"STRUCTURAL PHASE TRANSITIONS IN NANOCRYSTALLINE METAL OXIDES"

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R. F. HAGLUND, JR.,[1] L. C. FELDMAN,[1] C. M. LUKEHART[1] AND M. AZIZ[2]
[1]Vanderbilt University, Nashville, TN 37235
[2]Harvard University, Cambridge, MA 02138

MOTIVATION AND OBJECTIVE

It has been known for decades that vanadium dioxide (VO_2) thin films exhibit reversible switching behavior, changing from semiconducting to metallic at a temperature of about 70˚C, and reverting to a semiconductor when cooled to around 40˚C. This change is accompanied by a structural transition from monoclinic semiconductor to the tetragonal metallic structure, accompanied by a hundred-thousand-fold increase in electrical conductivity and similarly striking changes in the optical transmission. Our objective in this NIRT research program is to understand the nanoscale origins of this and similar phase transitions in a variety of model oxides, and to demonstrate possible enabling applications to technology.

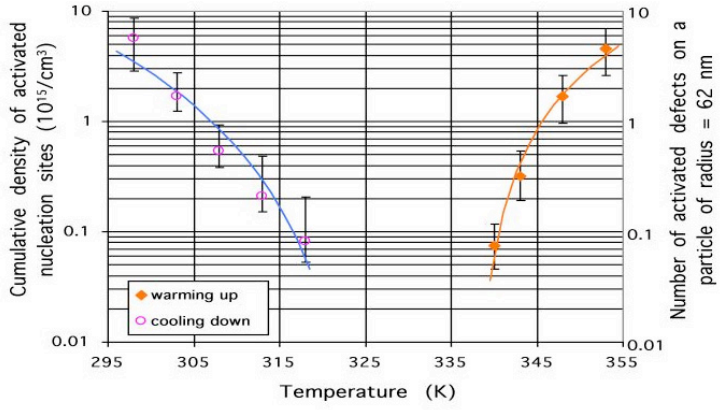

Figure 1. Density of activated sites for the structural phase transition of VO_2 nanocrystals as a function of absolute temperature, during the cooling (metal to semiconductor) and warming cycles (semiconductor to metal). From Ref. [1].

Shortly before beginning this project, we mapped the kinetics of the nanophase semiconductor-to-metal (SMT) in VO_2 as a function of size by measuring changes in optical properties during heating and cooling cycles.[1] Figure 1 shows, for example, that during the heating cycle, a 60 nm diameter VO_2 nanocrystal, which has on average one nucleation site, will change from semiconducting to metallic at 72˚C.

This behavior has potential applications ranging from optical limiting to non-volatile memories and optically triggerable sensors. For example, we have demonstrated that a thin layer of VO_2 nanorods inside an optical fiber exhibits strong switching action with even more pronounced hysteretic behavior than thin films.[2] When a near-infrared laser (1.5 μm) was focused through the fiber, with a heating element and a thermocouple attached near the nc-VO_2, the hysteretic signature of the phase transition was observed. As the temperature was raised, optical transmission remained high until the transition temperature was reached; as the nanocrystals became metallic upon heating, the transmission dropped abruptly as the layer of VO_2 nanocrystals reflected the incident light. As the optical fiber cooled, the transmission remained low until near 40˚C, where the material became semiconducting and transparent.

RESEARCH ACTIVITIES AND FINDINGS — AUGUST 2002-DECEMBER 2003

During this period, we have focused our research activities on three major technical challenges relating to synthesis and patterned growth of nanocrystalline VO_2 and V_2O_3; ultrafast dynamics of the phase transition in nanoparticles; and optical microscopy of nanocrystalline VO_2.

New synthesis techniques for preparing embedded nanocrystals. Our previous studies of nanocrystalline VO_2 were made possible by implanting V and O ions in a stoichiometric mixture in silica glass, then annealing to induce nucleation and growth in a thin layer near the surface of the silica. While this was especially useful for making prototype nanocrystals, ion implantation can only be used to prepare nanocomposite samples embedded in solid matrices.

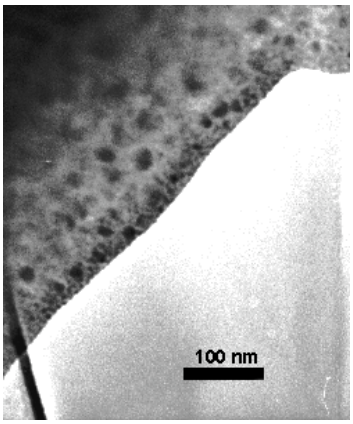

Figure 2. V_2O_3 nanocrystallites in a silica xerogel.

We are investigating both chemical and physical methods for synthesizing nc-oxides in transparent matrices. Lisa Sullivan, a graduate student in the laboratory of Professor Lukehart, has produced V_2O_3 nanocrystals in a silica matrix by a xerogel process. A transmission electron microscope picture is shown at left; analysis indicates that the nanoparticles have quite uniform sizes in the 20 nm range. The crystallinity of the nanoparticles is excellent, as confirmed by X-ray diffraction studies. These samples will be used in the high-pressure Raman and infrared measurements planned for the new diamond anvil cell (Aziz, Harvard), as well as for near-field microscopy. The xerogel technique, first used to make nc-Ge as a calibration standard, is now also being used to produce nc-$BaTiO_3$.

