanically stable, optically clear monoliths. The researchers said that before organic polymerization, composites could be spin-cast as microstructured, bicontinuous thin films. Previous studies have assumed that room-temperature sol-gel processing without templates leads