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Picosecond Soft X-ray Absorption Measurement of the Photo-induced Insulator-to-metal Transition in VO_2.

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Abstract

We directly measure the photo-induced 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 red-shift in the Vanadium L_3 edge at 516 eV, which is associated with the transient collapse of the low-Temperature bandgap. We identify a two-component temporal response, corresponding to an ultrafast transformation over a 50-nm surface layer, followed by 40-m/sec thermal growth of the metallic phase into the bulk.

The study of photo-induced 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 non-equilibrium, possibly vibrationally coherent physical pathways. Probing the transient behavior of the system as it is undergoing its phase change provides new 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 photo-excited coherent acoustic[9,10,11] and optical phonons[12], solid-liquid[13,14,15] and solid-solid[16,17] phase transitions have 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/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 timescale for melting of semiconductors[19] and for selected cases of gas[20] and liquid phase photochemistry[21].

Here, we report on ultrafast soft x-ray absorption measurements of the insulator-to-metal transition in photo-excited VO_2. This non-magnetic 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 experiments[16] on the photo-induced transition in VO_2 show that changes in both atomic and electronic structure occur on the sub-picosecond timescale, 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 timescale[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 nm ± 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_2O_5 were also found, indicative of a sample composed by approximately a 70% VO_2 and 30% V_2O_5, with micro-crystallites of different size distribution.

The optical reflectivity response of 50-nm and 200-nm thick films is reported in figure 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 (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 photo-excitation fluence of 50 mJ/cm^2, i.e. well in excess of the 10-mJ/cm^2 threshold for the photo-induced insulator-to-metal transition. In the fluence regime between 25 mJ/cm^2 and 80 mJ/cm^2 (damage threshold) the optical response was observed to saturate and did not vary with fluence. Because V_2O_5 does not exhibit a phase transition and does not absorb laser light at 1.5 eV, photo-induced changes reported here relate only to polycrystalline VO_2 with inert inclusions.

At early times, a sub-picosecond 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/probing light, no dynamics on the picosecond timescale is observed, indicative of a prompt transformation of the whole

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film. The reflectivity of the metallic state is preserved for tens of nanoseconds, due to thermalisation 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-timescale is likely related to dynamics in the regions of the film immediately beneath the promptly transformed 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 non-transformed semiconducting layer of thickness (200 nm - Δx), a 200-nm Si_3N_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 over a thickness Δx of approximately 70 nm or higher. However, due to the limited penetration depth of the probe light (120 nm and 90 nm for the semiconducting and metallic phase, 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_3N_4 buffer layer, which we know within 10%. Thus, the optical measurements on the 200-nm film only indicate 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 non-transformed volume in the region beneath the sample to reach temperatures equal 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 the photo-induced phase change, i.e. at growth velocities of the order of tens to hundreds m/sec, 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 XAS experiments were performed at beamline 6.3.2 of the *Advanced Light Source*. 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 (figure 2a, continuous curve). These measurements were performed in transmission geometry through free-standing Si_3N_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 ^{O}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 figure 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 O1s absorption edge appears different in the films used here when compared with what 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 O1s states and directional π^* and $\overset{*}{\sigma}$ orbitals. This effect that is averaged in our

experiments. XAS measurements on commercially available, 99.9%-pure VO_2 powders (reported in figure 2a, 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 "cam-shaft" 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 cam-shaft pulses, radiated once every 656 ns (roundtrip 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 eV and 800 eV, with a resolution of approximately 4 eV at 500 eV. The spectra were detected using either a gated MCP (Micro Channnel Plate)-Phosphor-CCD (Charge Coupled Device) assembly or using an avalanche photo-diode 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 performed 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 bandgap. 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 figure 3 are fit (solid line) with a fast response corresponding to $\Delta T/T \approx 1\%$, followed by a slower decrease at a rate of approximately 1%/ns. The cross-correlation measurement shown in the figure has been 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 static temperature-dependent XAS experiments of figure 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/sec. 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 the first picosecond, soft X-ray absorption measurements of a photo-induced insulator-to-metal transition in a strongly correlated compound. The shift of the Vanadium L_3 edge, associated with the collapse of the bandgap, is observed

directly and is shown to evolve on two different timescales. The prompt component is attributed to the direct photo-induced 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/sec. 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 timescale. These experiments will provide new information, especially by probing the fundamental transition times at both V 2p and O 1s edges, where the electronic structure may exhibit distinct dynamics.

