

Picosecond Soft X-ray Absorption Measurement of the Photo-induced Insulator-to-metal Transition in VO₂.

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Abstract

We measure the photo-induced insulator-to-metal transition in VO₂ using time-resolved Near-Edge X-ray Absorption. Picosecond pulses of synchrotron radiation are used to detect the red-shift in the Vanadium L₃ edge at 513 eV, which is associated with the collapse of the low-Temperature bandgap. We identify a two-component temporal behavior, corresponding to an ultrafast transformation occurring over a 50-nm surface layer, followed by thermal growth of the metallic phase into the bulk at 40 m/sec.

The study of photo-induced phase transitions with time-resolved spectroscopy is an important research direction in condensed matter physics. Controlled excitation of the system can lead to formation of the product phase along non-equilibrium physical pathways and provide interesting insight into the underlying physics. However, the amount of quantitative information that can be extracted from measurements at visible wavelengths is rather limited, motivating the 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^{1,2}, early laser-e-beam interaction schemes^{3,4}, fast x-ray detectors⁵ and synchrotron radiation pulses⁶. Direct detection of photo-excited coherent acoustic^{7,8,9} and optical phonons¹⁰, solid-liquid^{11,12,13} and solid-solid^{14,15} phase transitions have recently been demonstrated.

X-ray spectroscopy techniques are important complements to diffraction, particularly for systems where important changes in the electronic and magnetic structure are concomitant with atomic-structural rearrangements. In the strongly-correlated transition metal oxides, there is strong interplay between electronic and atomic structure that can be elucidated by Near-edge X-ray Absorption Spectroscopy¹⁶. 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 tunability requirements on the source, time-resolved soft XAS has been demonstrated only on the picosecond timescale for melting of semiconductors¹⁷ and for selected gas¹⁸ and liquid^{19,20} phase photochemistry.

Here, we report on ultrafast soft x-ray absorption measurements of the insulator-to-metal transition in photo-excited VO₂. This non-magnetic compound undergoes a transition between a monoclinic insulator and a rutile metal when heated above 340 K. The nature of the semiconducting ground-state is quite controversial and encompasses a delicate balance between electron-electron correlations (characteristic of a Mott-Hubbard insulator) and long-range structural symmetry (characteristic of band insulator)^{21,22}. Ultrafast optical and x-ray diffraction experiments on the photo-induced transition in VO₂ show that changes in both atomic and electronic structure occur on the sub-picosecond timescale, where the detailed relationship between atomic motion and renormalization of the electronic structure is yet to be fully understood. Thus, new ultrafast tools for the direct measurement of the latter 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 timescale²³.

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 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 the fundamental wavelength of the Ti:Sapphire laser (790 nm). A lock-in amplifier was used to measure changes in the VO₂ optical properties with high accuracy. The pump beam diameter was reduced before the focusing lens, resulting in a pump spot radius significantly larger than the probe and ensuring a 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 properties of the system were measured at a photo-excitation fluence of 50 mJ/cm^2 . At early times, a sub-picosecond decrease in the reflectivity is observed in both films, indicative of a transformation between the optical properties of the low-T phase ($n=2.9$, $k=0.5$) and those of the High-T ($n=2.3$, $k=0.72$).

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, suggestive of a prompt and complete transformation of the whole film to the metallic phase. On the other hand, the thicker 200-nm film shows a two step response, with a further decrease of the reflectivity with 3-ps time constant after the initial 35% drop. The picosecond-timescale evolution of the reflectivity is likely related to dynamics in the regions of the film beneath the excited surface. However, due to the complicated interplay between excitation, thermalization and coherent acoustic response over a non-homogeneously excited region, a quantitative interpretation is difficult. Based on the 35% drop in reflectivity, the transformed thickness 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 $(200 \text{ nm} - \Delta x)$ for the, 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 50 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. Thus, the optical measurements on the 200-nm film indicate the formation of the metallic phase over a thickness Δx of at least 50 nm.

