Universal phase dynamics in VO₂ switches revealed by ultrafast operando diffraction

Aditya Sood1,2,†, Xiaozhe Shen3, Yin Shi4, Suhas Kumar5,†, Su Ji Park3,†, Marc Zajac4,‡, Yifei Sun4,¶, Long-Qing Chen4, Shriram Ramanathan6, Xijie Wang3, William C. Chueh1,2, Aaron M. Lindenberg1,2,3,§

Understanding the pathways and time scales underlying electrically driven insulator-metal transitions is crucial for uncovering the fundamental limits of device operation. Using stroboscopic electron diffraction, we perform synchronized time-resolved measurements of atomic motions and electronic transport in operating vanadium dioxide (VO₂) switches. We discover an electrically triggered, isostructural state that forms transiently on microsecond time scales, which is shown by phase-field simulations to be stabilized by local heterogeneities and interfacial interactions between the equilibrium phases. This metastable phase is similar to that formed under photoexcitation within picoseconds, suggesting a universal transformation pathway. Our results establish electrical excitation as a route for uncovering nonequilibrium and metastable phases in correlated materials, opening avenues for engineering dynamical behavior in nanoelectronics.

The insulator-metal transition (IMT) in correlated oxide semiconductors is a notable example of an emergent phenomenon arising from the complex interplay between lattice and electronic degrees of freedom. Electronic and optical properties change drastically across the IMT, motivating applications in computing and photonics (1). In vanadium dioxide (VO₂), an archetypal correlated material, the IMT can be driven primarily in three ways—through thermal (2–4), optical (5–11), and electrical (12–14) excitation. Among these, the electrically triggered IMT (E-IMT) is arguably the most useful for future solid-state devices. It has been used in applications including steep sub-Boltzmann switching transistors (15), neuromorphic circuits (16, 17), and reconfigurable photonics (18–20). In fact, almost all envisioned (and, to date, demonstrated) applications of VO₂ involve two-terminal devices that are driven electrically. However, despite its importance, very little is understood about the mechanisms underlying E-IMT. Notably, the transformation pathway from the insulating monoclinic (M1) to metallic rutile (R) phase under an electric field remains unknown. In general, understanding the structural processes mediating electric field-driven phase transitions remains a challenge in condensed-matter physics. A major roadblock in addressing these issues has been the lack of a direct structural probe of the electrically triggered transient state.

By contrast, there is a rich history of fundamental studies probing the ultrafast photo-induced IMT (P-IMT). Several spectroscopic and structural techniques have shown that femtosecond optical pulses trigger the transformation of M1 to R on a picosecond time scale (5–7). In some cases, the structural and electronic transitions have been observed to be decoupled, which points toward a photo-induced isostructural, metallic monoclinic (mM) phase (7, 8, 21). Given that E-IMT and P-IMT occur on very different time scales and are often studied under different experimental conditions, it is still unclear whether there is a connection between the pathways followed by the two types of transformations. In particular, although the existence of an electrically driven mM phase has been hypothesized previously (13, 22), a direct structural observation of this transient state in operating devices has remained challenging.

To further our understanding of electric-field effects and engineer the next generation of electronic switches based on correlated oxide semiconductors, it is essential to visualize atomic motions within the electrically triggered transition state on fast time scales. Here, we introduce a stroboscopic mega–electron volt ultrafast electron diffraction (MeV-UED) technique and report time-resolved measurements of atomic structure in electrically excited VO₂ switches. By simultaneously probing changes in both structure and electronic transport under a pulsed electrical bias, we directly probe the mechanisms underlying E-IMT. Figure 1A shows a schematic of the operando experiment built at the MeV-UED facility (23, 24) at the SLAC National Accelerator Laboratory [see fig. S1 and (25) for details]. Two-terminal devices were fabricated using 60-nm-thick polycrystalline VO₂ films deposited on 50-nm-thick free-standing silicon nitride membranes. The device was pumped by a periodic train of voltage pulses synchronized to the 180-Hz clock of the UED system (Fig. 1B, top). After excitation by a voltage pulse, the time-dependent structural response was probed through diffraction of a delayed ~100-fs electron pulse. The resistance of the device was simultaneously monitored using a high-speed oscilloscope. In addition to electrical excitation, we also separately pumped the samples using synchronized ~100-fs, 1.55-eV optical pulses to study the dynamics during P-IMT (Fig. 1B, bottom). The devices display typical threshold-switching behavior, as shown by the current-voltage curve in Fig. 1C. When biased above a threshold voltage, the current increases abruptly as a result of the formation of an electrically conducting state (figs. S2 and S3). Figure 1D shows the resistance of the VO₂ channel (R_{VO₂}) as a function of time after a step voltage is applied. The three curves correspond to voltage magnitudes of 4 V (red), 4.8 V (blue), and 5.6 V (green). R_{VO₂} decreases strongly after a finite incubation time (26); this time scale is smaller at higher voltages. The transient characteristics are repeatable over millions of cycles, which is a crucial requirement for stroboscopic measurements. This is shown in Fig. 1E, where we plot the resistance ratio between the insulating and metallic states (top) and the incubation time (bottom) versus cycle number.

