

Note: This is a draft of a paper submitted for publication. Contents of this paper should not be quoted or referred to without permission of the author(s).

Submitted to:
CLEO/QELS 2002
Long Beach, California
May 19-24, 2002

**Optical Spectroscopy of the Structural Phase Transition of VO₂
Nanocrystals in Optical Fibers and Thin Films**

R. Lopez, ^a L. A. Boatner, ^a T. E. Haynes, ^a L. C. Feldman, ^b and R. F. Haglund, Jr. ^b

^a Solid State Division

Oak Ridge National Laboratory

P. O. Box 2008, MS-6056

Oak Ridge, TN 37831-6056, USA

^b Department of Physics and Astronomy

Vanderbilt University

Nashville, TN 37235

November 20, 2001

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

Prepared by the
SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Managed by
UT-BATTELLE, LLC, for the
U.S. DEPARTMENT OF ENERGY
Under Contract No. DE-AC05-00OR22725

Optical Spectroscopy of the Structural Phase Transition of VO₂ Nanocrystals in Optical Fibers and Thin Films:

R. Lopez, L. A. Boatner, and T. E. Haynes

Solid State Division, Oak Ridge National Laboratory Oak Ridge TN

L. C. Feldman and R. F. Haglund, Jr.

Department of Physics and Astronomy, Vanderbilt University, Nashville TN 37235
Telephone 615-322-2828, Fax 615-343-7263, e-mail richard.haglund@vanderbilt.edu

Abstract: The optical spectroscopy of VO₂ nanocrystals in planar and fiber-waveguide geometries shows a size- and doping-dependent structural semiconductor-to-metal phase transition and a shape-dependent surface plasmon resonance, with unusual linear and nonlinear applications possibilities.

0200 Optical Society of America

OCIS codes: (310.1860) Deposition and fabrication

Vanadium dioxide exhibits a semiconductor-to-metal phase transition near $T_c \sim 67^\circ\text{C}$ that is due to a change from the monoclinic low-temperature form to a tetragonal rutile structure at higher temperatures. Here we report the detailed exploration of the size- and shape-dependent optical properties of VO₂ nanocrystals prepared in both planar, thin-film configurations and in optical fibers, and we describe a variety of possible applications.

We have employed the stoichiometric ion implantation into a fused SiO₂ layer on crystalline Si or into the end of a silica optical fiber to synthesize assemblies of isolated crystalline VO₂ nanoparticles [1] that reveal the heterogeneous nature of the nucleation process for the VO₂ structural phase transition. Vanadium and oxygen ions were implanted in the near-surface region in stoichiometric proportion and at equal depths; high-temperature annealing (1000 °C) in an argon atmosphere induced the precipitation of VO₂ nanocrystals whose size was controlled by limiting the growth time in the furnace from two to sixty minutes. The initial faceted nanocrystals grow with increased annealing times into elongated bars with typical widths of ~50 nm and aspect ratios as large as 1:4. The process produces an altered layer some 200 nm thick whose centroid is approximately 150 nm below the surface.

The linear optical response at wavelengths near the optical communications wavelength of 1.5 μm shows a wide, size-dependent hysteretic response, which has a width in temperature of almost 40°C and an optical transmission that decreases from a relative value of 1 in the semiconducting state to 0.65 in the metallic phase. The size dependence of the hysteresis has been used to model the nucleation mechanism that initiates the phase transition [2]. The hysteresis loop, is almost an order of magnitude wider in temperature than that typically observed in VO₂ thin films, confirming the importance of the size effects. The surface plasmon resonance shows the expected red shift and broadening in the plasmon wavelength with increasing aspect ratio. In fact, the plasmon resonance in this case enhances the optical switching induced by the phase transition in the communication wavelength band, in contrast to the behavior of conventional VO₂ thin films where the maximum switching occurs closer to 3 μm.

The hysteretic response in the optical transmission could represent the basis for a number of "smart-materials" applications, including optical switching, holographic memory, and optical limiting. These applications could be facilitated by appropriate doping of the material. Doping with either Ti or W ions can change both the width of the hysteresis loop in the optical transmission, and move the transition temperature for the semiconductor-to-metal phase transition. Indeed, with tungsten doping it is possible to move the transition even below room temperature. This possibility is particularly intriguing for applications to optical limiters.

1. R. Lopez, L. A. Boatner, T. E. Haynes, L. C. Feldman and R. F. Haglund, Jr., "Enhanced hysteresis in the semiconductor-to-metal phase transition of VO₂ precipitates formed in fused silica by ion implantation," *Appl. Phys. Lett.* 79, 3161-3163 (2001).
2. R. Lopez, L. A. Boatner, L. C. Feldman, R. F. Haglund, Jr. and T. E. Haynes, "Size Dependence of the Phase Transition in Vanadium Dioxide Nanocrystals," submitted to *Physical Review Letters* (2001).