Focused ion-beam lithography. Because we particularly wish to generate arrays of metal-oxide nanocrystals for scanning near-field microscopy and to study interactions between nanoparticles, we have used lithography followed by pulsed laser deposition of the oxide. The focused ion beam (FIB) is particularly well-suited for lithography; the beam width is only 10 nm, and the straggling in a photoresist is substantially less than one finds in electron-beam lithography. Moreover, the FIB can be programmed pixel by pixel so that arbitrary patterns can be produced.[3] The scanning electron micrograph in Fig. 3 shows a section of a large array of nc-VO_2 disks prepared by focused ion beam lithography of PMMA resist on indium-tin oxide (ITO), following which VO_2 was deposited by pulsed laser deposition. The stoichiometry of the nanodisks was confirmed by Rutherford backscattering analysis. Such samples can be used for long path-length interaction studies in waveguide geometries.

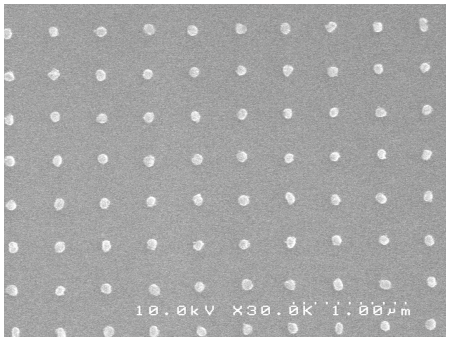

Figure 3. VO_2 nanoparticle array prepared by focused ion-beam lithography and pulsed laser deposition.

Microscopy and spectroscopy of VO_2. We are studying the phase transition in single nanoparticles of VO_2 using a scanning near-field optical microscope (SNOM); the first images were submitted with our annual project report in June 2003. We have also discovered that the integrated confocal microscope in our SNOM is exceedingly useful for studying the nc-VO_2 arrays. Figure 4 shows confocal microscope images of arrays with varying interparticle spacing.

Figure 4. Confocal microscope image of nc-VO_2 arrays ordered by increasing interparticle spacing.

A central unanswered questions about the structural semiconductor-to-metal (SMT) transition in vanadium dioxide is, how fast does it occur? Several groups have measured the transition in thin films using ultrafast laser and X-ray techniques; the phase transition in this case is initiated by a pump pulse that is strongly absorbed by the VO_2, creating dense electronic excitation. So far, there is agreement only that the transition occurs on a sub-picosecond time scale.

We have used femtosecond white-light continuum spectroscopy to see more clearly the temporal signature of the extremely broad surface plasmon resonance (SPR) at 1.2 μm. The probe beam, tightly focused into a thin silica plate, produces a continuous spectrum of light coherent with the pump beam; the pump beam heats the sample, generating the semiconductor-to-metal transition. We recently carried out the measurement shown in Figure 5 on a thin-film sample to demonstrate the application of the technique. The spectrum of the probe light, generated by focusing the light into an IR filter-glass plate, is nearly constant over the range 400-800 nm. Figure 5 shows the two-dimensional spectrum of sample transmission *vs* probe wavelength and pump-probe delay time. The advantage of displaying the data in this way is that one sees immediately the incipient plasmon response near 800 nm, whereas there is little change in the probe signal for wavelengths in the visible portion of the spectrum away from the SPR. Hence this spectroscopic technique is specific for the SMT in a way that ordinary pump-probe measurements might not necessarily be. The semiconductor-to-metal transition occurs on a time scale much shorter than 1 ps.

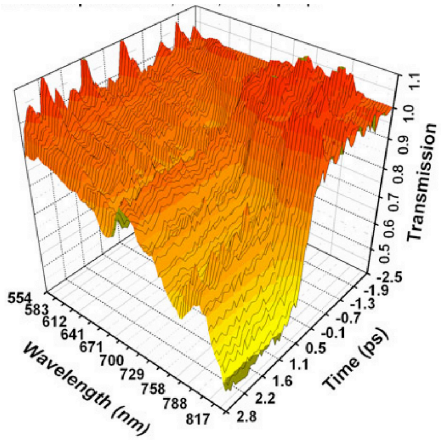

Figure 5. White-light continuum pump-probe measurement of the evolution of the surface plasmon resonance in VO_2/

Near-Term Activities and Directions

With fabrication techniques for nanocrystals increasingly well in hand, the near-term focus is on optical characterization experiments. High-pressure Raman experiments are underway at Harvard, with xerogels from Professor Lukehart's laboratory. Recently, we have begun to compare the third-order nonlinear response of VO_2 in thin-film and nanocrystalline forms using the Z-scan to generate simultaneous information on the nonlinear absorption and nonlinear dispersion. As in measurements of the second-harmonic signal reported in June 2003, we find that there is a clear distinction between the third-order nonlinear response of thin-film VO_2 *vs* nanocrystalline VO_2 . Specifically, the sign of the nonlinear index of refraction is positive for the nanocrystals, but negative for the thin films, probably indicating a different mechanism for the metal-insulator transition. We have also developed a novel concept for ultrafast optical switches and transistor structures based on nc-VO_2 that has been fabricated and is now being tested.

References

1 "Size effects in the structural phase transition of VO_2 nanoparticles," R. Lopez, T. E. Haynes, L. A. Boatner, L. C. Feldman and R. F. Haglund, Jr., *Physical Review B* **65**, 224113 (2002).

2 "Temperature-controlled surface plasmon resonance in VO_2 nanorods," R. Lopez, T. E. Haynes, L. A. Boatner, L. C. Feldman and R. F. Haglund, Jr., *Optics Letters* **27**, 1327 (2002).

3 For example, a 2.3x2.3μm replica of Picasso's pen-and-ink drawing of *Don Quixote* in VO_2 was produced by this same technique, and submitted earlier as a "Nugget" to the Division of Materials Research. The smallest feature size on this replica was less than 40 nm across.