Microscopy and Spectroscopy Open New Vistas in the Emerging World of Nanotechnology: Part 1

by Barbara Foster

An exciting new world is dawning: nanotechnology. Dealing with new properties and forms of matter at dimensions smaller than 100 nm, nanotechnology promises to provide stronger, lighter materials engineered with 100% accuracy; new modes of medical analysis and treatment; and a new age of ultrafast and super-performing computers.

A recent informal survey of microscope and imaging manufacturers conducted by Microscopy/Marketing & Education, Inc. (MME, Springfield, MA) revealed that microscopy has been and will continue to be pivotal to understanding and implementing nanotechnology. Five key trends emerged from this study:

- Nanomachining is becoming increasingly important for testing and repair and nanomanipulation will be a catalyst for nanostructure self-assembly.
- New nanoproperties will have a profound effect on the macroworld. The imaging and analysis of these nanoproperties will become increasingly important for both research and commercialized processes.
- Nanoanalyses are requiring new methods of sample preparation and a new integration of sciences that, in the more traditional macro- and microworlds, tended to be highly compartmentalized.
- Both micro- and nanoanalyses are driving the growth of hyphenated technologies.
- High-throughput techniques, based on combinatorial chemistry, are crossing over from drug discovery and biotechnology to chemistry and the materials sciences.

Using representative findings from the MME survey, this article discusses the impact of these trends, both on instrument development and new directions of research and commercialization. (Note: A more complete listing of microscopy and imaging techniques from this study is available at www.MicroscopyEducation.com.)

The new world of nanotechnology

First hypothesized by K. Eric Drexler in his book, *Engines of Creation*,[1] nanotechnology is emerging from fiction and pure R&D into the very real light of everyday life. Television commercials show khaki pants that will not stain because of their nanofiber surface, and cars are taking on a new, long-lasting shine because of nanoengineered coatings. Quantum Polymer Technologies (Sonoma, CA) has announced a new conductive polymer that builds its own wiring harness, depending on how voltage is applied. Even prime time evening television has caught the excitement: The lead character in "Jake 2.0" (Wed., 9:00 P.M. ET, UPN) enjoys superhuman abilities reminiscent of a cross between Spiderman and the Six Million Dollar Man, thanks to an infusion of "nanobots" (nano-sized robots).

Figure 1 shows the size relationship of the macroworld to the microdomain and the realm of nanoevents. As one travels further into the nanoworld, matter loses its bulk properties and quantum effects emerge. The transition is similar to the difference between classical Newtonian physics and quantum mechanics.

Matter in the nanoworld possesses unique characteristics. For example, it can be self-assembling, that is, individual atoms, under the influence of the appropriate driving forces such as voltage, chemistry, or atomic forces, can

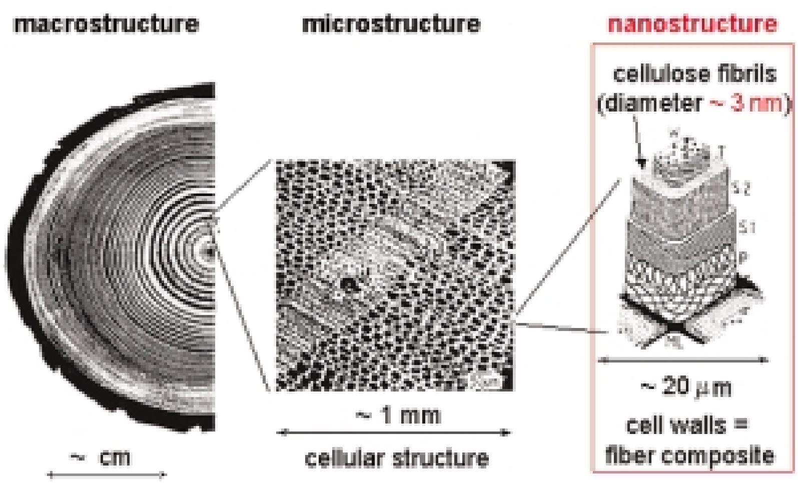

Figure 1 *Relationship of macro to micro to nano. (Image courtesy of Bruker-AXS, Madison, WI.)*

build machines to accomplish specific tasks. Proteins are a naturally occurring nanomaterial familiar to everyone. Under the proper influence of enzymes, amino acids self-assemble, then fold into unique structures to perform specific functions. Carbon nanotubes are a common synthetic nanomaterial (*Figure 2*). They are of considerable commercial interest because of their ability to form extremely strong but light structures.

