Optical nonlinearities in VO_2 nanoparticles and thin films

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(Received 11 June 2004; accepted 6 October 2004)

Z-scan and pump-probe measurements with ultrafast, 800 nm laser pulses were used to compare the ultrafast optical nonlinearities of VO_2 nanoparticles and thin films in both semiconducting and metallic states. In the metallic state, both the nanocrystals and thin films exhibit a positive, intensity-dependent nonlinear index of refraction. However, the nonlinear effects are relatively larger in the VO_2 nanocrystals, which also reveal a saturable nonlinear absorption. When the semiconductor-to-metal phase transition is induced by the laser pulse, VO_2 thin films exhibit a negative equivalent nonlinear index of refraction while the nanocrystals exhibit a smaller but still positive index. Both the VO_2 nanocrystals and thin films undergo the phase transition within 120 fs. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1826232]

Nonlinear materials in which light can be controlled on ultrafast time scales by optical means are critical to the development of all-optical photonic devices.[1] In VO_2, abrupt changes in electronic properties occur via a solid-solid phase transition[2] (PT), and are thus of particular interest. Above the critical PT temperature, $T_c \sim 67\ ^\circ C$, VO_2 has a rutile structure and metallic properties; below T_c, VO_2 becomes a monoclinic semiconductor[3] with 10^4 higher electrical resistance. This PT is accompanied by discontinuities in the VO_2 optical characteristics that recommend this material for fast optical switching and related applications (e.g., ultrafast optical limiters). Cavalleri *et al.*,[4] using time-resolved light and x-ray diffraction, have demonstrated that the transition occurs in less than 500 fs in VO_2 thin films.

In this letter we use the *Z*-scan technique[5] with ultrafast laser pulses to compare the absorptive and refractive nonlinearities in VO_2 nanoparticles and thin films above and below T_c. The nonlinear responses of the nanoparticle and thin-film forms of VO_2 were correlated with the properties of the semiconducting and metallic phases. The nanostructured VO_2 exhibits a substantial increase in the effective nonlinear absorption and refraction per unit volume compared to the thin film, while both show essentially identical ultrafast response.

Thin films of VO_2 were grown on silica substrates held at 550 °C by pulsed laser deposition from a 99.95% pure vanadium metal target in an oxygen pressure of 11 mTorr. The KrF ablation laser ($\lambda = 248$ nm) was set to a fluence of 4 mJ/cm^2 at 25 Hz. VO_2 nanoparticles were fabricated by implanting[6] vanadium and oxygen ions in stoichiometric ratio at equal depths in a 200-nm-thick surface layer of a SiO_2 substrate. Annealing (1000 °C) in an argon atmosphere induced the precipitation of ~50 nm VO_2 nanorods.

Figure 1 illustrates the linear optical transmittance at $\lambda = 800$ nm for both VO_2 nanoparticles and a 210-nm-thick VO_2 film undergoing the PT. The VO_2 PT manifests itself by a marked decrease in optical transmission when the metallic phase is formed in both film and nanocrystalline samples; however, the magnitude of the change in transmission is larger in the film since it contains five times more VO_2 by mass than the nanocrystalline composite.[7] The VO_2 nanoparticles exhibit a significantly wider hysteresis than the thin-film sample due to size effects.[8]

In most nonlinear materials, the complex refractive index $n = n_o + i\alpha_o/2k$, where n_o is the refractive index, α_o the absorption coefficient and k the modulus of the wave vector, undergo pump-induced changes of the form: $\Delta n_o = \gamma^* I$ and $\Delta \alpha_o = \beta^* I$, where I is the light intensity. While this situation is typical of most third order nonlinear materials and certainly for VO_2 in the metallic state, a fundamentally different situation is observed for VO_2 that is initially in the semiconducting state since the absorbed laser light can induce the conversion from semiconductor to metal.

