Femtosecond laser excitation of the semiconductor-metal phase transition in VO2

Michael F. Becker, A. Bruce Buckman, Rodger M. Walser, Thierry Lépine, Patrick Georges, Alain Brun

Femtosecond laser excitation of the semiconductor-metal phase transition in VO_2

Michael F. Becker, A. Bruce Buckman, and Rodger M. Walser
Laboratory for Smart Materials and Devices, Department of Electrical and Computer Engineering, The University of Texas at Austin, Austin, Texas 78712

Thierry Lépine, Patrick Georges, and Alain Brun
Institut d'Optique Théorique et Appliquée, Unité de Recherche Associée au CNRS No. 14, Université Paris-Sud, B.P. 147, 91403 Orsay Cedex, France

(Received 27 May 1994; accepted for publication 18 July 1994)

We have measured the subpicosecond optical response of a solid-state, semiconductor-to-metal phase transition excited by femtosecond laser pulses. We have determined the dynamic response of the complex refractive index of VO_2 thin films by making pump-probe optical transmission and reflection measurements at 780 nm. The phase transition was found to be largely prompt with the optical properties of the high-temperature metallic state being attained within 5 ps. The ultrafast change in complex refractive index enables ultrafast optical switching devices in VO_2.

The dynamics of solid-state phase transitions are amenable to study by ultrashort pulsed lasers. Ultrafast optical techniques effectively probe the cooperative structural change in the time domain in order to study precursors, soft modes, metastable states, and post-transition relaxations. We have employed femtosecond laser pump-probe techniques to investigate the dynamics of the solid-state phase transition in VO_2 near 68 °C. This is the first time that any phase transition incorporating both a lattice type (symmetry) change and an electronic band change (semiconductor to metal) has been studied on a femtosecond time scale. Femtosecond laser pulses have previously been used to probe the dynamics of solid-state phase transitions in the ferroelectric materials $PbTiO_3$,[1] $KNbO_3$, and $BaTiO_3$.[2] In that case, there was a lattice symmetry change, but the transition was from a nonconducting ferroelectric low-temperature phase to a similarly nonconducting paraelectric phase. In another study of solids, the purely electronic Mott transition in CuCl had been investigated using femtosecond laser pulses.[3]

The first attempt to measure the switching speed of the optically induced phase transition in VO_2 was made by Roach and Balberg[4] exciting with 20 ns ruby laser pulses at 694 nm and probing with a cw HeNe laser. They found the transition to be faster than their experimental resolution. Subsequently, Becker[5] and Walser[6] conducted the first pump-probe measurements on the VO_2 phase transition using 30 ps pulses from a mode-locked Nd:YAG laser, exciting and probing at 1064 nm. Again, the transition was abrupt and proved to be faster than the experimental resolution. Other experiments in which VO_2 films were excited with picosecond pulses at 532 and 1064 nm did not always show an abrupt transition to the metallic state.[7,8] In some cases an intermediate state was observed. However in all the cases where an abrupt transition was observed, the speed was faster than the experimental resolution dictated by 25–30 ps pulses. The important measurement of the switching time for the phase transition had not yet been made and was a motivation for our work.

In the experiments reported here, we have measured the subpicosecond response of the optical parameters of VO_2 thin films for laser excitation through the first-order phase transition. Femtosecond laser excitation at 780 nm for an amplified, self-mode-locked Ti:sapphire laser was used in a pump-probe configuration to excite the VO_2 film through the phase transition, from the low-temperature equilibrium state, a semiconductor with a monoclinic unit cell, to the high-temperature state, a metal with a rutile unit cell. The transient optical reflection and transmission were measured on a femtosecond and picosecond time scale by a delayed probe pulse at 780 nm. The slower behavior for nanosecond and longer times was measured using a cw HeNe laser at 633 nm and a fast photodiode ($\tau_{rise} \approx 1$ ns). We have transformed the raw measurements of dynamic reflection and transmission to complex refractive index using a thin film model.

