RESEARCH/RESEARCHERS

CNT Packing Density in Anodic Aluminum Oxide Templates Depends on Pore Aspect Ratios

Potential applications for carbon nanotubes (CNTs) include electron-field emitters, quantum wires, molecular filters, and artificial muscles. Fundamental to many applications is the packing density of aligned CNTs standing normal to a substrate. Densely packed, aligned CNTs have recently been fabricated using anodic aluminum oxide nanotemplates (AAOTs) that contain pores and are embedded with Co catalysts. The length and packing density of the resulting CNTs match the pore length and number density of the pores in the AAOTs. Researchers at the Departments of Chemical Engineering and Materials Science and Engineering, Pohang University of Science and Technology, Korea, have demonstrated a method to control the packing density of CNTs fabricated from AAOTs.

As reported in the October issue of *Chemistry of Materials*, the research team led by K.-H. Lee exploited a competition between two processes to control the packing density: CNT growth in AAOTs from Co-catalyzed C_2H_2 pyrolysis and amorphous-carbon deposition on the pore walls of the AAOTs. The degree of competition was controlled by varying the pore aspect ratio in the AAOTs, which were formed using a previously published two-step anodization process. A clean, highly pure, electropolished Al sheet was anodized at 40 V in 0.3 M oxalic acid solution at 15°C for 12 h and then etched using a mixture of phosphoric and chromic acids. A second anodization, performed under the same conditions as the first, but for only 10 min or 20 min, resulted in highly ordered AAOTs with pore depths of 1 μm and 2 μm, respectively. In order to facilitate uniform Co electrodeposition, the voltage was dropped from 40 V to 14 V in 1-V increments, which decreases the thickness of the alumina barrier at the pore bottoms. Subsequent treatment with 0.1 M phosphoric acid widened the pore diameters to 40 nm or 80 nm and also acted to decrease the barrier layer. Co catalyst was electrochemically deposited with uniform height at the bottom of the pores.

Three distinct AAOTs were fabricated, all with the same pore density (~10^{10} cm^{-2}) but differing in pore dimensions: (1) 1-μm pore depth, 80 nm diameter; (2) 2-μm pore depth, 80 nm diameter; and (3) 2-μm pore depth, 40 nm diameter. After reducing the Co particles, the CNTs were grown by catalytic pyrolysis in a tube reactor using 10% C_2H_2 and 20% H_2 in an Ar carrier gas for 20 min at 650°C. After the flow of C_2H_2 and H_2 was stopped, the samples were cooled to room temperature in an Ar atmosphere.

Lee and co-workers found that the CNT packing density depends on the pore aspect ratios; estimates of packing density from scanning electron microscope (SEM) images are ~10^9 cm^{-2} for (1), 10^7 cm^{-2} for (2), and 10^5 cm^{-2} for (3). The SEM images also reveal that the CNT diameters nearly match the pore diameters. Lee and co-workers found that packing density did not change with time even as the CNTs continued to grow and become curved. High-resolution transmission electron microscope images reveal that the CNTs consist of ~40–50 well-ordered graphitic layers surrounding a hollow core. Lee and the research team believe that in the initial stages of their experiments, CNT growth and carbon deposition on the pore walls occur simultaneously. Furthermore, the deposited carbon inhibits the growth of CNTs by Co catalysis, which results in short CNTs inside the pores. Carbon is deposited to a greater degree in smaller, deeper pores because, as the researchers point out, C_2H_2 is transported by Knudsen diffusion. The num-

Correction

Kyo-Se Choi's name was misspelled in the October 2002 issue of *MRS Bulletin*, page 752.

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ber of CNTs able to escape from the pores therefore depends on the pore dimensions. The researchers plan further investigation in order to quantify this geometric effect and said that "this approach should facilitate novel possibilities for the fundamental characterization and applications of microelectronic devices such as CNT-based field emitters."

STEVEN TROHALAKI

Metalloporphyrin Zeolite Analogue Demonstrates Selective Absorption of Polar Solvents

A highly crystalline solid-state material similar to that of zeolites has been synthesized using carboxylic functionalized metalloporphyrins and cobalt ions. Researchers from the University of Illinois at Urbana-Champaign led by Kenneth S. Suslick demonstrated this synthetic method to produce such zeolite analogues in their article in the October issue of *Nature Materials*.