It is crucial to recognize that this light-induced phase transition is neither a two-photon process nor a typical third order nonlinearity. The effect in this case, because of the existence of the PT threshold, is more step-like than proportional and is a function of the fluence rather than the inten-

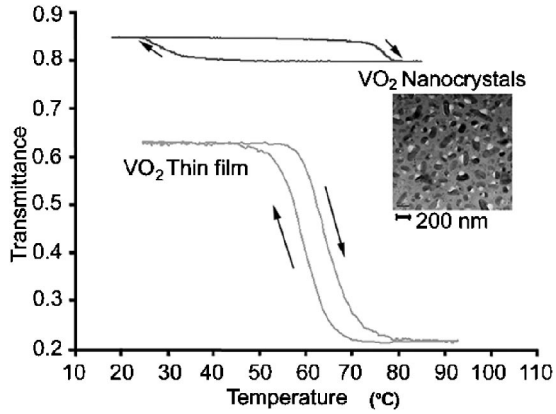

FIG. 1. Linear optical transmittance at $\lambda = 800$ nm of a nanocrystalline VO_2/SiO_2 composite and a standard VO_2 thin film cycled through their phase transition. The inset shows an electron transmission micrograph of the nanocrystalline sample.

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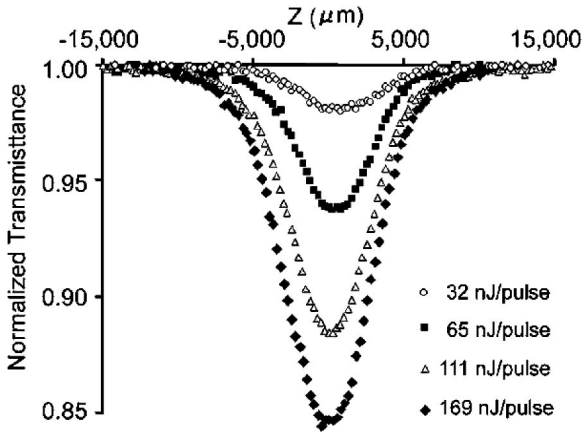

FIG. 2. Normalized transmittance of an open-aperture *Z*-scan trace obtained at different energy densities for a 210-nm-thick VO_2 film.

sity. However, despite its fundamentally different origin, this response produces similar looking *z*-scan profiles to those of true intensity proportional nonlinearities. In view of this experimental fact, we will use γ and β "*equivalent*" coefficients as other researchers have done in similar situations[9,10] in dealing with nonlinearities arising from phase transitions, in order to quantify the effects.

Figure 2 shows how this nonlinearity develops in a standard open-aperture *Z*-scan procedure for a VO_2 thin film. Regeneratively amplified Ti:sapphire laser pulses (120 fs, 1 kHz, $\lambda = 800$ nm) were focused using a 10 cm lens to a waist diameter of 50 μm. The total energy of the transmitted beam was measured in the far field as a function of sample position along the beam axis *Z*. Near the beam waist ($Z=0$), a large transmission decrease is observed, signaling the PT onset in the area irradiated by the central part of the beam. Open aperture *Z* scans at several energy densities were then normalized to obtain absolute transmittance values far from the waist region in order to determine the equivalent coefficient $\beta_{\text{film}}^{22\,^\circ\text{C}} = 270 \pm 30$ cm/GW. The PT induced in this way follows a nonthermal path,[5] but the energy absorbed is thermalized on the nanosecond time scale without overall temperature increase above 22 °C. No transmission change was detected at a fluence of ~ 2 mJ/cm^2, thus establishing the PT fluence threshold. Using the same protocol, sample damage was observed at fluences above 45 mJ/cm^2.