Strong governmental push

Nanotechnology is receiving intense attention from the U. S. Government. A National Nanotechnology Initiative (NNI) (www.nano.gov) was formed during the Clinton Administration. Comprised of 10 federal departments and independent agencies, NNI members share a common goal: "long-term fundamental research aimed at discovering novel phenomena, processes, and tools;...support of new interdisciplinary centers and networks of excellence, including shared user facilities; support of research infrastructure; and addressing research and educational activities centered on the societal implications of nanoscience and nanotechnology."[2] Participants in NNI include the Departments of Agriculture, Commerce, Defense, Energy, Justice, and Homeland Security, as well as NASA, the National Institutes of Health and National Science Foundation, and the U.S. EPA.

The government is providing strong funding for this effort. For fiscal year (FY) 2003, President Bush requested \$710 million, an increase of 17% over FY 2002. In actuality, Congress voted \$774 million. Funding is even stronger for FY 2004: \$847 million, a 9.5% increase over this year's budget.[3]

Robust growth in nanotechnology is expected to continue for well over a decade. According to a report from *Biotaq Newswire*, "the NSF predicts the total market for nanotechnology products and services will reach \$1 trillion by 2015."[4]

Two of three new NNI prime focus areas are especially important to microscopists and spectroscopists: manufacturing processes at the nanoscale and development of instrumentation and metrology.

Familiar territory and new opportunities

Conventional microscopy is no stranger to nanoimaging. Responding to MME's survey, Mr. Tom Calahan of **Zeiss** (Thornwood, NY) reminded us that darkfield, a routine light microscopy technique, detects (as differentiated from resolving) particles on the 30-nm range.

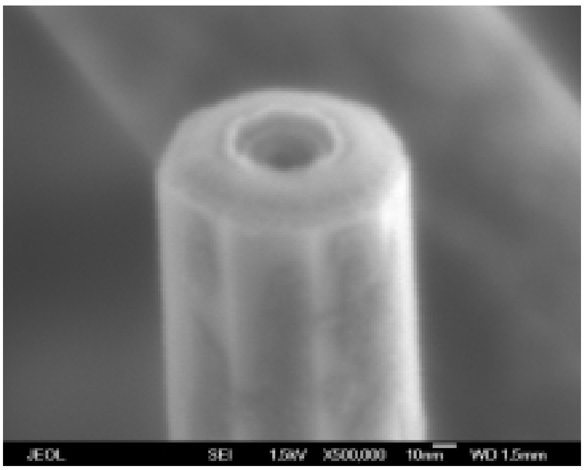

Figure 2 SEM image of a single-walled carbon nanotube (SWCT). (Image courtesy of JEOL, Peabody, MA.)

Scanning and transmission electron microscopes (SEMs and TEMs) have routinely imaged structures below 100 nm for well over 60 years. TEMs, especially, have long been used for elucidating atomic lattice structure and spacing. Ms. Patricia Corkum of **JEOL** summarized the impact of nanotechnology on this sector of the industry: "Seeing is believing. [These] instruments offer scientists a 'reality check' for clarity, contrast, and control to help make their process more efficient."

Electron beam lithography, a close sibling to conventional EM technologies and available from companies such as **Leica** (Bannockburn, IL) and **Nikon** (Melville, NY), is used routinely to etch circuitry and other unique structures for sensors and actuators smaller than 100 nm. In a detailed response to the survey, Dr. Bernie Wallman, a consultant to **Leica**, provided one of the more intriguing applications: the ability to select and grow cellular materials using patterned substrates with structural dimensions programmed to match specific cellular characteristics.