The diffraction data were analyzed by azimuthally integrating the polycrystalline diffraction pattern and computing changes in intensity relative to the unexcited M1 phase (25). Figure 2A displays a two-dimensional (2D) color map of the normalized intensity change, δI(Q, t) = I(Q, t) − I₀(Q))/I₀(Q), as a function of momentum transfer Q and delay time t. I₀(Q) corresponds to the unexcited state at t = 0. A lineout at a delay of 500 μs is shown in Fig. 2B, where three peaks of interest are indexed, namely (302), (313), and (220). To compare the structural dynamics during E-IMT with Pt-IMT, we excited the same device with ~100-fs optical pulses at 1.55 eV. As seen in Fig. 2C, photoexcitation induces ultrafast structural dynamics on the picosecond time scale. Figure 2D plots a lineout at a delay of 5 ps.

To resolve the time scales of the structural transformation after electrical excitation, we plot time-dependent δI₁₀₀, δI₁₁₃, and δI₅₈₀ at different voltages V = 4, 4.8, and 5.6 V (Fig. 3, A to C). Three distinct regimes are identified. (i) As the voltage is turned on, the intensities of the (302) and (313) peaks decrease, whereas the intensity of the (220) peak increases. As shown by structure factor calculations (fig. S4A), the (302) and (313) peaks are present
in the M1 but absent in the high-symmetry R phase. Therefore, $\delta I_{302}$ and $\delta I_{313}$ capture the $M1 \rightarrow R$ structural phase transformation (SPT)—i.e., the nucleation and growth of the metallic R phase under electrical excitation. As we show below, the dynamics of the (220) peak encode information about the nonequilibrium structural changes occurring during the E-IMT. (ii) After the voltage is turned off, the structure persists for a finite duration, possibly owing to hysteresis in the phase transition as the device cools and the associated barrier for the reverse $R \rightarrow M1$ transformation (12). (iii) The structure returns to the $M1$ phase in a quasi-exponential manner within ~2 ms, consistent with time scales for lateral heat transport along the membrane into the Si substrate.

In Fig. 3, D to F, we zoom in to the rising edge of the voltage pulse and probe structural dynamics and transport with higher time resolution (see fig. S5 for the corresponding device characteristics). A delay is observed in the structural response (through $\delta I_{302}$ and $\delta I_{313}$), which is temporally correlated with the delayed response in $R_{\text{VO2}}$. We do not find any evidence of the $R$ phase in this incubation state to within the experimental detection limits, which suggests that the direct electric field-induced transformation is small and that thermal effects are dominant (26) [see additional measurements and electrothermal simulations in (25) and fig. S6]. To understand the dynamics of $\delta I_{220}$, we first note that the (220) peak is present in both equilibrium phases. Structure factor calculations predict that the intensity of the (220) peak in the $R$ phase is higher than that in the $M1$ phase (fig. S4A). To investigate whether this equilibrium transformation completely describes the observed positive changes in $\delta I_{220}$, we performed static electron diffraction measurements while heating the sample slowly (fig. S7). A broad transition beginning at 340 K was observed, with a width of ~20 K. In fig. S7B, we plot the temperature-dependent ratios of the normalized intensity changes $\delta I_{220}/\delta I_{302}$ and $\delta I_{220}/\delta I_{313}$. Evaluating these at a temperature well above the transition temperature $T_c$—where the entire sample must transform to the $R$ phase—enables us to quantify the maximum relative change in (220) intensity that can be caused by the equilibrium $M1 \rightarrow R$ transition. In Fig. 3G, we calculate these relative normalized intensity changes for the time-resolved E-IMT and compare them with the equilibrium limits, which are indicated by the dashed lines. Notably, at time delays smaller than 100 $\mu$s, we find that the structural transformation under electrical excitation cannot be described solely by the formation of the $R$ phase. At longer times, the relative peak changes trend toward their equilibrium values, which suggests the eventual completion of the $M1 \rightarrow R$ SPT. For additional analysis, see figs. S8 to S10 and (25).

