semi™

Nano News Reprint

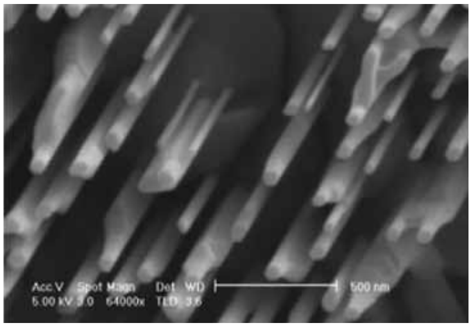
FEBRUARY 2007

Nanowire Applications and Production Methods

Sales Currently Limited to R&D but Developers Expect Range of Products in Few Years

Most actual nanowire products for sale are equipment and materials to research groups, but companies are working on developing a wide range of applications, ranging across sensors, semiconductor heat management, batteries, flexible circuits, display backplanes, medical diagnostics, and nonvolatile memory.

After five years in the business of building commercial process tools for nanotube and nanowire research, Atomate Corp.'s new growth in equipment sales over the last couple of years has largely come from vapor-liquid-solid (VLS) process tools for growing nanowires. "We've seen a huge shift," says CEO Brian Lim. Most of the Simi Valley, CA, company's CVD (chemical vapor deposition) tools initially went to university and government research labs, but are now migrating, along with graduating Ph.D. students, into large corporate research labs. Lim reports the company now has its process equipment in almost all major universities and government labs, and on six continents. Some of these tools are growing nanowire structures across 100 mm wafers, and the company is working on a roadmap for commercial fab equipment to produce the nanowire devices that may start to appear in the next three to five years. "We take our experience of the last five years—which is about as much as anyone has had in building commercial nanowire synthesis equipment—and try to brainstorm ways to get the results the university groups have shown with processes that are scalable," says Lim. This apparently involves taking an atomic layer deposition (ALD)-type process to new levels of faster switching between precursors, and replacing metal-organic (MO) CVD bubblers with other ways to deliver more precisely controlled liquid precursors for growing III-V type materials. "You can't just use the conventional semiconductor fab tools, you really have to think outside of the box and come up with something different," he notes. "This next generation of control is really complicated, but the scientific discovery was the hardest part. Now it is just a lot of innovative engineering, though it will take time and money." First applications, he figures from what he sees at users, are likely to be for flexible circuits, in printed or low power devices, and for military applications, where the particular benefits of the nanowires can justify the high development costs.



Source: Atomate Corp.

ZnO array grown by Atomate's low pressure CVD tool.

Nanosys is close to commercialization of its first product using its vapor-grown nanowires: a plate for mass spectrometers that uses the large surface area of a dense array of nanowires to increase sensitivity. The Palo Alto, CA, company says it's now contracting for distribution of the plate, which plugs in to existing instruments and enables faster analysis of small molecules in complex samples of bio fluids directly—without need for sample preparation—for efficient drug development, or rapid drug detection directly from urine.

In a far more significant market, CFO Pete Garcia reports that in early 2007 the company will identify the first specific target product—perhaps large displays or displays for cell phones—for its development of LCD backplanes with Sharp, as the joint effort progresses into its second of two years. The process of growing the nanowires is fairly well established, and "we've made a lot of progress on assembly," says Garcia. "Now the next step is integration." Initial applications will be for rigid displays, though the process should be extendable to flexible substrates, as the high temperature growth steps are done before the wires are flowed on to the actual product substrate.

Nanosys' work on nonvolatile memory with Intel and Micron aims to replace Flash in the 35 nm generation, aiming at ultra high density storage for memory-intensive applications like video, potentially within two to three years. Though the company's initial efforts in solar cells didn't turn out to be cost effective, Garcia notes that the solar technology developed did conveniently turn out to be very similar to what is now being used in the memory devices.

The strategy is to supply the nanostructures in dispersion for the backplanes or memory chips. And even with the intense cost pressures in the Flash memory and display markets, Garcia argues the nano products should be cost competitive with more conventional alternatives. "It's scalable, analogous to chemical processing," he points out. "and even for memory, the amounts of nanostructures needed would only be in kilograms."