A constant energy of ~ 160 nJ/pulse (~ 8 mJ/cm^2 at $Z=0$) was used in the *Z*-scan configuration with open and closed apertures to measure γ and β for both the thin-film and nanoparticle samples at 22 and 100 °C (i.e., above and below the PT). Figures 3(b) and 3(d) show the *Z*-scan results for VO_2 nanoparticles and thin films, respectively, at 100 °C. In the metallic state, a conventional intensity dependent nonlinearity occurs and the coefficients have the standard meaning from a third order nonlinearity. Hence the word equivalent is not used in this case. In the open-aperture measurements, no change was observed in the absorption of the film, thereby setting an upper limit of $|\beta_{\text{film}}^{100\,^\circ\text{C}}| < 1$ cm/GW. In contrast, the nanoparticles in the metallic state exhibited a negative nonlinear absorption coefficient of $\beta_{\text{nano}}^{100\,^\circ\text{C}} = -21 \pm 2$ cm/GW, as is typical of a saturable optical nonlinearity. Similar contrasting nonlinearities between bulk materials and nanoparticles are commonly observed for "true" metal nanocomposites such as gold nanoparticles in silica, where the incident flux saturates the transitions and bleaching can occur.[11] The closed/open-aperture ratios in Figs. 3(b) and 3(d) were used to extract the metallic-phase nonlinear index of refraction for both samples, yielding values of $\gamma_{\text{nano}}^{100\,^\circ\text{C}} = 3.1 \pm 0.3 \times 10^{-12}$ cm^2/W and $\gamma_{\text{film}}^{100\,^\circ\text{C}} = 7.5 \pm 0.5 \times 10^{-12}$ cm^2/W. Although the magnitude of γ is larger for the VO_2 film, the nonlinear index of the nanocomposite is twice that of the film per unit volume of VO_2. This is probably because the optical properties of the VO_2 nanoparticles in the metallic phase are enhanced by the dielectric confinement effect of the SiO_2 matrix.[1,7]

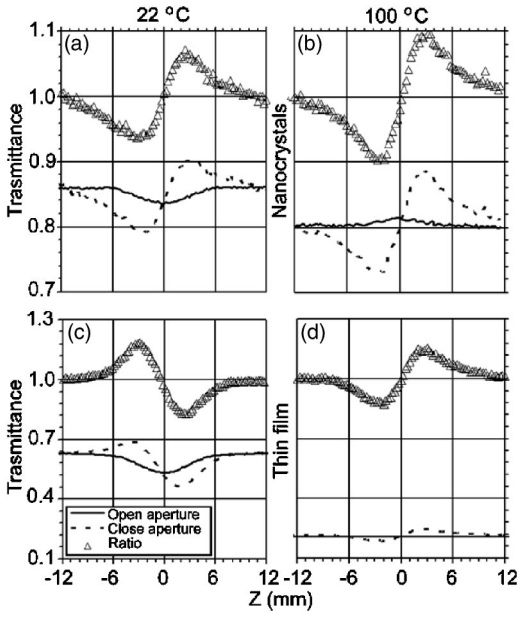

FIG. 3. *Z*-scan traces for VO_2 thin film and VO_2/SiO_2 nanocomposite samples. Panels (a) and (b) show nanocrystalline sample measurements at 22 and 100 °C, respectively. Panels (c) and (d) present the results for the 210-nm-thick VO_2 film.

The nonlinearities are more complex in the semiconducting phase at room temperature due to the laser-stimulated induction of the PT as the *Z*-scan fluence reaches the PT threshold. Nevertheless, as explained above, *equivalent* nonlinear coefficients can be obtained. Figures 3(a) and 3(c) show the *Z*-scan results for the VO_2 nanoparticles and thin film, respectively, at $T = 22$ °C. In the open-aperture measurement, the nanocrystal sample shows, as the thin-film case, a decrease in transmittance near the waist of the beam as a result of the PT—corresponding to an equivalent nonlinear absorption coefficient $\beta_{\text{nano}}^{22\,^\circ\text{C}} = 32 \pm 3$ cm/GW. It is important to note that this parameter has changed from a negative to a positive value as compared with the high-temperature phase. The change in sign arises because VO_2 nanocrystals become less transparent in the metallic phase after undergoing the PT (see Fig. 1), therefore we can expect less transmittance when the nanocomposite material in the central portion of the beam spot is illuminated with fluences above the threshold as is the case near the focus.

An additional reversal of sign, as compared to the metallic state, occurs in the nonlinear index of the VO_2 thin film. Here the peak-valley trace of the open/closed-aperture curve is inverted, corresponding to an equivalent $\gamma_{\text{film}}^{22\,^\circ\text{C}} = -7.1 \pm 0.5 \times 10^{-12}$ cm^2/W. This equivalent nonlinear index of refraction is expected to turn negative with the PT since $n_{\text{metal}} \sim 1.98$ is considerably smaller than