XAS experiments were then performed by taking advantage of bend-magnet radiation at the *Advanced Light Source*. In a first set of experiments (figure 2), the static absorption spectrum around the Vanadium $L_{3,2}$ edges (513 and 519 eV) and the Oxygen K edge (543 eV) was measured for the two phases. In these experiments, performed at beamline 6.3.2 of the ALS, 50-meV resolution spectra were taken in transmission geometry. For the transmission XAS experiments, windows of ~ 1 mm were created by removing the Silicon substrate from the samples with a combination of room-temperature etching using CP4A (acetic acid, HF and HN O_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 figure 2 for two temperatures across the transition temperature and on either side of the 50-K wide hysteresis cycle. As previously reported by Abbate et al.²⁴ in XAS measurements from single-crystal VO_2 , the metal-insulator transition is evidenced by changes at both V 2p and O 1s edges, which are associated with the collapse of the bandgap. There is good qualitative agreement between the two sets of measurements, however, the relative weight of the π^* and σ^* resonance near the O1s absorption edge appears different than that observed by abate et al. This is likely related to the fact that our experiments are performed in transmission in polycrystalline films, as opposed to total yield photo-emission in single crystals. Due to the bulk sensitivity of transmission experiments, we exclude the influence of oxygen or water contamination in the measured O1s edge.

Time-resolved XAS was used to measure the shift of the Vanadium L 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. The train of x-rays was focused onto the VO₂ sample using a toroidally bent silicon mirror, imaging the e-beam in the storage ring into the experimental area. A mechanical chopper operating at 1 Khz was used to eliminate approximately 98% of the x-ray flux, leaving 50-μsec windows. 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 3 eV. The spectra were detected either using a CCD camera with a gated MCP (Micro Channel Plate)-Phosphor assembly or using an avalanche photodiode in the image plane (single wavelength detection). In either case, the isolated x-ray pulses served as 70-ps long x-ray probe pulses. The excitation laser was synchronized to the storage ring within better than 2-ps.

.....XAS measurements were performed by mutually delaying laser and x-ray pulses over a 1-ns time interval and measuring differential transmission between pairs of x-ray pulses that interacted with the sample in coincidence with the laser (pumped) or arrived 656 ns earlier to provide a reference probe of the unperturbed sample. The data show the expected decrease in the transmission of the sample, due to the creation of states within the gap. It is important to point out that because of selection rules, the L₃ edge shift is sensitive primarily to the dynamics of the unoccupied orbitals of d

symmetry, in contrast with measurements performed at visible wavelengths, which are sensitive to 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 $\Delta T/T=1\%$, followed by a slower decrease at a rate of approximately 1%/ns. In the temperature-driven XAS experiments of figure 2, an 8% maximum transmission drop is observed for 50-meV resolution and 200-nm transformed thickness, which corresponds to approximately 5% for 3-eV resolution. The thickness of the transformed layer extracted from the data is shown on the left axis in figure 3, where a fast transformation over the first 50-nm occurs within the x-ray probe pulse, followed by slower thermal growth at 40 m/sec. The transformation depths are consistent with the estimates from the optical data.

In conclusion, we report a picosecond, soft X-ray absorption measurements of a photo-induced insulator-to-metal transition in VO₂. The shift of the V L-edge, associated with the collapse of the semiconducting bandgap, is observed directly and is shown to evolve on two different timescales, associated with different depths in the film. 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 is attributed to 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 flux and 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 evolution of the electronic structure may exhibit distinct dynamics.

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FIGURE CAPTIONS

Figure 1: Time resolved change in the reflectivity of non-etched, 50-nm and 200-nm VO₂ films, grown on a Silicon substrate with a 200-nm Si₃N₄ buffer-layer. The optical response indicates a sub-picosecond transition in the optical properties over a fraction of the VO₂ film, corresponding to 50-nm or more. A slower response occurring at longer time-delays is related to energy-thermalization/transformation of layers beneath the surface. The existence of acoustic effects makes the interpretation of the slower behavior challenging and not unique. Experiments performed on 50-nm films, exhibit only the fast, sub-100 fs component, confirming this effect.

Figure 2: Static x-ray absorption spectra of VO₂ in the region around the V L_{2,3} and the O K edge. The experiments are performed on 200-nm VO₂ films on 200-nm thick Si₃N₄ free-standing windows. The resolution of the measurement is 50 meV. A shift in both V Ledges and O Kedges is associated with the closure of the semiconducting bandgap.

Figure 3: Time-resolved transmission changes at the Vanadium L₃ 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.