Nanotechnology is also prompting development in the analytical techniques so closely tied to electron microscopy. In his survey response, Dr. Del Redfern of **EDAX** (Mahwah, NJ) indicated that "over the next five years, the minimum particle size for compositional analysis within the semiconductor industry is predicted to be reduced to 33 nm." These new resolution requirements have prompted **EDAX** to develop novel, low-energy technologies, ranging from complex Auger accessories to simple X-ray techniques such as microcalorimetry and wavelength-dispersive X-ray spectrometry (WDS).

AutoQuant (Watervaliet, NY), a key player in the image processing arena, cited new applications of its adaptive blind deconvolution algorithms to improve the resolution of both optical and SEM images. This technique is especially important for SEM users because it reduces the need for coating specimens.

The emergence of nanotechnology is also engendering new techniques and prompting new focus. **Nanoptek**

(Concord, MA) has applied the sophisticated physics of near-field evanescent wave theory to an elegantly simple modification of a light microscope to produce a photon tunneling microscope. This video-rate profilometer boasts a lateral resolution of 150 nm and subnanometer vertical resolution over fields of 150 µm *XY* and a *Z* range of 400 nm.

Sesa Corp. (Santa Clara, CA) has developed microphotoluminescent and photoconductivity equipment for measuring emission of micro- and quantum structures such as quantum wire and vertical cavity surface emitting lasers (VCSELs).

Small structure size does not seem to present the expected barrier to using existing equipment in the nanoworld. Camera companies such as Cooke (Auburn Hills, MI) are developing high-speed cameras for testing microelectromechanical (MEMS) chips, while the *Retiga* (QImaging, Richmond, VA) made the journey on the space shuttle to conduct microgravity experiments for new nanomaterials. Although the *XY* limit of resolution on a typical Raman system is far larger than nanoscale, some new nanomaterials turn out to be very Raman responsive. Using multiple excitation wavelengths from the UV through visible spectrum into the near-infrared (NIR), the LabRam (Jobin Yvon, Edison, NJ) has successfully studied both molecular and polymorphic properties of carbon nanotubes, fullerenes, and other nanomaterials.

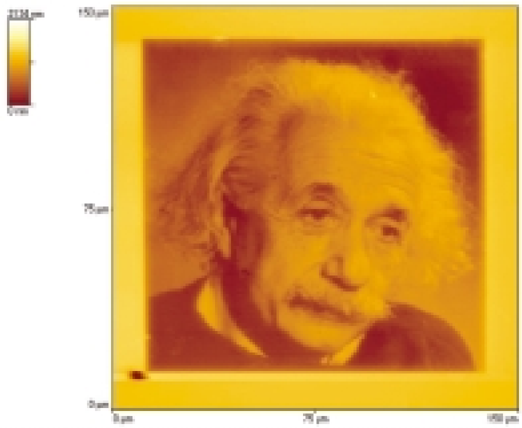

Figure 3 Nanolithography. *(Image courtesy of Raith, Inc., Ronkonkoma, NY.)*

Nanomachining and nanomanipulation

The rise of this technology is pushing the envelope for nanomovement and nanomanipulation. Companies such as Applied Scientific Instruments (Eugene, OR) report that nanotechnology is driving them to develop new encoder feedback technology for *XY* and *Z* stage movement on the order of 1–5 nm. Laser tweezers that can manipulate single cells and small particles in the microdomain have been available for more than a decade, but new technologies span the micro–nano boundary. For example, a proprietary holographic technique enables the Bioryx® 200 system (Arryx, Chicago, IL) to independently steer 200 individual particles—moving, placing, and aligning them at the user's command.

Focused ion beams (FIB), a derivative of the more conventional scanning electron microscope, have been used for a number of years in the electronics industry to section and repair semiconductor devices. E.A. Fischione, Inc. (Export, PA) recently announced the model 1030 automated sample preparation (ASaP) system, which combines ion beam etching (IBE), reactive ion beam etching (RBE), reactive ion etching (RIE), high-resolution coating (HRC), and plasma cleaning.