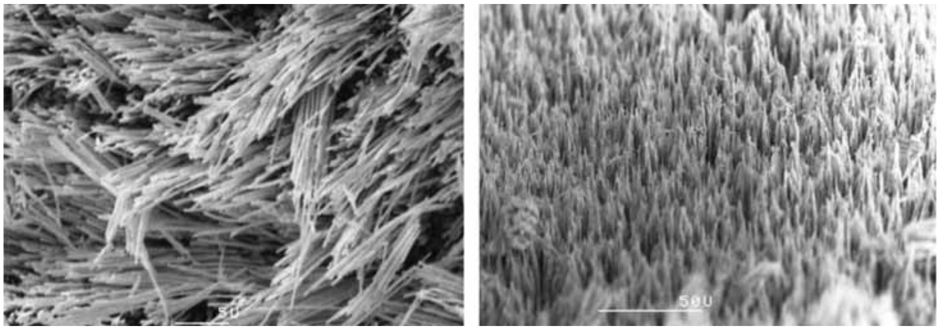
Nanosys is also working with Sharp on a better membrane for fuel cells that allows more electrons to pass through, and uses less catalyst, for methanol cells for portable electronics; with NTT DoCoMo on wireless communications technology; and says it is about to announce some other new applications. "2007 is a key year for us to move in to real development and commercialization," says Garcia.

Start-up Nanosens in the Netherlands is supplying its chips with etched arrays of

continued on page 2

Nanowire Applications and Production Methods

SALES *continued from page 1*



Source: Illuminex

50-micron long copper nanowires grown electrochemically by Illuminex for thermal management.

nanowires in a variety of materials in volume to its research partners, and says it will also soon start taking small orders from other labs. It etches out 20–500 parallel wires on its chips, in diameters of 5–50 nm and lengths of 1 to 1000 microns. Nanosens is working with several companies and universities to develop sensors based on these nanowire arrays, from hydrogen and environmental gas sensors to those for cancer diagnosis. Co-founder Hien Duy Tong points out his company's wire arrays are ready to use in research projects—and are inexpensive. The scalable semiconductor processes bring production costs down to less than $1 for a chip with an array of 100 individually addressed gold (Au) nanowires, or considerably less in volume production. "Actually we've come to the point where the main nanowire chip costs are from manpower and the silicon substrate," says Tong. He says yields are close to 85%–90%, and the electrical properties of the metal nanowires match or exceed those reported by other research groups, though the properties of the semiconductor wires are limited by the properties of the initial substrates.

The high surface area of the nanowires means a single molecule binding to the wire can change its electrical properties, potentially allowing highly sensitive and fast acting sensors. Several groups have demonstrated prototypes of hydrogen sensors based on palladium (Pd) wires made with various process technologies. Others have sensitized silicon wires with receptor groups that bind to target molecules to demonstrate detection of pH, DNA sequences, protein markers of cancer and other diseases, and single influenza viruses.

Illuminex, somewhat to its surprise, is selling its metallic and silicon nanowire arrays on glass substrates to university and commercial research labs for their own R&D work. But the Lancaster, PA, company is really focused on commercializing devices enabled using nanowires. The product closest to commercialization provides better heat management devices for temperature regulation in high performance computer chips. Working with Thermacore, Illuminex is using nanowires to improve heat pipe performance. Illuminex produces nanowires using electrochemical processes, with a wet chemical process that could be cheaper and more scalable than vapor deposition, and can conveniently leave the vertically aligned wires with one end attached to the substrate (similar to bristles on a toothbrush), as grown, for its applications. "We're getting very good data," says CEO Youssef (Joe) Habib. "If we can develop the mass production technology we're looking at commercialization sometime next year." In a heat pipe, the tight packing of the wires in the array provides high capillary pressure to promote fluid flow through the wick, while the aligned array arrangement provides a clear path for the vapor to escape, increasing the fluid flow and cutting thermal resistance by 30 percent or better at heat fluxes of 150–300 W/cm^2.

Illuminex is also working on a sensor for detecting ovarian cancer markers and other bio-molecules indicative of disease. The company grows metallic nanowires directly on the tip of an optical fiber probe, again using the electrochemical process, and attaches antibodies or nucleic acids to the wires to bind to target proteins or genes. Binding molecules changes the highly light absorbent nanowires' optical properties, so the target material can be identified by optical spectroscopy. Habib figures the technology is about a year away from prototyping, and is seeking to partner with a large medical diagnostic company to bring the sensor to market. The company is also developing nanowire-based solar cells that can be incorporated into fabrics.