To gain further insight into the unusual behavior of the (220) peak, we turn to the optical pump experiments. As shown in Fig. 3H, photoexcitation triggers the ultrafast $M1 \rightarrow R$ SPT within ~0.5 to 0.7 ps, as indicated by a quenching of the (302) and (313) peaks. In marked contrast, the (220) peak intensity increases on a much slower time scale of ~2.9 ps. These observations of dissimilar time scales for the evolution of different peaks are consistent with the unusual behavior of the (220) peak in the E-IMT and suggest that the electric field plays a role in the transformation process.
with previous optical pump–UED probe experiments, which showed that the slower response of $\delta I_{220}$ is related to a purely electronic (i.e., isostructural) transition from $M1$ into the metastable $mM$ phase \(7, 8, 25\). In particular, these experiments correlated $\delta I_{220}$ with changes in the terahertz conductivity and to symmetry-preserving charge reorganization, showing that the fluence-dependent ratio $\delta I_{220}/|\delta I_{313}|$ serves as an indicator of the $M1\rightarrow mM$ transition. This is consistent with the analysis of our P-IMT data, where, in a manner similar to E-IMT (Fig. 3G), we compute the relative normalized intensity changes and compare them with the thermally driven SPT (Fig. 3H, inset). The changes are larger than can be explained purely by the $M1\rightarrow R$ transition. Taken together, our photoexcitation measurements provide clear evidence for the creation of a $mM$ phase on picosecond time scales. Returning to the analysis presented in Fig. 3G, this interpretation of P-IMT dynamics reveals an important discovery: Electrical excitation creates, on microsecond time scales, a transient $mM$ phase in addition to the stable $R$ phase. This causes the peak intensity ratios $\delta I_{220}/|\delta I_{313}|$ and $\delta I_{220}/|\delta I_{322}|$ to exceed their equilibrium values. As the voltage is maintained, the $mM$ domains convert fully to the thermodynamically stable $R$ phase on a time scale of ~100 $\mu$s. This represents a direct observation of this transient isostructural state during the electrically triggered IMT in VO$_2$. Furthermore, this similarity between the pathways of E-IMT and P-IMT involving the intervening $mM$ phase is exemplified by the close correspondence between their structural dynamics across eight orders of magnitude in time scale (Fig. 2).

To gain insight into the phase coexistence and conditions leading to the emergence of the $mM$ phase during E-IMT, we perform time-dependent phase-field simulations of a VO$_2$ device under an electric field \(27, 28\) [Fig. 4A and (25)]. The state of the material is characterized by the structural and electronic order parameters, $\eta(r, t)$ and $\mu(r, t)$, respectively, where $r$ is the spatial coordinate and $t$ is time. The $M1$ phase is characterized by $\eta = \mu = 1$ and the $R$ phase by $\eta = \mu = 0$. The nucleation and growth of new domains is described by the spatiotemporal evolution of $\eta$ and $\mu$, free carrier density, and temperature, driven by the free energy reduction that includes contributions from the bulk chemical energy, interfacial energy, and the free energy density of electrons and holes. To capture the intrinsic heterogeneity of the material, we assume a spatially varying $T_c$ (Fig. 4B). In a polycrystalline film grown on a non-lattice-matched substrate, this could be caused by subtle variations in the oxygen stoichiometry, strain, or other nanoscale disorder associated with grain boundaries \(29, 30\). Atomic force microscopy measurements of the morphology provide an approximate length scale for this heterogeneity (Fig. S11). Based on this, and the temperature-dependent diffraction measurements that show a broad transition (fig. S7A), we model the inhomogeneous $T_c$ as a spatially correlated random field with a correlation length of 25 nm and a range of $T_c$ variation of 20 K.

Under the action of an electric field applied to the $M1$ phase at $t = 0$, after an incubation period, the $R$ phase first begins to nucleate in regions with lower $T_c$ (Fig. 4C, movie S1, and fig. S12) followed by the local formation of the metastable $mM$ phase domains ($\eta = 1, \mu = 0$). Although the metastable $mM$ is not a stable equilibrium phase in the bulk, it is stabilized here through interfacial interactions with the $R$ phase. An interface between $M1$ and $R$ involves a variation in both $\eta$ and $\mu$ and thus has a higher interfacial energy compared with that between $mM$ and $R$, through which only $\eta$ varies. When the size of $M1$ domains neighboring the growing $R$ phase domains shrinks below a critical length scale (on the order of 10 nm), $mM$ is locally stabilized, which leads to a reduction in the total free energy of the inhomogeneous system. This mechanism is consistent with a previous study of temperature-dependent IMT in epitaxial VO$_2$-VO$_{23}$ heterostructures \(2\). Furthermore, our simulations show that the intrinsic time scale for the formation of a single $mM$ domain (white regions in movie SI) could be smaller than 1 $\mu$s, which suggests that the 10- to 100-$\mu$s lifetime measured in the experiment is caused by the integration of the UED signal over the device area.

In two-terminal devices made of VO$_2$ or similar materials, it has been suggested that the E-IMT turn-on time is limited by electrical and thermal parasitics \(16\). Although switching times of 0.5 to 10 ns have been demonstrated, the intrinsic speed limits of material transformation under electrical bias have been unclear \(14, 20, 26\). Our observation of similar transient phase dynamics during ultrafast
P-IMT and slower E-IMT points toward a universality in their transformation pathways, thereby identifying the speed limits for electrically triggered switching. Furthermore, given that the isostructural mM phase exists on microsecond or shorter time scales, it is likely that neuromorphic Mott oscillators operating at megahertz and higher frequencies sample a complex phase space of structural and electronic states (17, 31). Finally, taken together with recent transport studies (32), our results establish ultrafast electrical excitation as a promising method for inducing nonequilibrium phase transitions—in much the same way that ultrafast photoexcitation has been used to uncover hidden order in materials (33). We anticipate that our work will motivate a search for electrically induced metastable phases across the broad spectrum of solid-state devices.

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