Atomic force microscopes (AFMs), which have been available commercially for 15 years, also provide a capable tool for both delicate nanolithography (*Figure 3*) and nanomanipulation (*Figure 4*).

Nanomanipulation requires a stable base. According to Mr. Bob Munkachy, his company, Vistek (Tempe, AZ), faces new requirements due to nanotechnology. The engineering in the company's new antivibration tables has reduced vibrational error from 15 Å to less than 5 Å. In its survey response, Prior (Rockland, MA) discussed new motorized technology for both *XY* and *Z* motion, with theoretical resolution of 10 nm *XY* (1⁄250th of a step, reproducible over several steps) and theoretical resolution of 1 nm in *Z*.

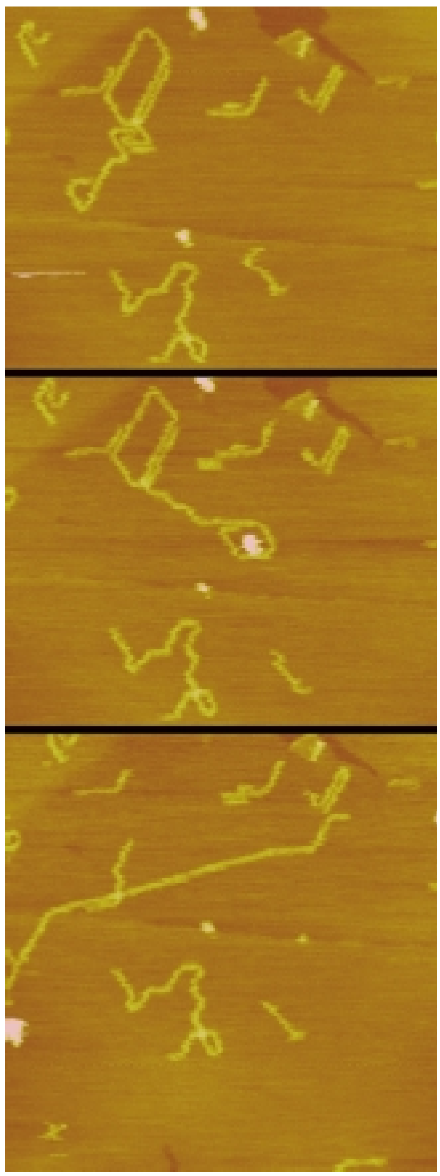

Figure 4 Nanomanipulation of polystyrene beads. *(Image courtesy of Veeco Corp., Santa Barbara, CA.)*

continued

Testing nanoproperties

How has nanotechnology made such amazing progress in such a short time, moving from pure theory through R&D to commercialization in less than 15 years? Mr. Thomas Wyrobek, President of Hysitron (Minneapolis, MN), well-known manufacturer of nanoindentation and nanoscratch devices, proposed one very real hypothesis: "The development of new materials that will affect all our lives in our lifetime are in process today as a result of being able to measure mechanical properties at the nanoscale." *Figure 5* illustrates an unusual combination of sample and technique. The sample is a MEMS device, another new technology that is having a significant impact on microelectronics, biotechnology, and drug discovery. While a cursory look reveals the nanoscratch test, closer examination of this figure reveals three small nanoindentations on the top of the right branch of each structure. The extremely high surface area:volume ratio of MEMS devices requires careful characterization of the surface tribological behavior. Nanoindentation and nanoscratch provide that information. Studies charting force to displacement in these tests show repeatability of the indentation measurements, even at depths below 25 nm.