The VO_2 samples used in these experiments were fabricated by a new low-temperature process compatible with polymer substrates.[9] In summary, the process involved sputtering vanadium in an oxygen-hydrogen-argon plasma at a temperature <250 °C, followed by annealing in a static nitrogen atmosphere at a temperature ≥290 °C. The films were verified to be polycrystalline, stoichiometric VO_2 by TEM/TED (transmission electron microscopy/transmission electron diffraction) and x-ray analyses. The electrical resistivity versus temperature and optical transmission and reflection spectra were identical to those for conventionally processed VO_2 films. The films used in our experiments were all deposited on glass microscope slides. During the transient optical experiments, the film was held just below the phase transition onset temperature, at 40±1 °C, by an electrically heated and insulated substrate holder. The optical transmission and reflection spectra of the film are shown in Fig. 1 for both the cold (semiconducting) state at 20 °C and the hot (metallic) state at 90 °C. The film used in our experiments was 32 nm thick as determined by fitting the measured transmission and reflection of the semiconducting state versus wavelength from 500 to 2000 nm to that calculated by a homogeneous thin-film model using reported values for the complex permittivity of a VO_2 thin film.[10]

The optical setup used to conduct the pulse-probe measurements was relatively conventional.[11] The laser source

 0003-6951/94/65(12)/1507/3/$6.00

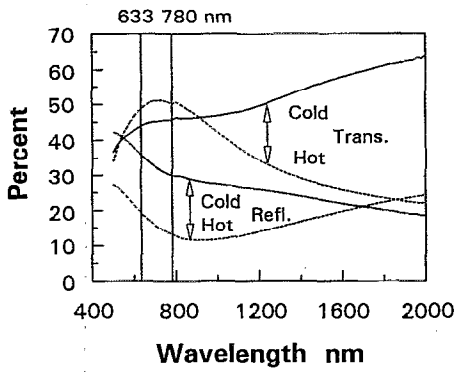

FIG. 1. VO_2 film transmission and reflection spectra for the cold (semiconducting) state at 20 °C and the hot (metallic) state at 90 °C. The vertical lines denote the cw probe wavelength of 633 nm and the pump-probe wavelength of 780 nm.

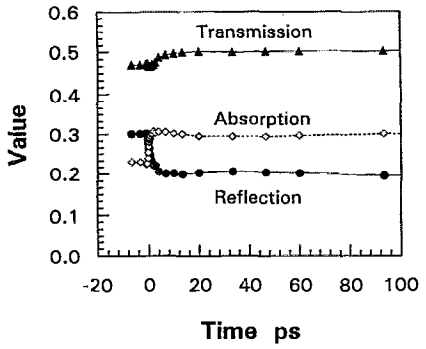

FIG. 2. Measured data for transmission and reflection for the VO_2 film vs time. Absorption was derived from this data as described in the text. The laser excitation fluence was 3.7 mJ/cm^2.

was a cw self-mode-locked Ti:sapphire laser at 780 nm wavelength with a regenerative amplifier operating at 20 Hz and a grating pulse compressor.[12,13] The pulse width was measured by background-free, sum-frequency generation to be in the range of 450–550 fs FWHM (assuming a sech^2 intensity profile). The femtosecond probe beam and the cw HeNe beam diameters at the sample plane were adjusted to be less than one-third of the pump beam diameter. Beam overlap and diameters at the sample plane were measured using a CCD camera. The pump beam average power at the sample was adjusted to be just sufficient to excite the complete phase transition. This resulted in a pump fluence of 3.7 mJ/cm^2 at the sample, in good agreement with the film temperature, heat capacity, and the latent heat of the phase transition. For each delay line position, both the desired peak voltage (reflection or transmission) and the peak reference voltage were measured using a digitizing oscilloscope. In addition, frequent measurements were taken with the pump beam blocked and used to correct for small changes in beam position as the delay was changed. Data for transmission and reflection were fit at large negative time delay to the transmission and reflection measured by the spectrometer at 780 nm. The resulting data is a record of transient transmission and reflection vs delay time from -7 to 400 ps.

