

## Lithography Process

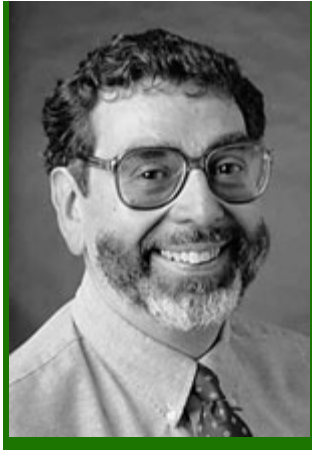
**W**hen the ion implanter facility at Oak Ridge National Laboratory closed, the Vanderbilt researchers had to come up with another method for making vanadium dioxide nanocrystals. They turned to a basic technique that has been used with great success in the semiconductor industry: lithography.

Lithographic techniques have been used in the microelectronics industry with great success. In the 1960's, silicon foundries began making the first integrated circuits with photolithography. In this technique, a silicon wafer is coated first with a sticky polymer, called a photoresist. Photoresists come in two flavors: negative, which hardens when exposed to light, and positive, which softens when exposed to light. When using a positive photoresist, a photographic "positive" of the circuit design is created and light is shown through the film onto the polymer layer, softening it in a predefined pattern. Next, the wafer is dunked in a chemical solution that dissolves the soft, exposed polymer and etches away the material below while the hardened polymer protects the rest of the chip's surface. The photoresist is then removed with a special solvent, leaving a complex surface that can be coated with another layer of semiconducting material. Typical integrated circuits contain dozens of such layers.

While the wavelength of light is small enough to make micron-sized features, it cannot be focused small enough to make nanometer-scale patterns. So scientists interested in nanoscience and technology use a variation of photolithography that uses a highly focused beam of ions or electrons, rather than photons, to create the exceptionally small patterns required. The Vanderbilt Institute for Nanoscale Science and Engineering (VINSE) obtained a focused ion beam writer and an ultra-high vacuum vapor deposition system designed specifically for nanoscale applications.

"The creation of new forms of materials on the nanoscale is a major enabler of new and exciting discoveries," says co-author Leonard Feldman, who directs VINSE.

## Nature's quickest change artist



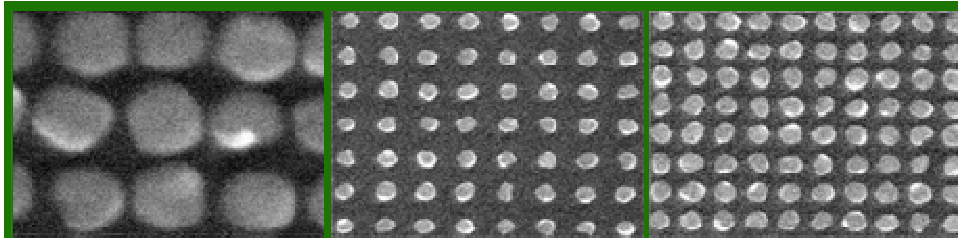
Leonard Feldman

So the Haglund group began experimenting with these new tools to see if they could make vanadium dioxide nanocrystals. They finally figured out how to do it, but it took them more than a year to do so.

The process the Vanderbilt researchers developed begins with a glass plate covered with the transparent conducting material indium-tin oxide (ITO). First, the substrate is coated with a thin, 60-nanometer layer of a positive resist, polymethyl methacrylate (PMMA). The focused ion beam (FIB) writer can be programmed to create complex patterns, so they set it to paint the surface with a pattern of closely spaced dots. After the FIB writer follows this pattern, washing the surface with alcohol dissolves the exposed PMMA, leaving a surface pock-marked with a regular array of tiny pits.

Next, the researchers move the plate from the FIB to the vapor deposition system, where they cover the partially masked surface with a thin layer of vanadium and oxygen atoms in a ratio of 85 oxygen atoms for every 50 vanadium atoms, slightly less than two to one. The sample is then removed from the deposition chamber and dunked in a tray filled with a solvent that removes the remaining PMMA, along with the portion of the vanadium oxide layer attached to it. This produces a surface covered by millions of tiny vanadium oxide bumps.

The final stage is to put the sample in an oven where it is annealed for 30 minutes at 450 degrees Celsius (840 degrees Fahrenheit). The heat causes the vanadium and oxygen to combine into vanadium dioxide crystals, pulling the extra oxygen atoms needed from the ITO layer.



Courtesy of Richard Haglund

Examples of vanadium dioxide nanocrystal arrays produced by the Vanderbilt group using FIB lithography.

This approach lets the researchers create nanocrystal arrays with a wide variety of crystal sizes, spacings and patterns. "As a result, we can tailor a sample to give us access to a variety of different properties of the vanadium dioxide," says Haglund. It has created several new avenues of research that they are just beginning to explore. For example, just arranging nanocrystal in regular arrays produces samples which exhibit optical coherence effects that reveal details of the transition from metallic to insulating phases of the vanadium dioxide.