Bio-assembled nanowires may also be within a few years of actual commercial use. Cambrios' nanowire transparent conductor film is being alpha tested at display makers as a replacement for ITO. And Angela Belcher reports her lab at MIT has made a thin film battery anode with two times to two and one half times higher energy density than current electrode materials, using a coating of wires of cobalt oxide and gold assembled on viral templates. Currently the thin film electrolyte and anode are attached to a conventional cathode, while researchers work on developing viruses that can grow the trickier three-material cathode. Still, Belcher projected the current proof of concept work could lead to a working thin film battery prototype in two years or so.

Also using wet chemical deposition, and leaving the upright wires on the substrate as grown, is Enable IPC. The Valencia, CA, company uses an alumina template to grow an array of vertical metal nanowires on the surface of a battery cathode to increase its surface area, to develop a thin film micro battery with higher energy density. It claims the growth method should allow scalable low-cost production. •

continued on page 3

Nanowire Applications and Production Methods

continued from page 2

Researchers Make Good Progress Controlling Nanowire Growth, with Multiple Technologies

Researchers are making impressive progress in growing nanowires with precisely controlled properties—with all sorts of different technologies. This better control could give nanowires an edge over carbon nanotubes in some of the same early applications like sensors and transparent conductive films. But early commercial applications are likely to use nanowires made by a wide range of technologies, ranging from conventional vapor deposition and electrochemical deposition to surfactant templates and biological assembly.

Vapor deposition work by groups at Harvard, Berkeley, CalTech and Lund universities, licensed by start-ups like Nanosys and QuNano, has demonstrated remarkable control of the structure and properties of semiconductor nanowires, suggesting it's likely to eventually be the technology of choice for advanced electronics applications. Companies are working on flexible circuits, Flash memory, sensors, display backplanes, and brighter LEDs using the vapor-deposited wires.

The vapor-liquid-solid deposition process, a variant of chemical or physical deposition, uses nano clusters of metal, often gold, as nucleation points to catalyze growth of nanowires. A feed gas, typically silane for growing silicon, condenses on the catalyst and the two mix into a liquid. As more gas condenses, the liquid becomes supersaturated, and a solid wire grows from the seed, directed by the substrate crystal order. With some substrate engineering, the wires can be grown vertically. Switching between precursors creates layers of different materials on the wire. Researchers can now grow single crystalline nanowires from about a third of the elements in the periodic table, and can control diameter by the size of the catalyst, and length by growth time. They can do both n- and p-type doping of silicon (Si), germanium (Ge) and gallium nitride (GaN) nanowires with boron (B) and phosphorous (P) bearing compounds to control the electrical properties. They can grow wires with different materials for the core and outer shells, and wires of stacked sections of different materials, such Si and Ge, or indium arsenide (InAs) and indium phosphide (InP).

Placing and connecting these wires on the wafer still remains, however, a rather rougher process. Though some work has grown wires horizontally by putting the catalyst on the sides of supporting structures, far more typical is to shake the wires off the substrate with sound waves and disperse them in solution, then use fluid flow to coat a new substrate with a monolayer of the wires all aligned in parallel. This coating of parallel nanowires can then be exposed and etched into strips of the desired pattern, and these pattern strips of wires topped with metal interconnects. Enough of the nanowires usually stretch all the way across the pattern to make a workable connection, but yields are typically problematic. Another layer of nanowires can be laid down perpendicular to the first, to make a crossbar system.

Others are working on extending somewhat more conventional semiconductor approaches to lift off or etch out the nanowire patterns. Hewlett Packard uses nano imprinting and a liftoff process to make its crossbar interconnects, using nanoimprinting to cut the nanowire lines through the resist, applying a platinum or platinum/titanium coating, then lifting off the metal when stripping the resist everywhere but in the cut-through lines.

The Netherlands startup Nanosens pushes the dry etching process, using rotation and different etch angles and recipes, to pattern continuous wires as small as 5 nm from metal or oxide thin films on the wafer surface. To make semiconductor nanowires it uses an initial set of metal wires as a mask to etch the silicon or other substrate to the same dimensions, then removes the mask to leave nanowires of semiconductor material. Recent work extends the process to most any material that can be deposited as a thin film and dry etched. Macro contact electrodes are added at each end of the wires by conventional microlithography.