This material, CoT(p-CO_2)PPC$o_{1.5}$, called PIZA-1, was synthesized by heating [H_5T(p-CO_5H)PP] and $CoCl_2$•$6H_2O$ in a sealed tube with a pyridine/KOH solvent at 150°C for 2 days. Single-crystal x-ray analysis revealed a neutral and highly crystalline network of ruffled Co(III) por-

Independent Committee Finds Scientific Misconduct in Investigation of Bell Labs Researcher Hendrik Schön

Bell Labs (Murray Hill, N.J.) announced on September 25 the findings of an independent committee it formed to investigate possible scientific misconduct, the validity of data, and scientific methodology used in a series of papers published by Hendrik Schön and co-authors. In its report, the committee concluded that Schön had engaged in scientific misconduct in 16 out of 24 allegations based on work published between 1998 and 2001. Schön's employment with Lucent Technologies/Bell Labs has been terminated. The committee cleared the other researchers who had contributed to the experiments, and who were co-authors on several published papers, of any scientific misconduct.

Bell Labs formed the committee in May after questions arose regarding the validity of data in several published papers authored by a total of 20 researchers from Bell Labs and other institutions. It named Malcolm Beasley (Stanford University) as chair; and as members: Supriyo Datta (Purdue University), Herwig Kogelnik (Lucent Technologies), Herb Kroemer (University of California—Santa Barbara), and Don Monroe (Agere Systems).

The research work in question encompassed a number of areas in condensed-matter physics and solid-state devices. These included field-induced high-temperature superconductivity in various materials, organic single-molecule transistors, organic field-effect transistors, organic junction lasers, plastic Josephson junctions, and tunable superconducting weak links.

The allegations under examination were grouped into three categories: (1) substitution of data, (2) unrealistic precision of data, and (3) results contradicting known physics. An example cited by the committee of the substitution of data includes work on self-assembled monolayer field-effect transistors (SAMFETs), published by Schön and co-authors in *Nature* **413** (2001), page 713. Very similar transistor diode curves for two reportedly different molecules, including detailed "noise," appear in two different figures in the same paper, with the vertical scale differing by a factor of two.

An example cited by the committee of unrealistic precision of data is Schön's work on normal-state resistance of gated C_{60}, which reportedly showed a superconductive transition up to 50 K for various gate voltages. This work was published with co-authors in *Nature* **408** (2000), page 549. The systematic variation of the resistance as a function of temperature as gate voltage was varied is remarkable. The derivative of the original plotting data shows striking linearity, including the data near 50 K.

In the third category, contradictory physics, one of the allegations cited in the report involves SAMFET transistor characteristics. A well-known constraint for any device using the FET principle is that a gate-voltage change of at least ~60 mV is needed to turn off the current by a factor of 10. The SAMFET molecular devices reported by Schön and co-authors in *Nature* **413** (2001), page 713, *Science* **294** (2001), page 2140, and *Applied Physics Letters* **80** (2002), page 847, took far less gate voltage to turn off than this minimum. Furthermore, the reported devices had very poor aspect ratios, with oxide thicknesses of more than 10 times the reported channel length. Standard FETs typically have channel lengths that are 10 times the oxide thickness so that the gate, rather than the drain, controls electrostatic potential.

The committee found scientific misconduct in these examples as well as in other instances listed in the report. The committee specifically cited data fabrication in the first two examples and data falsification in the third. The devices used and the physical measurements of the significant devices in the research in question were, for the most part, fabricated by Schön alone, and he was unable to present his data as requested by the committee. In addition, no measurement or demonstration of a significant physical effect or device characteristic was witnessed by any co-author or other colleague, with one possible exception.

The committee acknowledges Schön's dedication to research and that the allegations under review represented less than a quarter of his published work. Furthermore, the committee wrote, "As a result [of the committee's study] it is not possible to confirm or to refute the fundamental physical claims in the papers in question....In the end, the correctness of the fundamental physical claims in the work in question will come through the normal processes of science—specifically through the reproduction, or not, of the results."

In a response to the committee's report, Schön acknowledged that he had made various mistakes in his scientific work and apologized to his co-authors and the scientific community. Furthermore, Schön wrote, "I have observed experimentally the various physical effects reported in these publications, such as the quantum Hall effect, superconductivity in various materials, lasing, or gate modulation in self-assembled monolayers, and I am convinced that they are real, although I could not prove this to the investigation committee."

Jeff Jaffe, president of research at Bell Labs, said, "An experience such as this heightens everyone's awareness of the importance of ensuring scientific research integrity....We are reinforcing our policies and procedures for the publication of experimental results and encouraging more rigorous internal peer reviews. At the same time, we remain committed to maintaining the scientific freedom essential for discovery and innovation to flourish."

The committee's full report, including an executive summary, is available on the Web at http://www.lucent.com/news_events/researchreview.html.

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