Picosecond soft x-ray absorption measurement of the photoinduced insulator-to-metal transition in VO$_2$

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We directly measure the photoinduced insulator-to-metal transition in VO$_2$ using time-resolved near-edge x-ray absorption. Picosecond pulses of synchrotron radiation are used to detect the redshift in the vanadium L_3 edge at 516 eV, which is associated with the transient collapse of the low-temperature band gap. We identify a two-component temporal response, corresponding to an ultrafast transformation over a 50 nm surface layer, followed by 40 m/s thermal growth of the metallic phase into the bulk.

The study of photoinduced phase transitions in strongly correlated systems[1,2] with time-resolved spectroscopy is an important research direction in condensed matter physics. Impulsive optical excitation of the system can lead to formation of the product phase along nonequilibrium, possibly vibrationally coherent, physical pathways. Probing the transient behavior of the system as it is undergoing its phase change provides insight into the underlying, microscopic physics, which is sometimes hidden in time-integrated measurements. However, the amount of quantitative information that can be extracted from measurements at visible wavelengths is limited, motivating interest in short-pulse x-ray spectroscopy. To date, scientific applications of ultrafast x rays have concentrated primarily on time-resolved diffraction measurements. This has been driven in part by developments in tabletop plasma sources,[3,4] early laser–*e*-beam interaction schemes,[5,6] fast x-ray detectors,[7] and synchrotron instrumentation.[8] Direct detection of photoexcited coherent acoustic[9–11] and optical[12] phonons, solid-liquid[13–15] and solid-solid[16,17] phase transitions has been recently demonstrated.

X-ray absorption spectroscopy techniques are important complements to diffraction, particularly for systems where large changes in the electronic and magnetic structure are concomitant with atomic-structural rearrangements. In the strongly correlated transition metal oxides, there is important interplay between electronic and atomic structure that can be elucidated by time-resolved near-edge x-ray absorption spectroscopy.[18] Near-edge measurements probe unoccupied valence states by measuring transitions from core levels, rather than from extended occupied valence states as in visible spectroscopy. Element specificity, symmetry selection rules, and linear or circular dichroic effects are some of the most powerful aspects of this technique. To date, due to the stringent tunability requirements on the source, time-resolved spectroscopy with soft x rays has been demonstrated only on the picosecond time scale for melting of semiconductors[19] and for selected cases of gas[20] and liquid phase[21] photochemistry.

Here, we report on ultrafast soft x-ray absorption mea-surements of the insulator-to-metal transition in photoexcited VO$_2$. This nonmagnetic compound undergoes a transition between a monoclinic insulator and a rutile metal when heated above 340 K. The nature of the insulating ground state is quite controversial and is attributed to a delicate balance between electron-electron correlations (characteristic of Mott-Hubbard insulators) and long-range structural symmetry (characteristic of band insulators).[22,23] Ultrafast optical[24] and x-ray diffraction[16] experiments on the photoinduced transition in VO$_2$ show that changes in both atomic and electronic structure occur on the subpicosecond time scale, where their detailed relationship is yet to be fully understood. Thus, ultrafast spectroscopy tools for the direct measurement of electronic structure are necessary. The spectral region of interest is around 500 eV, encompassing the vanadium L edges and the oxygen K edge. This spectral range is poorly covered by high-order harmonics or plasma sources. The present work demonstrates measurements of the insulator-to-metal transition with 70 ps resolution using tunable pulses of synchrotron radiation, an important step toward future experiments on the femtosecond time scale.[25]

First, we characterized the ultrafast response of VO$_2$ by means of femtosecond optical measurements, which we briefly summarize here as supporting evidence for the time-resolved x-ray experiments. Thin films of vanadium dioxide on Si(111) wafers, with a 200 ± 10 nm silicon nitride buffer layer were used for the experiments. The transport properties of the films evidenced a thermally induced metal-insulator transition around 340 K, characteristic of VO$_2$. Resistivity changes of two orders of magnitude were observed. Powder x-ray diffraction exhibited dominant peaks from the VO$_2$ lattice spacing. Weaker and broader peaks corresponding to V$_2$O$_5$ were also found, indicative of a sample composed of approximately 70% VO$_2$ and 30% V$_2$O$_5$, with microcrystallites of different size distributions.

