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Optical switching in VO_2 films by below-gap excitation

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We study the photoinduced insulator-metal transition in VO_2, correlating its threshold and dynamics with excitation wavelength. In single crystals, switching can only be induced with photon energies above the 670 meV gap. This contrasts with the case of polycrystalline films, where formation of the metallic state can be initiated also with photon energies as low as 180 meV, which are well below the bandgap. Perfection of this process may become conducive to schemes for optical switches, limiters, and detectors operating at room temperature in the mid-infrared. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2921784]

Correlated electron systems are very sensitive to external perturbations, such as temperature, pressure, electric,[1] or magnetic fields,[2] and exhibit dramatic transitions between competing structural, electronic, or magnetic phases.[3] Such switching has potential applications, ranging from sensors to data storage. Light can also drive similar phase changes[4] on significantly shorter timescales, which may be conducive to high bit-rate applications.

The photoinduced insulator-to-metal transition in VO_2 is one of such photocontrol phenomena.[5–7] In its low-T phase ($T_c < 340$ K), VO_2 has a cell-doubled monoclinic structure, derived from the high-temperature rutile phase by the pairing and tilting of V^{4+} cations along the c axis. Concomitantly with this structural distortion, the V3d charge carriers localize into spin singlets on the V^{4+} dimers, causing a metal-insulator transition[8,9] (see Fig. 1). Photoexcitation across the gap depletes the localized states in the valence band, injecting electrons into the spatially extended conduction band. As a result of such prompt *hole photodoping*, the energy gain derived from the lattice distortion is lost, the atoms move coherently toward the higher-symmetry rutile structure and the metallic phase is formed. This process can also be seen as a displacive excitation of large amplitude coherent phonons,[10–12] where photoinjection of holes into the valence band shifts the equilibrium ionic position from the dimerized state to the high-symmetry phase.

Due to the technological potential of this process, we have also investigated the response of VO_2 at telecom wavelengths.[13] We have shown how the use of nanoparticles in glass makes the ultrafast phase transition compatible with optical fiber geometries and make an efficient room-temperature switch at 1.55 μm. Other experiments have reported ultrafast switching of VO_2 in opal-based photonic crystals.[14]

Here, we report on a study of the excitation wavelength dependence for this photoinduced phase transition, comparing the response to light tuned above and below the bandgap. The main conclusion of our work is that single crystals respond very differently from polycrystalline films. In the former, we show that no photoinduced phase transition can take place if the photon energy is below 670 meV. Interband optical absorption is the dominant mechanism driving the transition. On the contrary, in the thin films, the insulator-metal transition can be controlled also with photon energies below the gap, extending to 180 meV. The threshold follows the linear absorption coefficient, which is already significant at low photon energies. This is presumably indicative of the importance of hole photodoping to drive the insulator-metal transition, which is made possible by the existence of defect states in the middle of the gap.

Figure 1 shows the temperature-dependent resistivity for the single crystals and thin films. Single crystal samples were

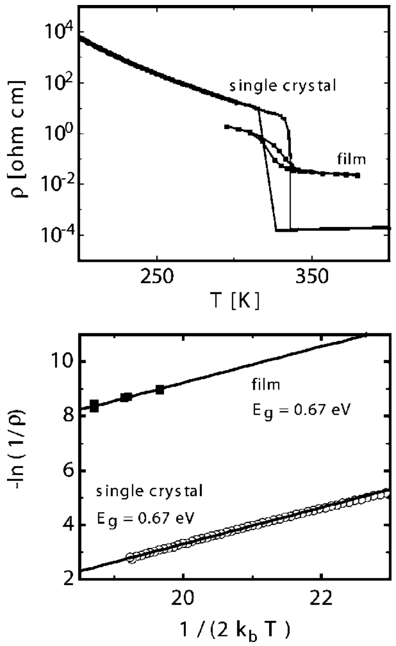

FIG. 1. Temperature-dependent resistivity of single-crystal and thin film VO_2. The insulator-metal transition occurs in both samples near 340 K, with similar hysteresis curves. A fit to the resistivity in the insulating phase gives an activation energy (bandgap) of 670 meV for both samples.

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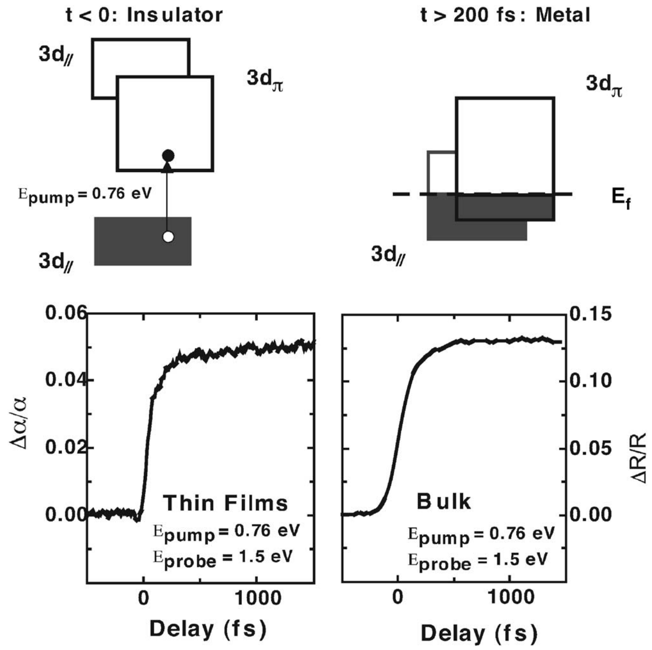

