Femtosecond Structural Dynamics in VO_2 during an Ultrafast Solid-Solid Phase Transition

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Femtosecond x-ray and visible pulses were used to probe structural and electronic dynamics during an optically driven, solid-solid phase transition in VO_2. For high interband electronic excitation ($\sim 5 \times 10^{21}$ cm^{-3}), a subpicosecond transformation into the high-T, rutile phase of the material is observed, simultaneous with an insulator-to-metal transition. The fast time scale observed suggests that, in this regime, the structural transition may not be thermally initiated.

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A number of oxides of vanadium exhibit insulator-to-metal transitions upon heating, most notably V_2O_3 ($T_M = 150$ K) and VO_2 ($T_M = 340$ K) [1]. In the latter case, changes in the electronic band structure are associated with atomic rearrangement between a low-T monoclinic and a high-T rutile phase. The intriguing nature of this process [2,3] and the importance of transition metal oxides in modern condensed matter physics [4] make this problem amenable to dynamic studies using ultrafast techniques. However, time resolved measurements of phase transitions in highly correlated materials are generally very demanding, because they require simultaneous access to the femtosecond dynamics of more than 1 degree of freedom of the system (e.g., electronic, structural, magnetic).

In this Letter, we report on ultrafast optical and x-ray diffraction [5] measurements of a photoinduced phase transition in VO_2. We demonstrate the first direct measurement of a femtosecond solid-solid phase transition and the combined measurement of electronic and structural dynamics in a correlated solid. For intense interband excitation ($\sim 5 \times 10^{21}$ carriers cm^{-3}), we directly observe the formation of the rutile phase, simultaneous with an insulator to metal transition, on a time scale that is comparable to or shorter than internal thermalization times of the photoexcited system. Thus, our results challenge the thermal model for a solid-solid transition in this excitation regime. This experiment raises several additional issues for future studies, including the questions of what microscopic process is responsible for initiating the structural distortion and what causes the disappearance of the band gap after optical excitation.

Optical measurements were performed combining the commonly used pump-probe technique with visible microscopy, i.e., spatially resolving the pumped/probed area of the VO_2 surface for different time delays. A 50 fs, 800-nm, p-polarized optical pump pulse, impinging at an angle of 60°, was used to excite 200-nm VO_2 crystalline films on glass substrates, while a variably delayed probe pulse provided reflectivity snapshots of the surface imaged onto a charge-coupled device (CCD). The peak pump fluence was set to 25 mJ/cm^2, significantly lower than the measured single-shot damage threshold of 63 mJ/cm^2. Figure 1 shows spatially dependent reflectivity curves, measured along the vertical direction on the individual images. The laser pulses were spatially filtered before interaction with the sample, resulting in a single-transverse-mode, Gaussian spatial profile. Thus, different positions corresponded to different local excitation fluences that were precisely known. As immediately evident in the plot, the reflectivity of the center drops most rapidly toward the equilibrium reflectivity of the metallic phase [6], reached well within hundreds of femtoseconds. At a time delay of about 10 ps, a larger area exhibits the same reflectivity, as parts of the sample that are pumped at lower fluence switch at a slower rate. The low-reflectivity area progressively enlarges, reaching a maximum after approximately 5 ns and slowly returning toward the optical properties of the low-temperature phase in several tens of nanoseconds. Similar to what was observed in a number of optical experiments investigating phase transformations [7], above a distinct threshold the reflectivity settles to the value characteristic of the new phase, independent of the local excitation fluence. Thus, a true phase change can be hypothesized, as opposed to simple carrier excitation, observed at the earliest time delays when the optical properties follow the spatial profile of the pump laser. A 7-mJ/cm^2 threshold was obtained by comparing the measured maximum transformed area and the pump-fluence profile [8]. Reflectivity evolutions sampled at three different positions of the photopumped spot are shown in the respective insets. Exponential fits to these curves indicate that for increasing pump fluence the insulator-to-metal transition time decreases from more than 50 ps to about 100 fs. A sharp decrease in