FIGURE CAPTIONS

Figure 1: Time resolved change in the reflectivity of non-etched, 50-nm and 200-nm VO_2 films, grown on a Silicon substrate with a 200-nm Si_3N_4 buffer-layer. The optical response indicates a sub-picosecond transition in the optical properties of the VO_2 film. A slower response occurring at longer time-delays is related to energy-thermalization/transformation of layers beneath the surface. The continuous curves are a bi-exponential fit to the data. The response of the 50-nm film could be fit 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.

Figure 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 Ledge and the O K edge observed above 340 K.

Figure 3: Time-resolved transmission changes at the Vanadium L_3 edge. The data are fit with a two-timescale 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.
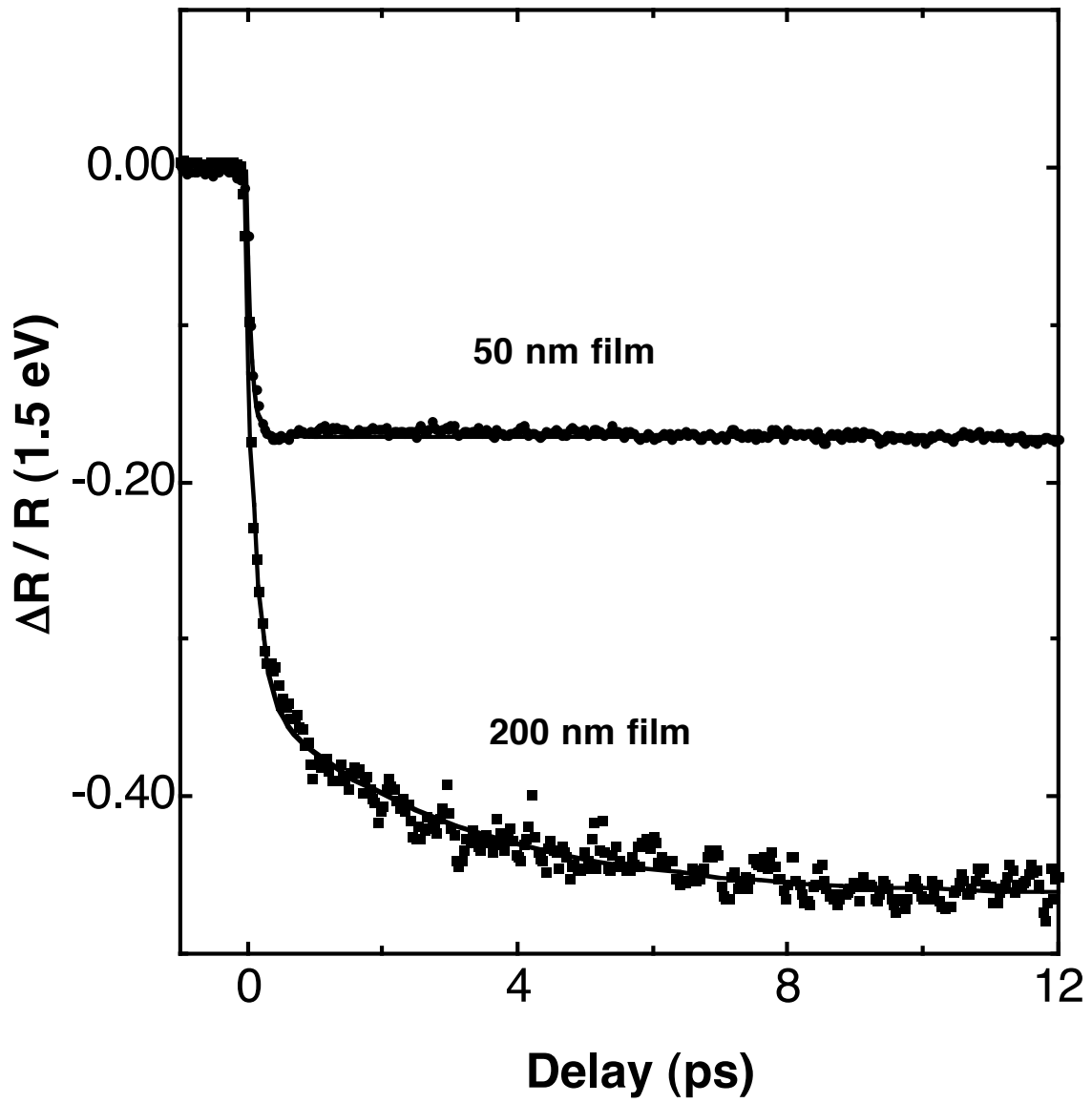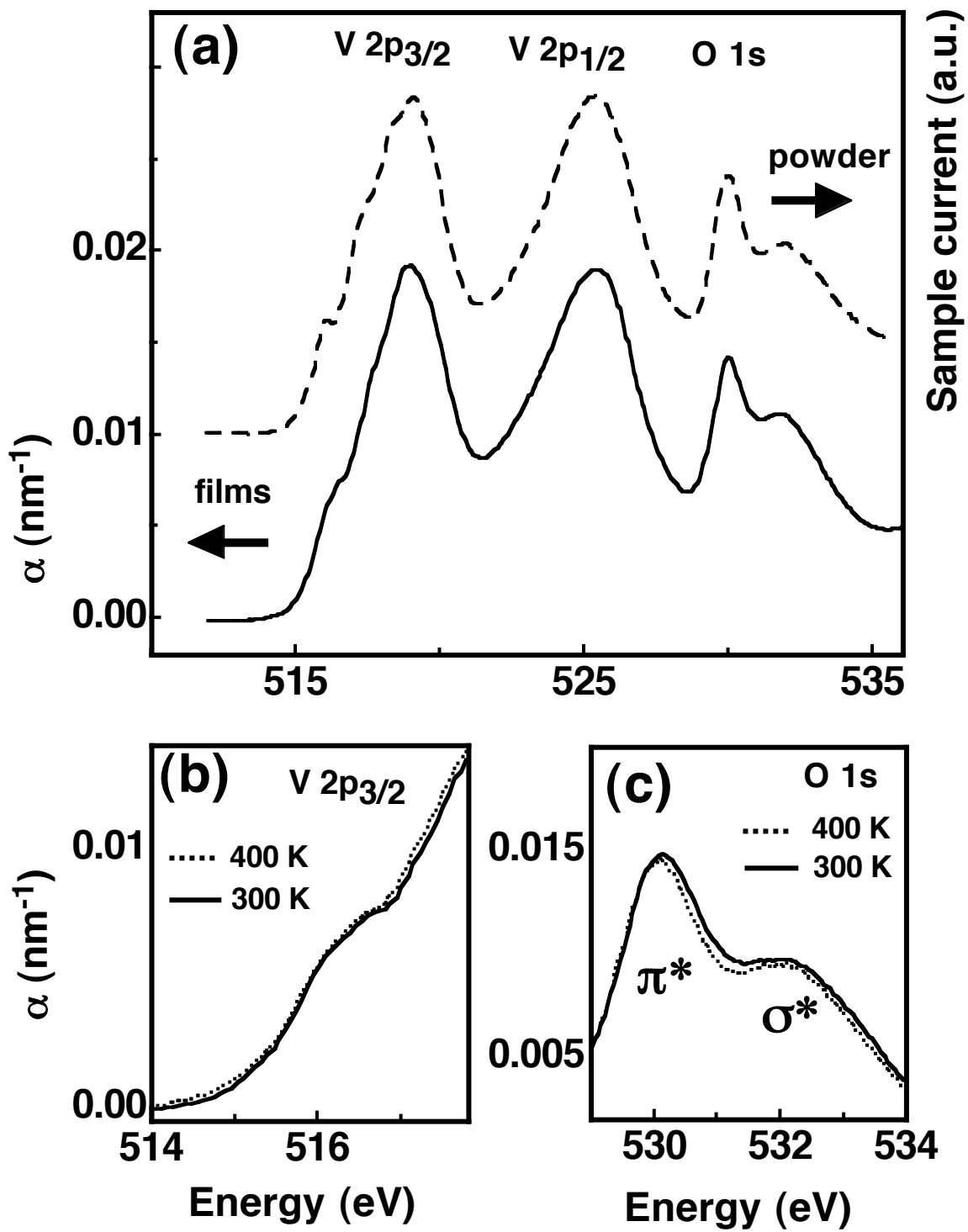
50 nm film

200 nm film

Figure 1

(a) V 2p$_{3/2}$ V 2p$_{1/2}$ O 1s

powder

α (nm^{-1})

films

Sample current (a.u.)