FIG. 2. Schematic band diagram of VO_2. In the insulating phase, a 670 meV bandgap is formed between the $3d_{\|}$ valence band and the $3d_{\pi}$ conduction band. A second empty conduction band has the same $3d_{\|}$ symmetry as the valence band, which is split by a Peiers distortion and by Hubbard energy. Photoexcitation at high photodoping energies is dominated by $3d_{\|}-3d_{\pi}$ transitions. The time-dependent optical response of single-crystal and thin-film VO_2 after photoexcitation with 0.76 eV pulses is shown in the lower part of the figure.

grown by chemical vapor transport,[15] whereas thin films polycrystalline samples were grown by reactive rf-magnetron sputtering.[16] Both samples evidence an insulator-metal transition near 340 K, with similar hysteresis curves. As expected, the transition region is sharper in the single crystal than in the thin films, both upon heating and cooling. The absolute resistivity change across the insulator-metal transition is higher in the single crystal samples than in the thin films. By plotting ln(1/resistivity) as a function of $(1/2k_bT)$ in the insulating phase, one finds an identical activation energy of 670 meV for both samples. The observation of a smaller resistivity change across the transition can be explained by higher defect density of the polycrystalline films, resulting in lower carrier mobility for the metallic phase and higher intrinsic dopant densities in the insulating phase.

Time-dependent reflectivity and transmission are reported in Fig. 2. The femtosecond pump pulses, continuously tunable between 1 and 20 μm, were obtained by optical parametric conversion of 800 nm pulses from a 1 KHz Ti:Sa amplified laser system. The time-dependent optical constants were probed only at the fundamental 800 nm wavelength of the same femtosecond laser. Because the 50 nm VO_2 film was thin compared to the absorption depth of both pump and probe pulses, we could directly convert our transmission measurements into the time-dependent absorption coefficient across the photoinduced insulator-metal transition. In the bulk samples, the penetration depth of the IR pump pulse was significantly larger than the 800 nm probe for all excitation wavelengths. Thus, a homogeneously excited region was probed.

In Fig. 3, we report the pump-fluence dependence of the differential absorption coefficient for the thin films at +300 fs time delay (qualitatively similar results were obtained for the bulk samples). The absorbed fluence was estimated by subtracting transmitted and reflected energies from the incident pulse energy, normalizing to the excitation spot size as measured *in situ* with knife-edge measurements and pin-hole transmission. A fluence threshold, a region of monotonic increase, and a saturation value are found. We take the value of the threshold as the intercept with the zero differential change in absorption at 300 fs.[17] The threshold for the transition is about 250 $\mu J/cm^2$, which, at 1 eV, corresponds to 8×10^{21} absorbed photons/cm^3, one absorbed photon for every 60 unit cells. No significant change in threshold was found for all the pump photon energies above the bandgap.

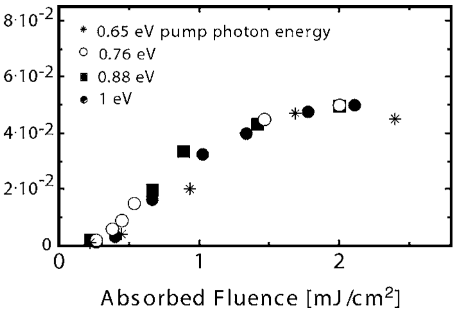

FIG. 3. Fluence dependence of the photoinduced phase transition in the thin films for various pump photon energies above the bandgap. A threshold of 250 $\mu J/cm^2$ is found for all photon energies, with a region of superlinear growth and saturation.