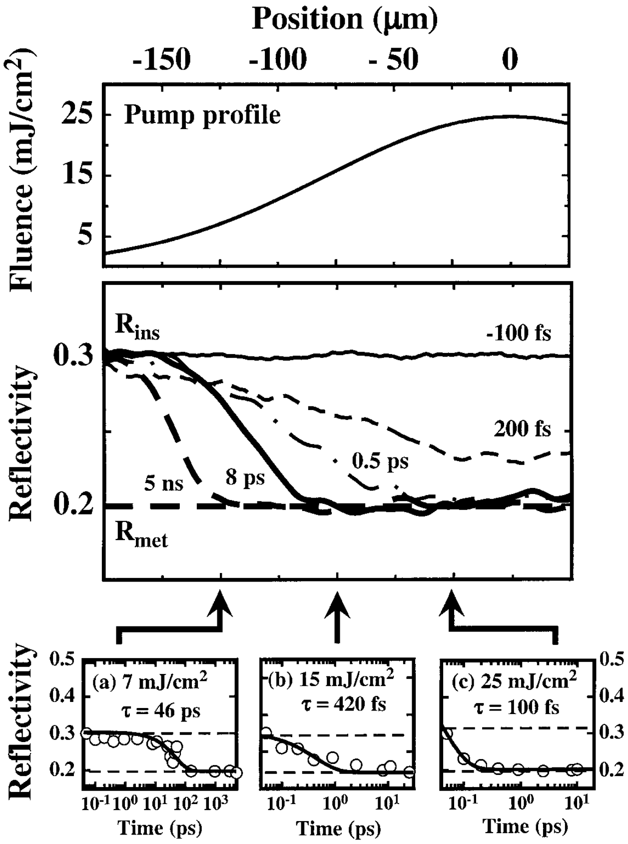

FIG. 1. Upper plot: Gaussian spatial profile of excitation. Middle plot: Plots of the reflectivity during the phase transformation. The probe light illuminates a region that is several millimeters in diameter, in order to provide homogeneous intensity conditions over the photopumped region. The spatially dependent reflectivity is measured along the vertical direction, where the nonzero angle of incidence of the pump pulse does not affect the pump-probe time delay. Lower plots: Time resolved evolutions of the reflectivity for three different positions on the sample, corresponding to local fluences of (a) 7 mJ/cm^2, (b) 15 mJ/cm^2, and (c) 25 mJ/cm^2. The time scale is logarithmic. The dashed line is the calculated reflectivity for a 200-nm-thick metallic phase on a glass substrate. The continuous curve along the experimental points is a one-parameter, exponential curve fit for the transition time constants, obtained by assuming exponential behavior.

the transition time, from 10 ps to 900 fs, was observed between 10 and 12 mJ/cm^2. We repeated our measurement using 0.5 ps pump pulses of the same fluence and found no significant variation in the threshold, as well as a longer minimum transformation time of about 2 ps, in good agreement with that reported in the literature [9]. To extract the transformed depth from the optical data, we calculated the reflectivity of a three-layer structure, composed by a metallic film of thickness Δx (high T phase at the surface), a 200 nm-Δx thick insulating film beneath (low T phase) and a semi-infinite glass substrate. Comparison of the calculated reflectivity with the measured value did not provide a unique value for Δx, which was found to be compatible with 80-nm, 150-nm, or 200-nm transformed depths. Thus, optical measurements provide no direct information on the structural dynamics and ambiguous indication on the transformed depth.

Ultrafast structural probing was achieved by using x-ray bursts of spin-orbit-split 8-keV (1.54-Å) Cu-K$_{\alpha 1}$ and Cu-K$_{\alpha 2}$ line radiation at 20 Hz, generated by focusing terawatt femtosecond laser pulses onto a moving copper wire [10]. The probing x rays, emitted into 4π steradians by the plasma point source, were focused using a pair of ellipsoidal grazing incidence reflectors in a Kirkpatrick-Baez configuration, providing about 2000 Cu-K$_\alpha$ photons/pulse in a 0.3° cone angle onto a 50-μm spot. The experiments were conducted on a bulk VO$_2$ sample, exhibiting the best crystalline quality and maximizing the diffracted signal. Angle and time dependent diffraction were measured in an optical pump, x-ray probe configuration, with excitation limited to the intermediate fluence range (15 mJ/cm^2), where no cumulative damage was observed [11]. The static temperature of the crystal was held below the transition temperature. The sample was excited over an area of several millimeters in diameter, resulting in an x-ray probed region that was homogeneously pumped. The diffracted signal was measured in the (110) direction of the low-T phase using an x-ray CCD, with the Bragg angle being 13.9°. For calibration purposes, the unpumped sample was reversibly heated across the transition temperature (340 K), where a shift of the Bragg angle to that of the high temperature rutile phase (13.78°) was observed.