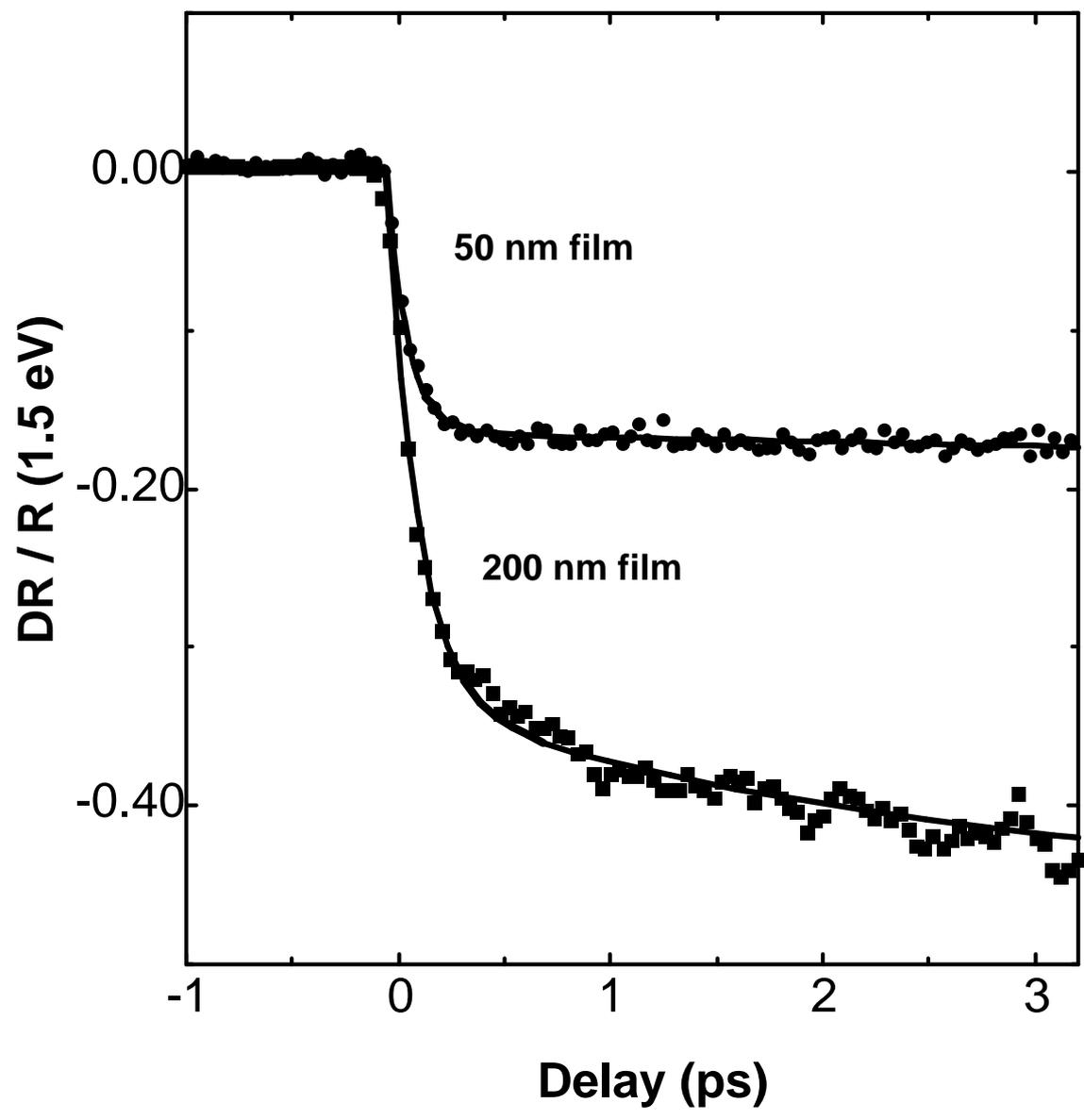


Figure 1