Figure 4(a) shows the most compelling observation of

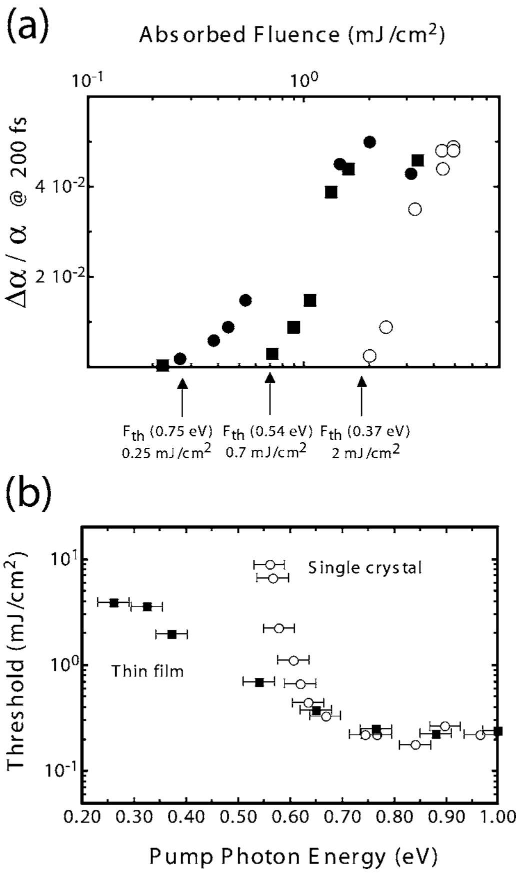

FIG. 4. (a) Fluence dependence of the photoinduced phase transition in the thin films for various pump photon energies below the bandgap. (b) Threshold for the photoinduced phase transition for various wavelengths in bulk and thin films.

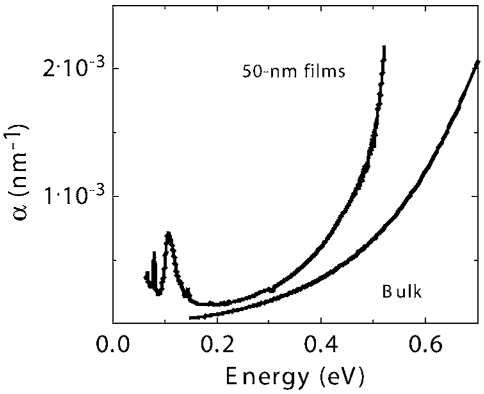

FIG. 5. Measurement of the IR absorption coefficient for VO_2 thin films. The absorption coefficient for single-crystal samples exhibits lower absorption at photon energies below the bandgap.

our paper, i.e., the response of the thin films to below-gap optical excitation. The fluence dependence is the same as that for above gap excitation, although the efficiency of the process is reduced. An approximately rigid shift of the curves toward higher fluences is observed. Figure 4(b) summarizes these observations, comparing them to the results for bulk samples. The value of the threshold is plotted as a function of pump photon energy for thin films and bulk. Strikingly, the threshold is seen to much more rapidly diverge for single crystals than for thin films.

Figure 5 displays the linear absorption coefficient for a range of wavelengths in the mid-IR for both thin films and for single-crystal samples.[18] The resonances near 0.1 eV correspond to IR active lattice vibrations. At a higher energy, the absorption is low but significantly grows in the films already near 200 meV. Thus, irradiation in the 200–670 meV region results in significant absorption in the thin films. While the main purpose of this paper is to report the observation of this effect, we note that this is consistent with our understanding of the photoinduced phase transition in a Peierls (or spin Peierls) insulator. Long-wavelength excitations in the thin films of VO_2 presumably take place between the valence band and nonmobile defect states below the bandgap, resulting in effective hole photodoping. Within this picture, it is possible to argue that the transition is solely driven by hole photodoping, i.e., by the removal of electrons from the singlet states that stabilize the low-T phase. Thus, the nature of the final states into which electrons are promoted does not effect the insulator-metal phase transition as long as the final states are not "binding" states of the V-V pairs.

In summary, we have shown that polycrystalline VO_2 films can be switched between the insulating and metallic phases by photoabsorption below the electrical bandgap. This is likely due to the existence of defect states in the middle of the gap, which allow for hole photodoping into the valence band. Our work may be conducive to schemes for optical switching, limiting, or sensing in the mid-IR.

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[15] V_2O_3 powders were first prepared by heating V_2O_5 at 973 K for 24 h. Next, polycrystalline samples were grown by heating a mixture of V_2O_3 and V_2O_5 at 1173 K for 24 h in nitrogen atmosphere. Resultant polycrystalline samples and $TeCl_4$ were sealed in a quarts tube, of which the high temperature part was 1323 K and the low temperature part was 1173 K. The result of the thermogravimetric analysis was VO {2.002\pm0.0002}. The lattice constants at room temperature were $a=5.764$ Å, $b=4.539$ Å, $c=5.393$ Å, and $\beta=122.61°$.
[16] A >99.9% pure vanadium target was used for the sputtering, which was performed in an argon and oxygen gas mixture at an operating pressure better than 10 mTorr, and deposited onto Si (100) substrate previously coated with 200 nm low-pressure vapor-deposited amorphous Si_3N_4 layer. The 50 nm film thickness was measured *ex situ* by cross sectional scanning electron observations. The samples were etched to have free-standing 50 nm/200 nm VO_2/Si_3N_4 structures. The films were also characterized by measuring x-ray diffraction, x-ray absorption spectra, and Raman scattering, which showed the same characteristics of pure VO_2 powders.
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