The measured diffraction profiles were, at negative time delays, identical to those measured from the unperturbed sample, thus evidencing no significant cumulative or prepulse effects. At positive time delays, a shoulder originating from the new crystallographic phase appeared at about 0.1° degrees from the center of the unperturbed curve (see Fig. 2a). Because the high-T phase is initially formed over a small fraction of the depth probed by the x rays (≈ 3 μm), the peak of the shoulder was observed to be only a few percent of the main lines. Figure 2b displays normalized diffraction curves at early times, obtained by dividing the measured time resolved signals by those from the unperturbed sample. As pointed out before, the curves at negative time delays resemble those from the unpumped case, whereas after a few hundred femtoseconds a significant shoulder is visible at the diffraction angle of the equilibrium, high-temperature rutile phase. At time delays of several picoseconds (not shown), a corresponding feature was observed at higher diffraction angles, due to a compressive response of the low-temperature monoclinic phase to the expansive transformation taking place at the surface. While no detail of the actual atomic dynamics during the growth of the metallic phase can be retrieved at this stage, the formation time at the very surface unequivocally appears to be of the order of a few hundred femtoseconds.

Figure 3 shows the integrated x-ray reflectivity from the new phase, normalized to the signal from the low-temperature monoclinic crystal. During the first 10 ps, the step in the integrated diffraction from the rutile phase

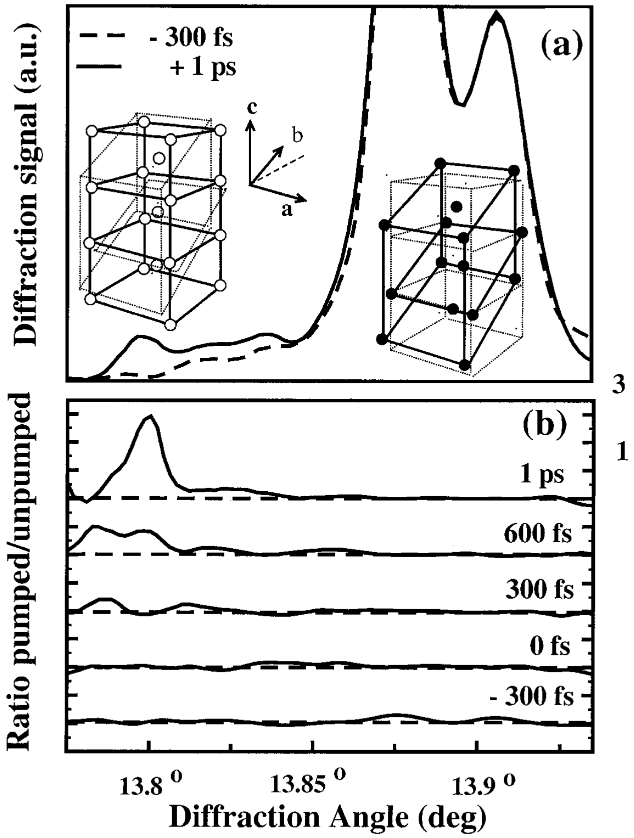

FIG. 2. Upper plot (a): Angle dependent x-ray diffraction signal measured for negative and positive time delays. The diffraction profiles originate from the convolution between the rocking curve of the dynamically strained/transforming crystal and the spectrum of the x-ray plasma source. The dashed and continuous curves correspond to delays of −300 fs and +1 ps, respectively. The two crystalline structures (monoclinic insulating phase and tetragonal metallic phase) are sketched by displaying only the vanadium atoms, which dominate the diffraction signal. Lower plot (b): Ratio between the x-ray reflectivity of the excited and unpumped crystal.

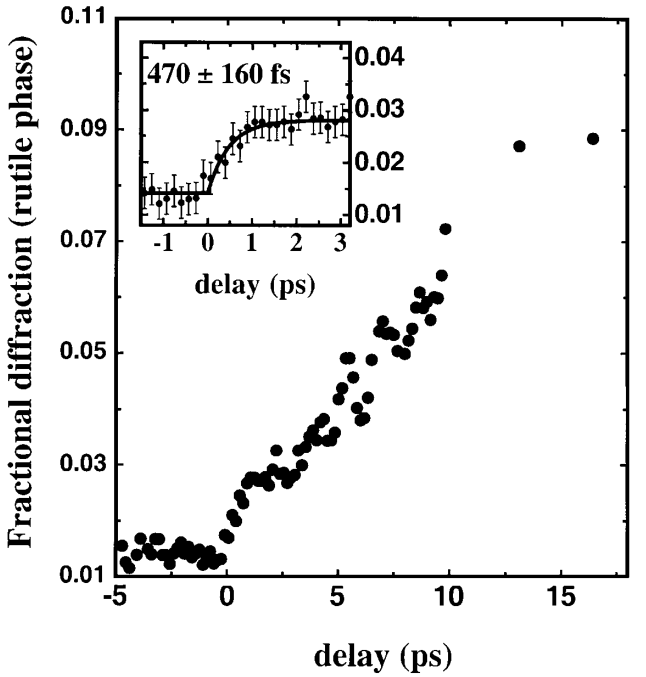

FIG. 3. Main plot: Time-dependent, integrated diffraction signal from the metallic rutile phase normalized to the integrated diffraction from the monoclinic phase. The integrals are calculated over a region of 0.1° around the center of the respective lines. Inset: Region near zero time delay. Continuous curve: exponential fit of the rise time.