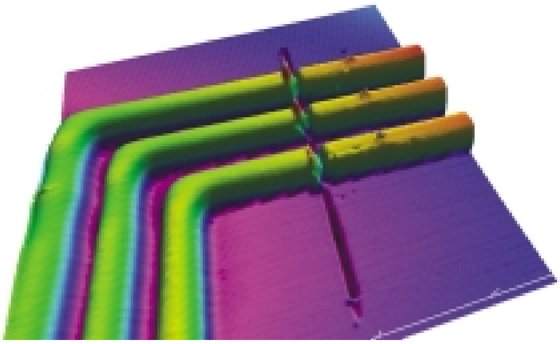

Figure 5 MEMs device showing both a nanoscratch test (middle) and nanoindentation tests for nanohardness. (Image courtesy of Hysitron*.)*

Atom probe microscopies are critical to nanoanalyses. Atomic force microscopy uses an atomically sharp tip to scan or hop across the surface, creating images based on the atomic attractions and repulsions between the probe tip and the surface. These images elucidate a wide variety of parameters, including topography (*Figure 6*, left), lateral forces, friction, and adhesion.

These microscopes are part of a large and energetically growing family more aptly called "scanning probe microscopy." While Veeco is still the acknowledged leader in the field, a number of other smaller companies are entering the fray, including now-veteran firms such as Quesant (Agoura Hills, CA) and Molecular Imaging (Tempe, AZ), and newcomers Asylum Research (Santa Barbara, CA), Pacific Nanotechnology (Santa Clara, CA), and the latest entrant, Nanotech-America (Springfield, MA) (a wholly owned subsidiary of NT-MDT, Moscow, Russia). The industry meta-site, www.microscopy.info, has detailed information and links for manufacturers for AFM/SPM/NSOM [near-field scanning optical microscopy], as well as other, more conventional microscopy modalities, sample preparation companies, and camera and image analysis firms. Between them, these companies offer a wide variety of probe–surface interactions that map everything from magnetism and electrical properties (spreading resistance, ion conductance, capacity) to quantum states. Uniscan (Derbyshire, U.K.) has also announced a scanning electrochemical microscope (SECM 270) for investigating surface coating technology and corrosion, biotechnology applications such as biosensors and enzyme stabilization, and MEMs properties.

Figure 7 (right) shows a new type of atomic probe technology, the local electrode atom probe (LEAP). Described as a "point projection microscope," this device uses an electric field to strip the surface of a sample, atomic layer by atomic layer. As they are ionized, the atoms are propelled toward a detector that records the location and time of impact of each atom. The result is a map that resolves millions of individual atom positions in three dimensions and identifies them by time-of-flight mass spectrometry.

Spectroscopy's role

The nanoworld presents important expansion opportunities for companies such as EDAX; PANalytical (previously Phillips Analytical) (Natick, MA); and Gatan (Pleasanton, CA). These firms all manufacture the conventional X-ray diffraction and energy-dispersive X-ray (EDX) spectrographs that are standard on many electron microscopes.

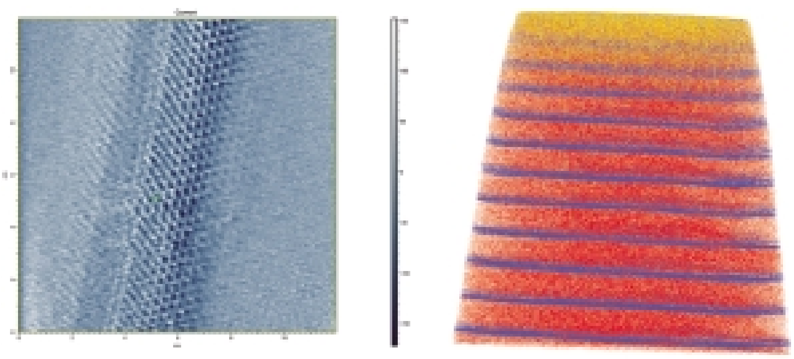

Figure 6 Atomic level imaging. Left: Structure detail of a carbon nanotube taken with a scanning probe microscope. (Image courtesy of NT-MDT*, Moscow, Russia.) Right: Multilayered Pt Mn Ga nanofilm taken with local electrode atom probe (LEAP). (Image courtesy of* Imago*, Madison, WI.)*