The optical reflectivity response of 50- and 200-nm-thick films is reported in Fig. 1. The experiments were performed in pump-probe geometry at near-normal incidence, using 100 fs laser pulses at the fundamental wavelength of Ti:sapphire
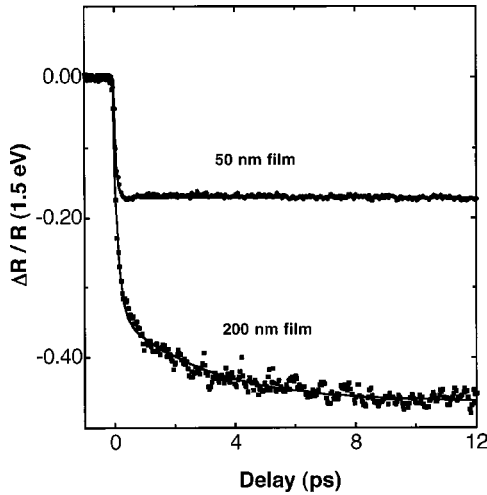
FIG. 1. Time-resolved change in the reflectivity of nonetched, 50 and 200 nm VO$_2$ films, grown on a silicon substrate with a 200 nm Si$_3$N$_4$ buffer layer. The optical response indicates a subpicosecond transition in the optical properties of the VO$_2$ film. A slower response occurring at longer time delays is related to energy thermalization and transformation of layers beneath the surface. The continuous curves are a biexponential fit to the data. The response of the 50 nm film could be fitted with a single exponential with a 90 fs time constant, whereas that of the 200 nm film yielded two time constants of 100 fs and 2.9 ps.

(790 nm). A lock-in amplifier was used to measure changes in the VO$_2$ optical properties with high accuracy. The pump spot was significantly larger than the probe, ensuring homogeneous excitation in the interrogated area. Pump and probe polarizations were crossed to minimize coherence artifacts near time zero. The reported changes in the optical reflectivity were measured at a photoexcitation fluence of 50 mJ/cm^2, i.e., well in excess of the 10 mJ/cm^2 threshold for the photoinduced insulator-to-metal transition. In the fluence regime between 25 and 80 mJ/cm^2 (damage threshold), the optical response was observed to saturate and did not vary with fluence. Because V$_2$O$_5$ does not exhibit a phase transition and does not absorb laser light at 1.5 eV, photoinduced changes reported here relate only to polycrystalline VO$_2$ with inert inclusions.

At early times, a subpicosecond decrease in the reflectivity is observed in both films, consistent with a transformation between the optical properties of the low-T ($n = 2.9$, $k = 0.5$) and those of the high-T phase ($n = 2.3$, $k = 0.72$). In the 50 nm films, significantly thinner than the 120 nm penetration depth of the excitation or probing light, no dynamics on the picosecond time scale is observed, indicative of a prompt transformation of the whole film. The reflectivity of the metallic state is preserved for tens of nanoseconds, due to thermalization of the system in the high-T phase and slow return to the low-T semiconductor via heat diffusion and nucleation. The thicker, 200 nm film shows a two-step response toward the long-lived metallic phase. After the initial 35% drop, a slower 10% decrease of the reflectivity with 3 ps time constant is observed. The evolution of the reflectivity on the picosecond time scale is likely related to dynamics in the regions of the film immediately beneath the promptly trans-

formed surface volume. However, due to the complicated interplay between excitation, thermalization, and coherent acoustic response with depth-dependent excitation, a quantitative interpretation is difficult. Based on the 45% drop in reflectivity, the transformed thickness at 5–10 ps time delay can be estimated by calculating the expected optical response of a four-layer structure, composed of a metallic surface layer of thickness Δx, a nontransformed semiconducting layer of thickness (200 nm$-\Delta x$), a 200 nm Si$_3$N$_4$ buffer layer, and a semi-infinite bulk silicon substrate. This analysis shows that in the 200 nm film the formation of the metallic phase occurs over a thickness Δx of approximately 70 nm or higher. However, due to the limited penetration depth of the probe light (120 and 90 nm for the semiconducting and metallic phases, respectively), and to thin-film effects, it is not possible to assign the thickness Δx uniquely. Furthermore, this value is affected by the exact thickness of the Si$_3$N$_4$ buffer layer, which we know within 10%. Thus, the optical measurements on the 200 nm film indicate only the prompt formation of the metallic phase over a thickness Δx, for which we can assess a lower limit of approximately 70 nm. At later times, we expect the nontransformed volume in the region beneath the sample to reach temperatures equal to or in excess of the transition temperature (340 K) and to be transformed thermally via nucleation and growth. The speed of such thermal transformation is expected to be significantly lower than for the photoinduced phase change, i.e., at growth velocities of the order of tens to hundreds m/s, depending on the degree of superheating of the interface. No information on this slower process can be retrieved based on the optical reflectivity data.