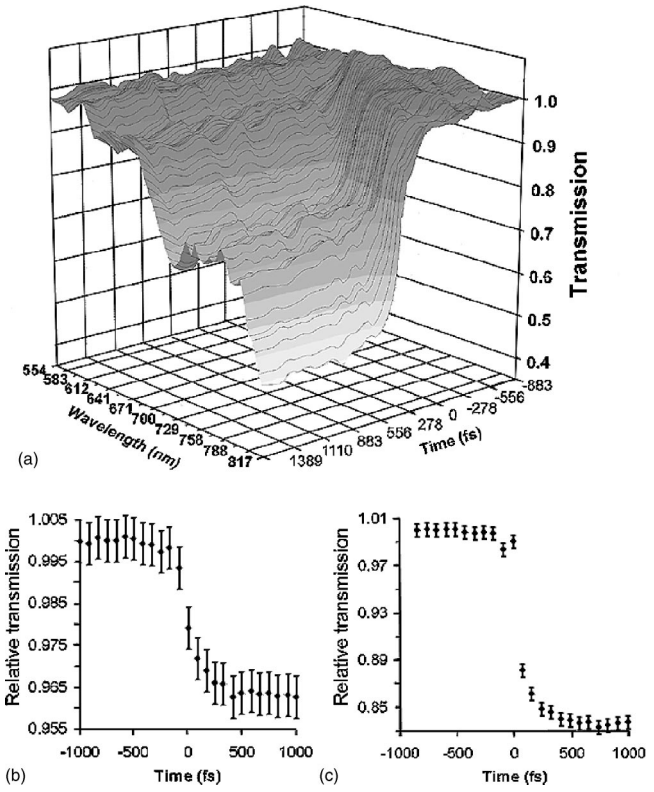

FIG. 4. (a) Ultrafast measurement of the laser-excited VO_2 thin-film phase transition. The measurement was taken in the pump-probe configuration with an 800 nm pump (Ti:sapphire laser with a 120 fs pulse width, 30 mJ/cm^2) at $Z=0$ and probed with white light. Panels (b) and (c) show the time resolution obtained for the sample of VO_2 nanorods and the VO_2 thin film, respectively (laser fluence 10 mJ/cm^2).

$n_{\text{semiconductor}} \sim 2.89$.[12] The net effect of this lower index occurring in a larger proportion of the beam spot proportion as the sample moves to the focus, is an effective negative lens focusing. The same tendency is also exhibited by the VO_2 nanocrystal sample: While it does not reach negative values, it does show a reduced equivalent $\gamma_{\text{nano}}^{22\,^\circ\text{C}} = 2.1 \pm 0.2 \times 10^{-12}$ cm^2/W. Given that the VO_2 nanoparticles are embedded in amorphous SiO_2, the nonlinear index of the composite could remain positive due to the small filling fraction of VO_2. Nonlinearities of a composite containing nonlinear nanoparticles is known to be sensitive to the nanostructure of the composite. Indeed, a similar behavior of the nonlinear index has been reported previously for Au-particle/$BaTiO_3$ nanocomposites.[13,14]

An important parameter in evaluating nonlinearities for optical limiting applications is the speed of the nonlinearity. The time evolution of the optical nonlinearity connected with the PT in both the nanoparticles and thin film was measured in the pump-probe configuration, with a laser pulse resolution of 120 fs. Figure 4(a) shows the results of an ultrafast measurement made for a VO_2 thin film using an 800 nm pump and probing with a white light continuum. The optical switching is clearly evident by a pronounced steep drop in the transmission with a magnitude that increases with increasing wavelength. Figures 4(c) and 4(b) show the time evolution for the thin-film and the nanocrystal samples, respectively, at $\lambda = 800$ nm. For both samples, the drop in transmission occurs faster than the 120 fs. This time scale does not clarify whether the system becomes metallic from the disruption of electronic correlations or from structural distortions,[4,15] but the ultrafast nature of the VO_2 PT is reflected in the nonlinear optical properties of the material. This combination of the femtosecond reversible PT that exhibits opposite-sign different origin nonlinearities across the critical temperature region makes VO_2 unique among nonlinear materials.

This research was sponsored at Vanderbilt University by the National Science Foundation (Grant No. DMR-0210785) and at Oak Ridge National Laboratory (ORNL), by the Laboratory Directed Research and Development program. ORNL is operated by UT-Battelle, LLC for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

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