continued

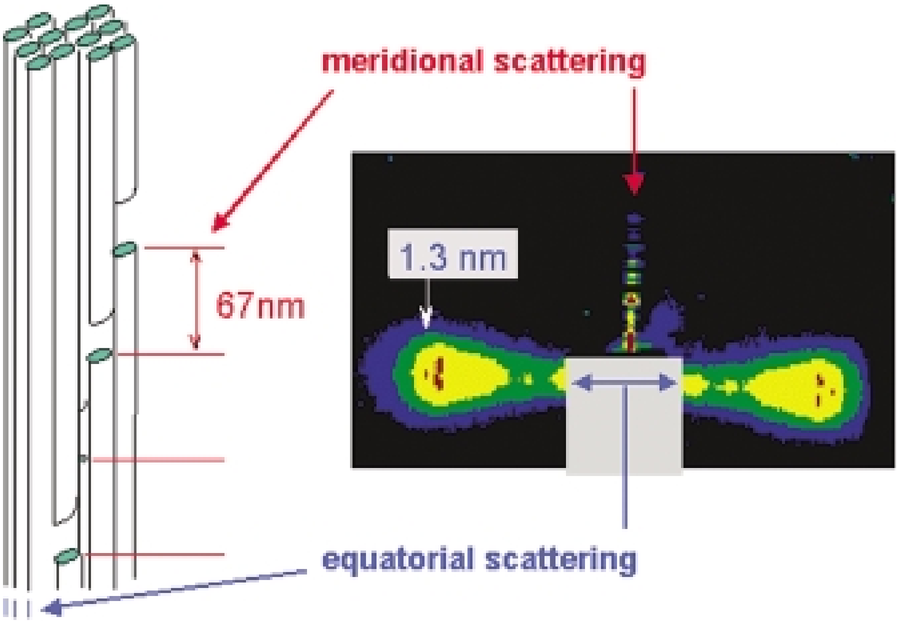

Figure 7 *Small-angle X-ray scatter (SAXS) spectrum of polymer fibrils. (Image courtesy of Bruker-AXS.)*

Bruker AXS has focused on this new niche with a number of products, including the Nanostar, its small-angle X-ray scatter (SAXS) system. Its customers are analyzing shapes and sizes of particles on the Å to 100-nm scale; the relationship of ordering to strength in lamellae and precipitates in super-alloys; as well as alignment versus structural property in a number of materials from polymers to nanotubes, solutions, wood, and bone.

Microscopy and spectroscopy are central to this new world of nanotechnology. Part 2 of this article will explore the impact of nanotechnology on sample preparation; innovative "microscopes within microscopes"; and high-throughput combinatorial chemistry, a new high-speed approach to conducting multiple chemical tests in parallel as well as a new method for initiating self-assembling processes.

References

1. *Drexler KE. Engines of change: the coming era of nanotechnology. New York, NY: Anchor Books, 1986 and 1990. Also published for the World Wide Web by Russell Whitaker and available for download at www.foresight.org.*
2. *Rocco NC. National nanotechnology investment in the FY 2003 budget request by the President. Presented at AAS/ASME briefing, Washington, DC, Feb 13, 2002.*
3. *National Nanotechnology Initiative. Research and development funding in the President's 2004 budget. Washington, DC: Office of Science and Technology Policy, Executive Office of the President.*
4. *Biotaq Newswire. Investor conference to address market capitalization in the nanotechnology industry, Mar 8, 2002.*

Ms. Foster is President, Microscopy/Marketing & Education, 126 Paridon St., Ste. 102, Springfield, MA 01119, U.S.A.; tel.: 413-746-6931; e-mail: bfoster@mme1.com. The author welcomes comments and questions on her articles.

New size regimes and new properties

A nano is one-billionth of a unit. Dr. Andrew Whitely of Jobin-Yvon (Edison, NJ) submitted the following comparisons:

- 1 nm = 1 billionth of a meter
- Head of a pin = 10,000,000 nm
- Human hair = 10,000 nm
- DNA molecule = 2.4 nm wide
- Individual atom = few tenths of a nm.