Irreversible metal-insulator transition in thin film VO₂ induced by soft X-ray irradiation

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Abstract: In this study, we show the ability of soft x-ray irradiation to induce a room temperature metal-insulator transitions (MIT) in VO₂ thin films grown on *R*-plane sapphire. The ability of soft x-rays to induce the MIT in VO₂ thin films is confirmed by photoemission spectroscopy and soft x-ray spectroscopy measurements. When irradiation was discontinued, the systems do not return to the insulating phase. Analysis of valence band photoemission spectra revealed that the density of states (DOS) of the V 3*d* band increased with irradiation time, while the DOS of the O 2*p* band decreased. We use these results to propose a model in which the MIT is driven by oxygen desorption from thin films during irradiation.

Introduction: As a strongly correlated transition metal oxide, VO₂ is an interesting and valuable material both for expanding our understanding of fundamental physics and for potential applications due to its particular metal–insulator transition (MIT). At 340K, the resistance of bulk VO₂ exhibits a large jump (up to 5 orders of magnitude), accompanied by first order crystal phase transition from a room temperature monoclinic phase to a high temperature tetragonal phase [1-2]. The origin of the MIT has been widely discussed since electron–phonon interaction (Peierls type) or electron–electron interaction (Mott–Hubbard type) could play a key role to induce the occurrence of the MIT [3-7]. Furthermore, these characteristics of VO₂ material make it suitable for applications in many fields such as sensors, memory devices, photoconductive infrared detectors, smart windows, and optical switching devices such as terahertz modulators [8-15].

 VO_2 does have a relatively high critical transition temperature (T_c) that limits its practical application. Thus modulating the phase transition behavior and decreasing T_c have become important topics that have recently been explored. Various models and approaches to decrease

the T_c value, such as interfacial strain [16-22], hydrogenation [23-24], oxygen vacancies [25-27] and element doping [28-30] have been employed. Among these, it has been shown that interfacial strain has been the most effective way to reduce the T_c to room temperature or lower.

Studies have also been conducted on the photo-induced properties of VO₂, including UV light irradiation (365 nm) [31], hard X-ray irradiation (10 keV) of W doped VO₂ thin films resulting in a persistent MIT at low temperatures [32]. Similar persistent effects have also been observed in VO₂ films with 10 keV X-ray irradiation [33]. Thus, it is clear that the MIT of VO₂ thin films can be tuned by light with photon energies between the meV orders to 10 keV.

In this work, we study the effect of soft x-ray irradiation on the MIT of VO₂ thin films using synchrotron radiation-based photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS). Our measurements suggest that continuous soft x-ray irradiation renders the insulating state metallic in the film. We focus on the effects of soft x-ray irradiation on the valence band structure and map the V 3*d* and O 2*p* partial density of states (*p*DOS) using PES and XAS. The formation of oxygen vacancies in areas exposed to soft x-ray irradiation is proposed as the underlying mechanism. Following the concept of chemistry driven MIT, we show that soft x-ray induced oxygen vacancies can be a key button to tune the MIT behavior for optoelectronic applications.

Methods: Thin films of VO₂ (~100nm) were grown on (0 1 2)-oriented substrates of *R*plane sapphire, as described previously [34]. The films are hereafter referred to as VO₂(100). Xray diffraction (XRD) using monochromatic Cu K_{α} radiation and atomic force microscopy (AFM) were used to characterize the structural properties of VO₂ thin films deposited on *R*-plane sapphire by magnetron sputtering [34]. XRD analysis indicated that the film orientations were along the (100) plane, with a thickness of ~100nm [34]. AFM verified that the films surface morphology was flat and smooth [1]. The MIT temperature was found to be 348K (for VO₂ (100)) using a four-point probe method performed using a physical property measurement system (Quantum Design PPMS) [34].