The transient transmission and reflection of the VO_2 film is shown in Fig. 2. The absorption is also shown, and was calculated using absorption=(1-transmission-reflection). It was particularly instructive to present the data in this way because, at the phase transition, the decreased reflection loss and increased absorption almost cancel, resulting in only a small change in transmission. It is immediately apparent that the VO_2 film attains an optical state very close to the final state in less than 10 ps. The observed change at 400 ps was equal to the change observed when the sample was heated through the phase transition by static means. This was determined by heating the sample through the phase transition, with and without femtosecond excitation applied, while monitoring the nanosecond and static optical parameters with the cw HeNe laser. Thus, the final reflection and transmission state reached by pulsed laser excitation was identical to that reached by equilibrium heating.

Conversion of the data to a refractive index format was done using a thin-film model for the VO_2 film and substrate. A coherent reflection was assumed from the film-substrate interface, and an incoherent reflection was assumed for the substrate rear interface since the 500 fs pulse was shorter than the substrate thickness. A numerical solver routine was used to obtain a best-fit value of n and k for each delay time given the measured values of transmission and reflection. The entire data set for complex refractive index, $\tilde{n}=n-jk$, is shown in Fig. 3(a) while the time interval near zero delay is expanded in Fig. 3(b). In the latter, the asymptotic values for both n and k are shown as horizontal lines. The real part of the refractive index, n, was just over halfway to the metallic value by the end of the 500 fs excitation pulse. It then decreased more slowly to the steady-state value by 5 ps. On the other hand, the imaginary part of the refractive index k, was equal to the metallic value by the end of the excitation laser pulse and overshot by 36% at 7 ps. After smaller fluctuations, both n and k had reached their final values by 300 ps. If the laser energy was not in excess of that required for the phase transition, decay back to the low-temperature semiconducting state was observed on a nanosecond time scale consistent with heat conduction to the substrate.

For the interval from 0.5 to 15 ps in Fig. 3(a), both n and k are greater in magnitude than their corresponding equilibrium metallic values. This deviation could be explained by a plasma of both higher electron density and higher electron collision frequency than is present in the equilibrium metallic phase. The permittivity of VO_2 is assumed to be of the form of a constant contribution plus a contribution due to free carriers, which can be written as

$$\tilde{n}^2=\tilde{\epsilon}_m+\tilde{\epsilon}_{fc}=\tilde{\epsilon}_m+\epsilon_0\left(\frac{-Ne^2}{\epsilon_0 m^*(\nu^2+\omega^2)}-j\frac{Ne^2\nu}{\epsilon_0 m^*\omega(\theta^2+\omega^2)}\right), \tag{1}$$

where $\tilde{\epsilon}_m$ is the constant contribution in the metallic phase, $\tilde{\epsilon}_{fc}$ is the contribution of the free carrier plasma, N is the electron density, m^* is the electron effective mass, and ν is