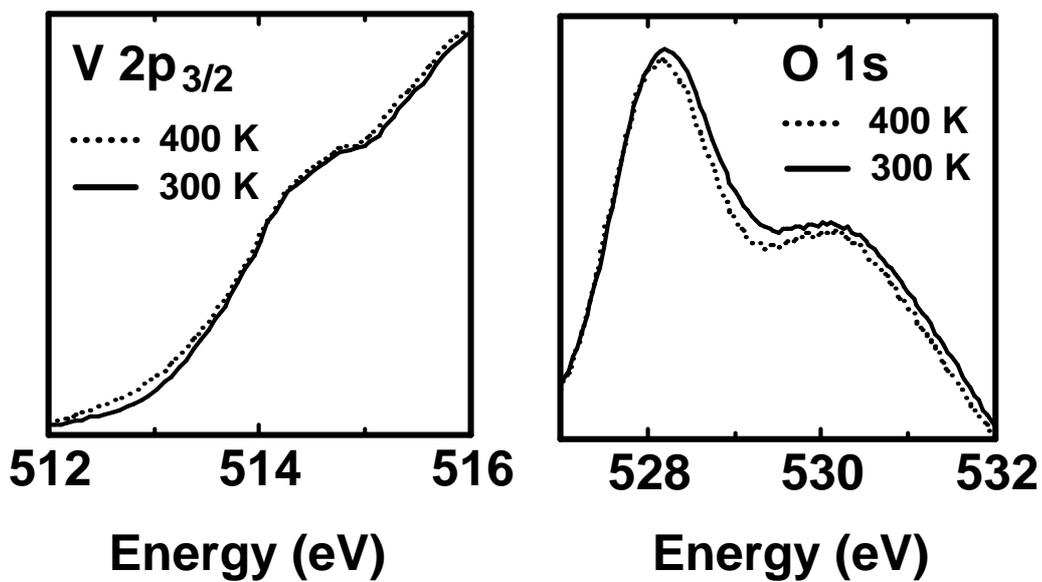
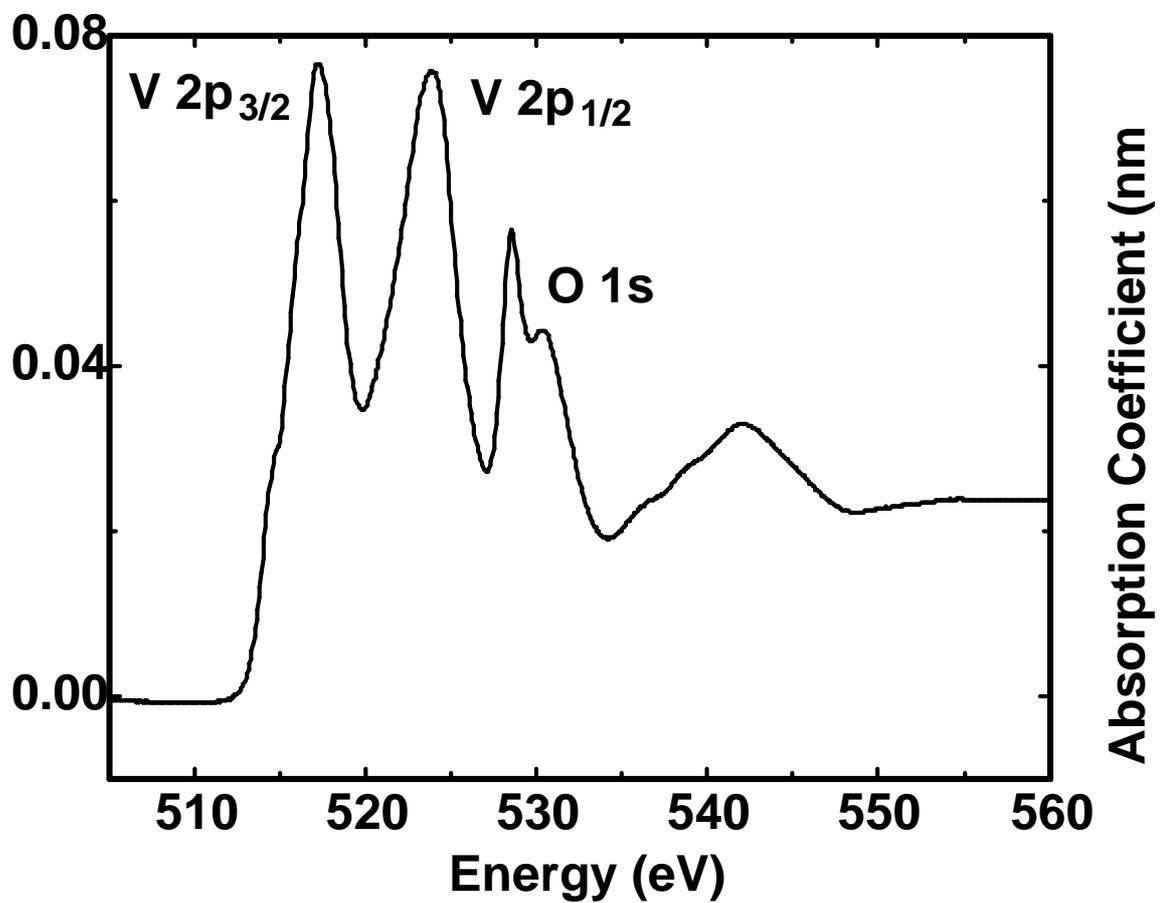