X-ray absorption and photoemission spectroscopy were performed at beamlines 8.0.1 and 10.0.1, respectively, of the Advanced Light Source, Lawrence Berkeley National Laboratory. To study the effects of soft X-ray irradiation on the MIT via XAS, the samples were exposed to 550 eV X-rays carrying a flux density of ~ 1.5×10^{16} photons s⁻¹cm⁻². XAS spectra were measured in the surface sensitive (~5 nm) total electron yield (TEY) mode. Since X-rays interact

with the materials surface even if this interaction may be very weak. By controlling the flux density one can use the photon-beam to create oxygen vacancies in a thin layer below the surface in a controlled but continuous way. This has been exemplified in a number of publications concerning the use of soft X-ray spectroscopy in the study of metal-oxide systems [34A]. The x-ray beam was perpendicular to the surface of the sample. XAS spectra were calibrated using the O *K*-edge of a TiO₂ rutile reference sample. The spectral resolution was 0.3 eV. Photoemission spectra were collected at room temperature using 55 eV incident photons and calibrated against the 4*f* peaks of metallic gold reference foil in electrical contact with the sample. Effects of soft X-ray irradiation on the MIT were investigated by exposing the samples to 250 eV photons and a flux density of 3×10^{15} photons s⁻¹cm⁻².

Results and discussions: Figure 1 shows valence band spectra of VO₂ (100) thin film following 0 and 60 min exposure times to 250 eV photons. The spectra are similar to our earlier PES measurements of vanadium oxide films and show the characteristic V 3*d* band stretching from 0 to 2.5 eV above the Fermi level (E_F) and a broad O 2*p* band from 2.5 to 10 eV [35-36]. Prior to irradiation, the V 3*d* states are relatively narrow and of lower intensity. The intensity of the V 3*d* states at E_F increases and the leading edge has a ~0.3eV shift toward lower binding energy after 60 min of irradiation. This suggests that a percentage of the material has transitioned from the insulating to the metallic phase. Furthermore, the valence band spectrum collected 60 min after irradiation was discontinued (red line) indicating that the soft X-ray irradiation damage was persistent and that the material undergoes a MIT.

To further investigate the influence of soft x-rays on the MIT, the valence band spectrum of the film was measured at 20-minute-irradiation intervals at particular spot on same sample as shown in Fig 2(a). We observed a finite intensity at E_F after 20 min and increasing until 40 min soft x-ray irradiation intervals of same sample and same particular spot. Thus, this result suggests that a minimum irradiation time is necessary for MIT induced by soft x-ray exposure. Since the spectral area correlates with the density of state (DOS) [37], we have calculated the change in spectral area of the V 3*d* and O 2*p* bands with irradiation time. We also calculated the ratio of the spectral area of V 3*d* to O 2*p* DOS obtained from valence band PES as a function of irradiation time. This is shown in Fig. 2(b). If we consider the ratio between the area of O 2*p* and V 3*d* states, it becomes apparent that irradiation is causing oxygen to desorb. It is observed that the DOS for V 3*d* increases due to a decrease in oxidation state of V, while the DOS for O 2*p*

decreases as a result of being freed from the lattice. At an exposure time of 40 minutes, oxygen desorption has reached its limit, as signified by the plateau in the peak area of Fig 2(b). This steady state indicates a saturation of the V 3*d* DOS.

The metallic phase induced by soft x-ray irradiation can be understood by examining the V 3*d* states. The lower part of Fig. 2(c) shows the valence band spectra near E_F at irradiation times 0 and 60 min. For comparison VO₂ thin films spectra near E_F are also shown in Fig 2(c) for both low-temperature (T~300K) insulating phase and high-temperature (T~380K) metallic phase. Our results indicate that as irradiation time is increasing, the shape of V 3*d* band changes and the spectral weight is transferred from a binding energy of about 0.3eV to a region near the Fermi level. This change in the shape of the spectra that coincides with the MIT cannot be explained by a rigid band model, where only the position of the Fermi level shifts without any change in shape of DOS when the number of electrons is varied. The observed temperatureinduced spectra (upper panel in Fig. 2c) appear to be similar to that of photo-induced spectra at low-temperature. These results indicate that irradiation can induce a metallic state that is equivalent to a temperature induced metallic state.