0.02

0.01

0.00

515   525   535

(b) V 2p$_{3/2}$

0.01

0.00

·········· 400 K
——— 300 K

514   516

(c) O 1s

0.015

0.005

·········· 400 K
——— 300 K

π^*

σ^*

530   532   534
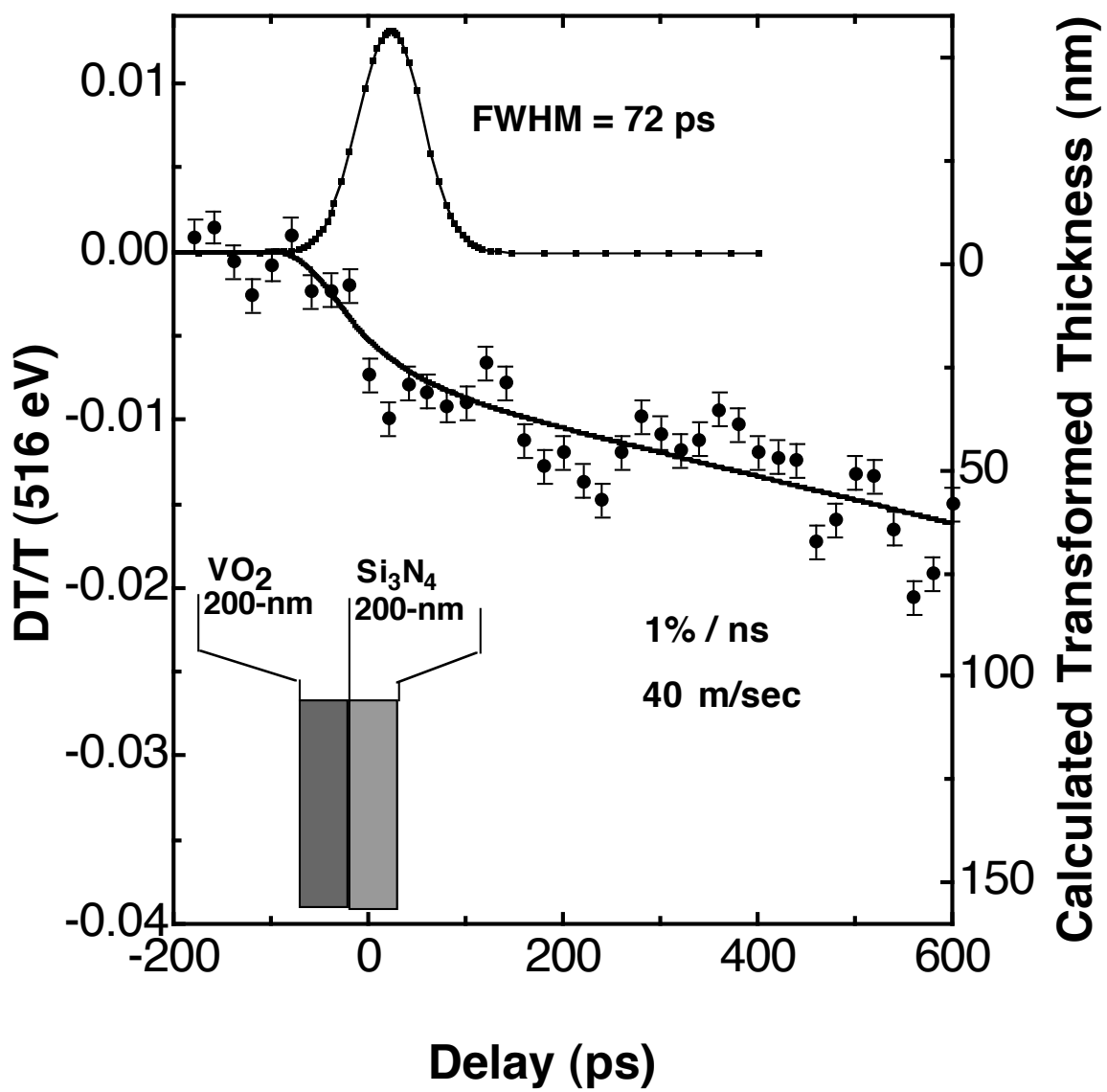
Energy (eV)   Energy (eV)

Figure 2

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Figure 3

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