Figure 2

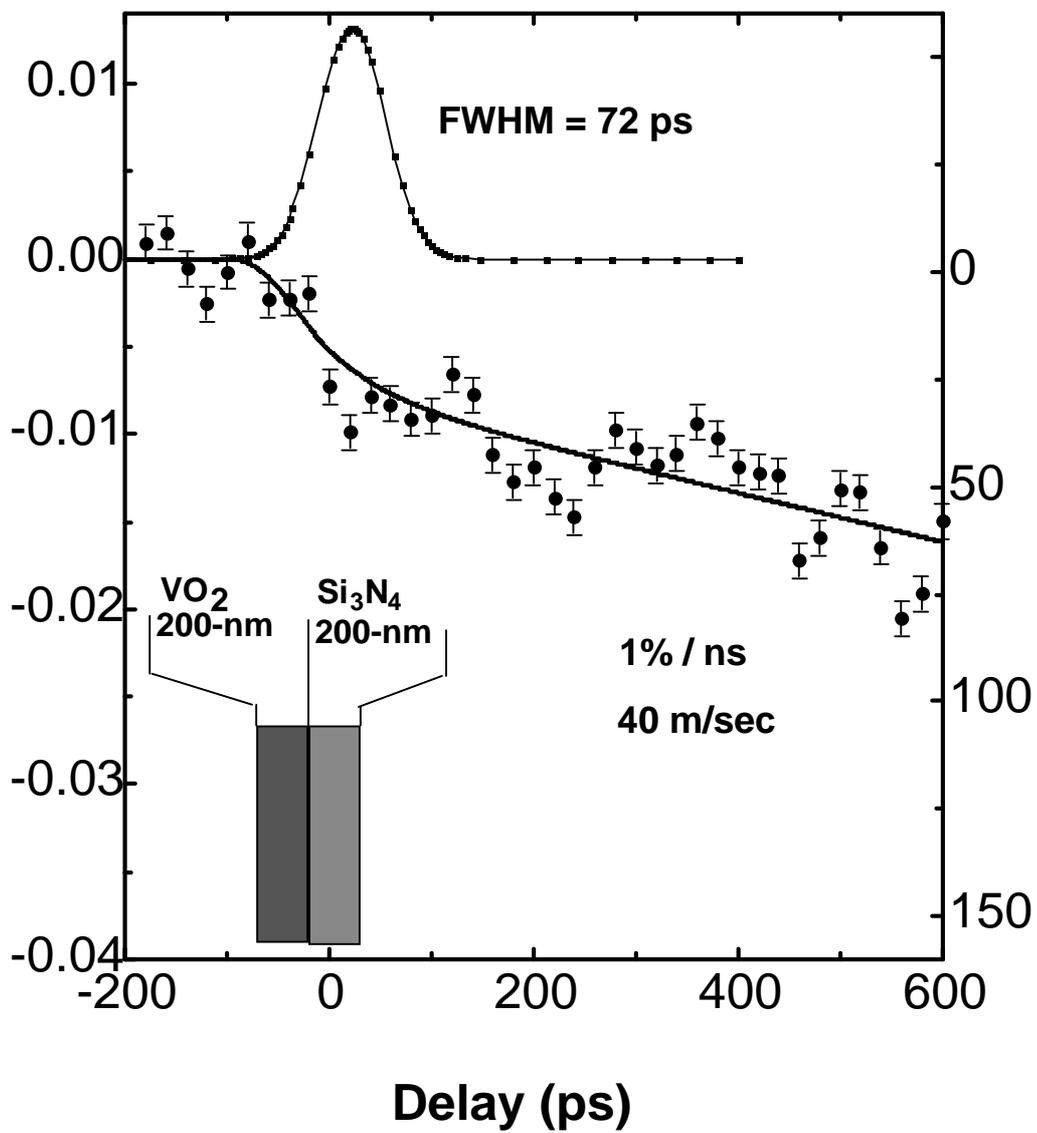


Figure 3

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