Static x-ray absorption spectroscopy (XAS) experiments were performed at beamline 6.3.2 of the Advanced Light Source (ALS). The absorption spectrum around the vanadium $L_{3,2}$ edges and the oxygen K edge was measured for the two phases with 100 meV resolution [Fig. 2(a), continuous curve]. These measurements were performed in transmission geometry through free-standing Si$_3$N$_4$/VO$_2$ windows, created by removing the silicon substrate with a combination of room-temperature etching using CP4A (acetic acid, HF, and HNO$_3$ in a 3:3:5 ratio) and KOH at 80 °C. Wax-based protective masks were deposited onto the substrate, while the VO$_2$ front layer was waxed to a sapphire plate, protecting it from the etchant. The transmission spectra are shown in Fig. 2 for two temperatures above and below the 20-K-wide hysteresis cycle, centered around $T_c = 340$ K.

Previous XAS measurements on single-crystal VO$_2$, reported by Abbate *et al.*,[26] evidenced qualitatively similar changes at both vanadium $2p$ and oxygen $1s$ edges due to the metal-insulator transition. However, the relative weight of the π^* and σ^* resonances near the O $1s$ absorption edge appears different in the films used here when compared with that measured in single crystals by Abbate *et al.* This is related to the polarized nature of the x rays and the use of polycrystalline samples in the experiments reported here. In particular, anisotropic absorption is expected in single crystals, due to transitions between O $1s$ states and directional σ^* and π^* orbitals. This effect is averaged in our experiments. XAS measurements on commercially available,
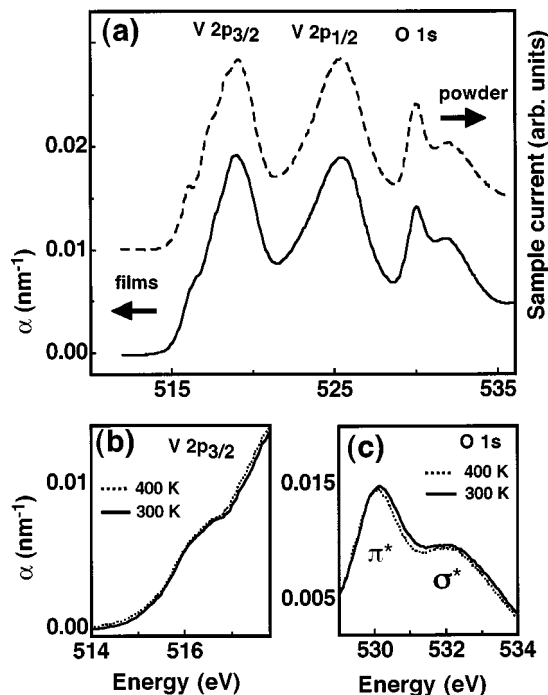
FIG. 2. Static, VO_2 x-ray absorption spectra in the region around the V, $L_{2,3}$ and the O K edge. (a) Continuous curve: Transmission XAS spectra from free-standing, 200 nm VO_2/200 nm Si_3N_4 structures. Dashed curve: Spectra taken on commercial VO_2 powder. The resolution is 100 meV. (b), (c) Spectral changes at the V L edge and the O K edge observed above 340 K.
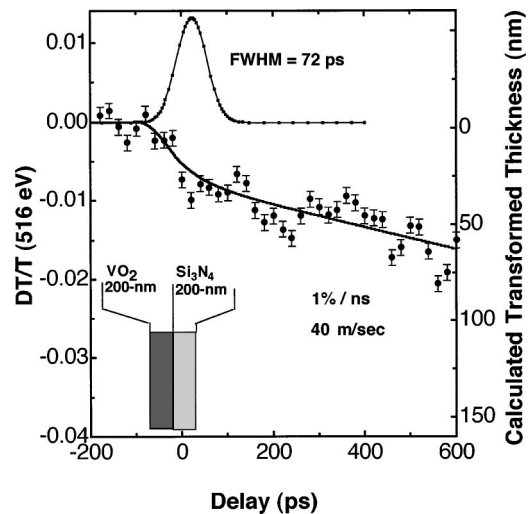

FIG. 3. Time-resolved transmission changes at the vanadium L_3 edge. The data are fitted with a two-time-scale model, obtained by convolving a rapid and a slow response with the duration of the 70 ps x-ray pulse, as measured by cross correlation of the laser with the visible part of the synchrotron radiation spectrum.