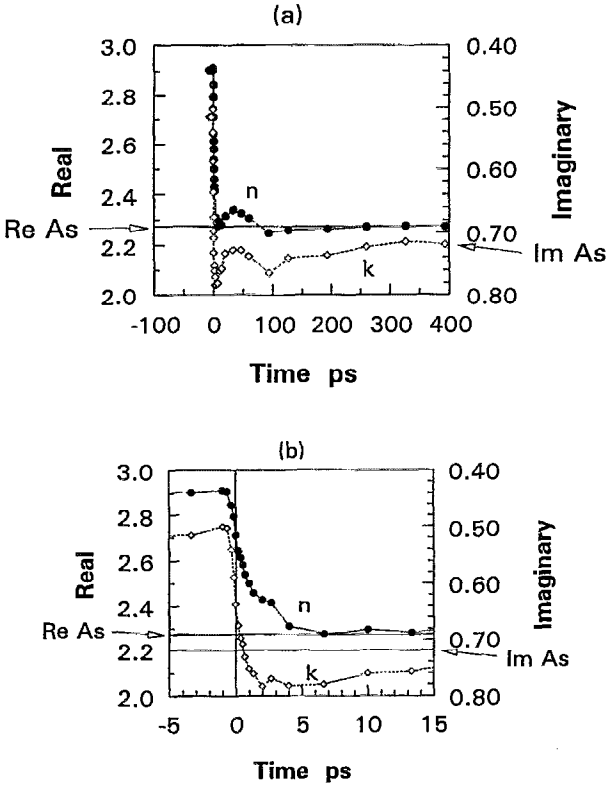

FIG. 3. Complex index of refraction for a VO_2 film vs time derived from the measured data in Fig. 2 for time scales: (a) -100 to 400 ps and (b) -5 to 15 ps. Note that the imaginary part of the refractive index, k, is plotted on the right-hand scale and that the direction of this scale is inverted. Arrows and horizontal lines denote the asymptotic values of n and k (determined at 400 ps).

the electron collision frequency. We plan to address the details of this plasma model in a forthcoming publication. We conclude that, if indeed the VO_2 state after 500 fs can be represented by its metallic phase plus a higher density electron plasma, then the transition to the metallic phase must have occurred during the interval of the pump phase. This then establishes an upper limit of roughly 500 fs for the switching time of the phase transition.

In generalizing the phase transition switching time results to the near IR and visible spectral regions, one can reasonably expect the VO_2 film to switch in less than a few picoseconds between the semiconducting and metallic transmission and reflection spectra shown in Fig. 1. Whether the same applies to the far-IR and microwave spectral regions depends on whether the VO_2 film truly has reached the high-temperature metallic phase in this short time. If so, then wide optical bandwidth, ultrafast switching devices incorporating VO_2 can be synthesized that take advantage of the rapid change in complex refractive index at the phase transition.

M. F. Becker acknowledges partial support from the University Research Institute at The University of Texas and from the University of Paris 11, Faculty of Physics. The VO_2 samples were fabricated under the sponsorship of the Energy Research in Applications Program of the Texas Higher Education Coordinating Board.

[1] D. P. Klein, J. C. Loulergue, and J. Etchepare, *Ultrafast Phenomena VIII*, edited by J.-L. Martin (Springer, New York, 1993), p. 368.
[2] T. P. Dougherty, G. P. Wiederrecht, K. A. Nelson, M. H. Garrett, H. P. Jensen, and C. Warde, Science **258**, 770 (1992).
[3] D. Hulin, A. Mysyrowicz, L. L. Chase, A. Antonetti, J. Etchepare, G. Grillon, and A. Migus, *Ultrafast Phenomena IV*, edited by D. H. Austin and K. B. Eisenthal (Springer, New York, 1984), p. 126.
[4] W. R. Roach and I. Balberg, Solid State Commun. **9**, 551 (1971).
[5] M. F. Becker, R. M. Walser, and R. W. Gunn, *Picosecond Phenomena*, edited by C. V. Shank, E. P. Ippen, and S. L. Shapiro (Springer, New York, 1978), p. 236.
[6] R. M. Walser and M. F. Becker, *Laser-Solid Interactions and Laser Processing—1978 MRS Conference*, edited by S. D. Ferris, H. J. Leamy, and J. M. Poate (AIP, New York, 1979), p. 117.
[7] A. A. Bugaev, V. V. Gudyalis, B. P. Zakharchenya, and F. A. Chudnovskii, JETP Lett. **34**, 430 (1982).
[8] A. A. Bugaev, V. V. Gudyalis, and A. V. Klochkov, Sov. Phys. Solid State **26**, 887 (1984).
[9] R. M. Walser, H. C. Joung, M. F. Becker, R. W. Bené, and A. B. Buckman, SPIE Symposium on Smart Structures and Materials '93, Albuquerque, NM (February 1993).
[10] H. W. Verleur, A. S. Barker, Jr., and C. N. Berglund, Phys. Rev. **172**, 788 (1968).
[11] M. F. Becker, A. B. Buckman, R. M. Walser, T. Lépine, P. Georges, and A. Brun, Proc. SPIE **2189**, 400 (1994).
[12] J. Squier, F. Salin, and G. Mourou, Opt. Lett. **16**, 324 (1991).
[13] D. Strickland and G. Mourou, Opt. Commun. **56**, 219 (1985).