To confirm the possibility of oxygen desorption during soft x-ray irradiation suggested by our PES measurements, we carried out another independent experimental study. Here, we used XAS in the surface-sensitive TEY mode to measure changes in the V $L_{3,2}$ - and O K-edge of the VO₂ thin films. The lower spectrum of Fig. 3(a) shows V $L_{3,2}$ and O K-edge XAS spectra for VO₂(100) thin film recorded at room-temperature prior to irradiation [38]. The absence of any shift in the bulk sensitive mode V $L_{3,2}$ spectra (not shown here) indicates that the vanadium ions in VO₂ thin films are in the expected V⁴⁺ oxidation state, with no indications of mixed valence states in either the surface-sensitive and bulk-sensitive modes. These spectra are also consistent with shape and peak positions from previous studies [38] which also confirm the purity of the VO₂ thin film.

To further probe the effects of soft x-ray irradiation with higher flux density on the electronic structure of VO₂ thin film, we performed V $L_{3,2}$ - and O K-edge XAS as a function of x-ray irradiation time in both; surface and bulk sensitive TEY and TFY mode, respectively. For XAS measurement we used same sample at different spot than PES measurements. Figure 3(a) shows V L-edge and O K-edge absorption spectra for VO₂ thin film following 0 and 60 minutes exposure times to 550 eV x-rays carrying a flux density of 1.5×10^{16} photons s⁻¹cm⁻². Shifts in

the spectral weight of the peaks away from the reported ratios, deviations of the intensity ratio between the spin-orbit-split $2p_{3/2}$ (L_3) and $2p_{1/2}$ (L_2) doublet from a 2:1 ratio, and a decrease in the apparent spin-orbit coupling in XAS at ~6.4 eV (as compared to an XPS value of 7.3 eV) are common features that display no dependence on irradiation time [39]. It is worth noting that there are two subtle features within the XAS spectra which show variation before and after the samples are irradiated. First, the V L_3 -edge, circled in red, shows an increase in weight after irradiation, which is consistent with the band gap closing upon exposure. However, the O *K*-edge region exhibits only slight changes before and after irradiation. Thus, the lower energy features are associated with the V-V bonds along the *c*-axis. Second, there is an evident change in the t_{2g} and e_g peak intensity ratio at the O *K*-edge following irradiation, indicated by the black circle, which is a likely result of structural distortions of the VO₆ octahedra [40-41]. This suggests that the V 3*d* states feel the effect of the crystal field more strongly, which increases the crystal field splitting energy, before irradiation. In other words, samples before irradiation should have a larger separation between t_{2g} and e_g states [40-41].

Oxygen desorption can also be probed by considering the peak area (V L-edge and O Kedge) of the x-ray absorption signal, as described in relation to PES (Fig. 2 (b)). From the plots at the V L-edge in Fig. 3 (a), it is clear that the irradiated spectra show a shift at the low energy edge and variations in the electronic features, resulting from changes in hybridization between V-O states. A clearer picture of this is portrayed by Fig. 3(b), which shows V L- and O K-edge spectral peak ratios for VO₂ as a function of soft x-ray irradiation time. From this plot, it becomes apparent that the intensities at the V L-edge are also increasing, while O K-edge intensities are decreasing (up to an irradiation time of 40 minutes) for VO₂ samples. We have also calculated χ which is equal to sqrt (integral ((x₁(E)-x₂(E))² dE) / (Delta E)) where x₁ and x₂ are intensities obtained from fig. 3(a) and the samples which were annealed in oxygen atmosphere for 1hr as shown in Fig.4 (black line). Thus, both XAS and PES support the desorption of oxygen atoms from the lattice, with a critical point for the saturation of the DOS in both the vanadium and oxygen sites at approximately 40 min of irradiation time. For comparison spectra of VO₂ thin film at V $L_{3,2}$ - and O K-edge are also shown in Fig 3(c) for both lowtemperature insulating phase and high-temperature metallic phase. With increasing irradiation time, the shape of the V L_{3, 2}- and O K-edge changes; the spectral weight is transferred towards lower photon energy. The observed spectral change seems to be similar to that of the

temperature-induced spectra (upper panel in Fig. 3c). This implies that the high-temperature metallic state is nearly equivalent to soft x-ray irradiation induced metallic state, obtained at low temperature, and that they are both in the rutile-type tetragonal phase. The role of oxygen desorption from the thin films was further verified by annealing soft x-ray exposed VO₂ films in oxygen atmospheres (10^{-6} Torr) at 673 K for 60 min. In comparison to the pristine sample, XAS spectrum is the slightly different, which could be due to the sample's damage due to X-ray irradiation but it is nearly identical in shape.