99.9% pure VO_2 powders [reported in Fig. 2(a), dashed curve] were performed at beamline 9.3.2 of the ALS with similar resolving power as those performed in transmission. They show very good agreement with the transmission measurements on our films.

Time-resolved XAS was used to measure the dynamics of the insulator-to-metal transition at the vanadium L_3 edge. The experiments were performed using bend magnet radiation at beamline 5.3.1 of the ALS. The storage ring was filled in a "camshaft" pattern consisting of 278 electron bunches at 2 ns intervals, followed by a 100-ns-long dark window which contained a single, isolated bunch at the center of the window. 70-ps-long x-ray pulses were radiated by a bend magnet and focused onto the VO_2 sample using a toroidally bent silicon mirror, which imaged the e beam in the storage ring into the x-ray hutch. A mechanical chopper operating at 1 kHz was used to eliminate approximately 96% of the x-ray flux. A fraction of the isolated camshaft pulses, radiated once every 656 ns (round trip time of the storage ring), were used for our experiments at 1 kHz repetition rate. A flat-field imaging spectrometer was used to disperse the transmitted soft x rays after the sample, generating spectra in the range between 100 and 800 eV, with a resolution of approximately 4 eV at 500 eV. The spectra were detected using either a gated microchannel plate–phosphor–charge-coupled device assembly or using an avalanche photodiode in the image plane for single wavelength detection. The excitation laser was synchronized to the storage ring within better than 2 ps.

Time-resolved, differential XAS measurements were per-

formed by delaying the laser with respect to the x-ray probe pulse over a 1 ns time interval. An x-ray pulse transmitted through the unperturbed sample 656 ns before the pump pulse was used as reference. The data at the vanadium L_3 edge show the expected decrease in the transmission of the sample, due to the collapse of the band gap. It is important to point out that because of selection rules the L_3 edge shift is sensitive primarily to the dynamics of the unoccupied orbitals of d symmetry, in contrast with measurements performed at visible wavelengths, which measure the joint density of states and are less sensitive to symmetry, due to band mixing. The time-resolved data in Fig. 3 are fitted (solid line) with a fast response corresponding to $\Delta T/T = 1\%$, followed by a slower decrease at a rate of approximately $1\%/ns$. The cross-correlation measurement shown in the figure was obtained by mixing visible pulses of synchrotron radiation with the 100 fs pump-laser pulses in a nonlinear optical crystal, a procedure that allows for monitoring of laser–x-ray synchronization and duration of synchrotron pulses while acquiring the data. In the static temperature-dependent XAS experiments of Fig. 2, an 8% maximum transmission drop is observed for 100 meV resolution and 200 nm transformed thickness, which corresponds to approximately 5% for 4 eV spectral resolution in the time-resolved experiments. Since the thickness of the transformed layer scales linearly with the signal, we conclude that a fast transformation over approximately the first 50 nm occurs within the x-ray probe pulse, followed by slower thermal growth at 40 m/s. The 50 nm transformation depth extracted from the x-ray data is consistent with the 70 nm depth estimated from the optical data.

In summary, we report picosecond, soft x-ray absorption measurements of a photoinduced insulator-to-metal transition in a strongly correlated compound. The shift of the vanadium L_3 edge, associated with the collapse of the band gap, is observed directly and is shown to evolve on two different time scales. The prompt component is attributed to

the direct photoinduced insulator-to-metal transition over a sample thickness determined by the absorption depth of the excitation pulse. The slower component originates from thermal growth of the metallic phase over the entire sample thickness at 40 m/s. Because of the reversibility of the experiment and the relatively large size of the effect, this experiment will nucleate future investigations using femtosecond pulses of synchrotron radiation from laser-modulated electron bunches. Foreseeable improvements in the available x-ray flux and spectral resolution of the experimental apparatus will also allow for energy-resolved spectroscopic measurements on the femtosecond time scale. These experiments will provide additional information, especially by probing the fundamental transition times at both V $2p$ and O $1s$ edges, where the electronic structure may exhibit distinct dynamics.

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