Meanwhile, other researchers at MIT and the University of Washington, and at start-ups like Illuminex and Enable IPC, are using potentially lower-cost wet chemical or electrochemical baths to grow metal nanowires. These batch solution processes may well be some of the first to be commercialized, in relatively simpler applications such as sensors, semiconductor heat pipes, and batteries. One variant of this approach anodizes porous alumina with weak acid to make a template of cylindrical channels; fills the pores by melt injection or electrochemical deposition; then dissolves away the structure to leave an array of vertical metal nanowires. Others skip the hard template to use what is essentially a template of surfactant instead, using the attraction and repulsion characteristics of molecular clusters of poly vinyl pyrrolidone or sodium dodeclysulfonate to direct metal growth from nanoparticle catalysts into wires.

Also a serious contender for some of the initial applications for nanowires, like transparent conductive films, sensors and thin film batteries, is biologic assembly, championed by players like MIT and start-up Cambrios. Angela Belcher reports her lab at MIT, in conjunction with colleagues Paula Hammond and Yet-Ming Chiang, has gotten better at making bigger changes in virus DNA, engineering viruses that can now evenly coat themselves with an orderly arrangement of inorganic material all along their long, thin bodies to build nanowires, and can even do so with two different materials at once. "New genetic engineering in the last year now allows alloys," said Belcher. Growing long skinny viruses that attach themselves in a dense monolayer to just about any desired material turns to be quite easy. "We have high school students do it, or visiting physicists, and we teach it in our undergraduate labs," she said.

continued on page 4

Nanowire Applications and Production Methods

NANOWIRE GROWTH *continued from page 3*

They pick a group of likely viruses from libraries developed by the drug industry, expose the viruses to the desired material to find ones that stick, wash off all those that don't, feed the few that do into bacteria to grow a new generation, and repeat the processes. It typically takes about five rounds to get an organism that attaches stably to the desired metal, insulator, or semiconductor, and which can then be engineered to coat itself with the desired wire material. A densely packed monolayer of crystalline nanowires can be made by simply coating the substrate with a solution of the viruses, and then with a solution containing the desired wire material.

"In my opinion," says Co-founder Hien Duy Tong, "the big breakthrough for nanowire technology is that it is recently getting considerable attention from leading research groups and companies around the world, and people who come from different sectors, with really different backgrounds, will push this technology forward." •

Multi-layered Nanowires Ease Manufacture of Transistors on the Wafer

Being able to make complex layered nanowires helps in the more complicated business of making volumes of transistors from these nanowires—by essentially moving more of the complicated processing over to the production of the wires themselves. Researchers are producing working field effect transistors (FET) by using nano structured multi-layered wires in the thin film that serves as the active channel, and by growing the gate directly around each nanowire to make arrays of vertical transistors.

Peidong Yang's group at UC Berkeley recently demonstrated working FETs made by growing surrounding gates directly around the Si nanowires in the vertical array, and topping them with metal contacts, using conventional semiconductor processes. These initial first generation un-optimized vertical devices showed transport properties similar to standard planar MOSFETS and other nanowire-based devices. Researchers say optimization could likely make them competitive with FINFETs at 10 nm.

To make these arrays of FETs, with the vertical Si nanowire cores as the active channels, researchers start by using fluid flow to lay down parallel rows of nanoparticles of metal catalyst across the wafer, then use silicon tetrachloride ($SiCl_4$) as the precursor and boron tribromide (BBr_3) as the dopant source to grow rows of upright Si nanowires. They coat the substrate and each wire with a thin layer of silicon dioxide (SiO_2) dielectric by thermal oxidation, then sputter on a coating of chromium (Cr) gate metal, and add another layer of SiO_2 dielectric with low pressure CVD. The dielectric and Cr are then removed to expose the Cr and the Si wire tips where needed, by standard photolithography, chemical mechanical planarization (CMP) and plasma etching, and metal contacts sputtered on to form the drain electrode above, and the source below. A bundle of somewhere between ~10–250 nanowires are attached to each contact pad.

Charles Lieber's group at Harvard is also making high speed FETs from its patterned coatings of nanowires, thanks to putting multiple layers of different materials in the nanowires themselves for the active channel. Researchers first introduce germane (GeH_4) to grow an array of Ge nanowires from gold nano cluster catalysts, then switch to silane (SiH_4) to coat them with a Si shell. A solution of the wires is then coated on a wafer in an aligned monolayer by fluid flow. The film of horizontal parallel wires is patterned and topped with electrodes by conventional semiconductor processes. They recently demonstrated a FET, with the Si/Ge channel under a high-κ dielectric and a gold gate, with transconductance and on-current values three times to four times greater than state-of-the-art MOSFETs, and hole mobility 10 times greater than a Si p-MOSFET with a hafnium oxide (HfO_2) gate dielectric. •