Based on our PES and XAS observations, a tentative model has been developed to explain soft x-ray induced phase transitions in VO₂ thin film. In this model, the MIT is driven by desorption of oxygen from the lattice on account of soft x-ray exposure. Oxygen desorption lowers the oxidation state of vanadium in VO₂ thin films, thus maintaining the charge balance and driving the MIT to completion [42-43]. Agreement between PES and XAS supports this conclusion and provides spectroscopic evidence for oxygen desorption as a function of irradiation time. This desorption will cause oxygen vacancies in the films, which would decrease the hybridization between V 3d and O 2p, resulting in the π^* band level shifting down and a narrower band gap in the insulator state. This implies that the occurrence of oxygen vacancies reduces the energy barrier for prompting the MIT rate [31]. Furthermore, desorbed oxygen will leave behind extra electrons, which partially occupy the empty π^* states, forming a local conduction band acting as the nuclei for MIT occurrence. The effect is similar to high valence state impurity. Due to the presence of these pre-MIT nuclei generated, the required thermal energy for the MIT of the VO_2 film decreases [31]. As a consequence, the extra electrons induced by the oxygen vacancies in the VO_2 film may trigger an earlier onset of the metal states. The conclusions suggest that disorder is present and unavoidable during the MIT in VO₂ thin films. Thus, the obtained results of V 3d and O 2p bands are informative for the understanding the nature of the MIT of VO₂ thin films induced by soft x-ray.

Conclusions: In this study, we used x-ray absorption and photoemission spectroscopy to show the ability of soft x-ray irradiation to induce a room temperature metal-to-insulator transition (MIT) in VO₂ thin films. Valence band spectra revealed that the V 3*d* DOS increases as a function of soft X-ray irradiation time, while the O 2*p* DOS decreased with irradiation time of up to 40 min at flux density of 3×10^{15} photons s⁻¹cm⁻². Photoemission results were in excellent agreement with XAS data which also demonstrated decreased oxygen DOS. We believe the MIT under soft x-ray irradiation in VO_2 thin films is driven by oxygen desorption. The ability to locally suppress and recover the MIT property of VO_2 film by soft x-ray, especially the low temperature writing and erasing of arbitrary spatial circuitry, provides a different route to build next generation reconfigurable electronic circuits using strongly correlated materials.

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Fig. 1. Valance band photoemission spectra at 0 min and 60 min irradiation for VO₂ (100) thin films. The samples were irradiated with 250 eV photons carrying a flux density of 3×10^{15} photons s⁻¹cm⁻². Spectra were recorded at room temperature and are offset for clarity. The red dotted line represents valence band spectra recorded 60 min after irradiation was stopped.



Fig. 2 Valence band photoemission spectra as a function of irradiation time for (a) VO₂ (100) thin film grown on a *R*-plane sapphire substrate. (b) Spectral area's ratio of the V 3*d* to O 2*p* DOS obtained from valence band photoemission spectra. (c) V 3*d* band spectra after soft X-ray irradiation for 0 and 60 min, together with (upper part) those of low-temperature (T~300K) insulating phase and high-temperature (T~380K) metallic phase for comparison.



Fig. 3 V *L*- and O *K*-edge X-ray absorption spectra for (a) VO₂ (100) thin films recorded as a function of soft X-ray irradiation time. (b) Spectral area's ratio of the V *L*-edge to O *K*-edge obtained from 3(a) and χ w.r.t. soft X-ray irradiation. (c) V *L*-edge and O *K*-edge spectra after soft X-ray irradiation for 0 and 60 min, together with (upper part) those of low-temperature (T~300K) insulating phase and high-temperature (T~380K) metallic phase for comparison.



Fig. 4 V *L*- and O *K*-edge X-ray absorption spectra for VO₂ (100) thin films recorded from pristine sample as shown in red line and black line represents that 1hr soft X-ray irradiated samples were annealed in oxygen atmosphere (10^{-6} Torr) at 673K.