reaches about 8% of the signal from the main peak. Since the scattering factors for these two phases are approximately equal, the ratio of the two diffraction signals directly yields the thickness of the transformed layer from the 3-μm x-ray penetration depth. This resolves the ambiguity on the transformation depth, indicating that for this intermediate fluence range (15 mJ/cm^2), a 250-nm thick layer of material undergoes transformation in about 10 ps. The inset displays the signal measured during the first few picoseconds, demonstrating that the first step in the structural phase transition occurs on this time scale over a depth of approximately 40–60 nm (consistent with an 80-nm-thick layer, as extracted from the observed transition in the optical properties). At long time delays (hundreds of picoseconds, not shown), slow oscillations were observed around the 8% value, probably due to coherent acoustic response [12,13] initiated by the ultrafast transformation. However, analysis of the response at longer times requires a full thermoelastic treatment and is beyond the scope of this paper. While we were not able to perform ultrafast x-ray measurements in the highest fluence regime (nonreversible), we believe that our data cover the essential features of the structural phase transition. Higher excitation energies are likely to result in similar dynamics and in a thicker layer being transformed in the subpicosecond time domain.

The measurements reported here point toward two different physical mechanisms for the phase transition. Close to threshold, the process requires tens to hundreds of picoseconds before completion. A thermal pathway governs the transformation, with the lattice being heated in several picoseconds above the critical temperature (340 K) and growth of the new phase proceeding incoherently and at spatially separated sites by statistical transitions across an activation barrier (nucleation and growth). This excitation regime corresponds to the conventional pathway for the first order phase transition and is not the main focus of our paper.

At higher degree of electronic excitation ($\sim 5 \times 10^{21}$ cm^{-3}), optical and x-ray data point toward a transition occurring over a macroscopic volume within 500 fs or less [14]. This time scale is comparable to that for energy transfer to the lattice, and it is shorter than the typical internal thermalization time of a nonequilibrium phonon distribution [15,16]. Excitation of a dense carrier population across the 600-meV band gap [17] may significantly perturb the potential energy surface of the electronic ground state and depress the barrier separating the two phases. This process could, for example, result from weakening of the covalent bonds, similar to the mechanism governing ultrafast melting [8,18]. Alternatively, direct laser excitation of coherent lattice displacements [19,20] or excitation of hot, nonequilibrium phonons may drive the phase transition along an unperturbed potential energy surface [21]. The current experimental data cannot resolve this issue. Further, it is not clear whether the system becomes metallic from disruption of electronic correlations or from structural distortion. This issue is intimately related to the nature of the insulating phase of VO_2 and represents an important question for future experimental studies [2,3]. In these respects, theoretical work is required to address the nature of the highly excited state of insulating VO_2 as well as the ensuing dynamics. Experimentally, future advancements in the ultrafast x-ray measurements will allow for improved signal to noise ratio, as well as for the simultaneous detection of several diffraction orders [22] and retrieval of atomic positions at the early stages of the transition.

In summary, we have reported the first conjunct optical and x-ray measurements during an optically driven solid-solid phase transition in the correlated oxide VO_2. While a variety of characteristic time scales are found, laser pulses of sufficiently high fluence can trigger a subpicosecond structural transition from the low-T monoclinic phase to the high-T rutile phase. Our results are suggestive of a nonequilibrium pathway between the two equilibrium crystalline structures.

Because the reported solid-solid transformation lasts only a few hundred femtoseconds and is reversible, it may be useful for an ultrafast Bragg switch [23], capable of selecting a subpicosecond portion of a longer x-ray pulse (e.g., from a synchrotron). Finally, as opposed to previous studies of nonthermal order-disorder phase transitions, this is the first experiment where the product state of a transformation is structurally identified, as opposed to indirect signatures such as loss of scattering efficiency [24]. This capability may have ramifications in femtosecond dynamics of condensed matter, such as the possibility of achieving coherent control of phase transitions by adjusting the excitation conditions to maximize a specific product state.

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