

# Atomic-scale origins of ultraviolet-driven phase transition behavior in strongly correlated vanadium dioxide heterostructures

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**ABSTRACT:** Precise control over multiple functional phases in strongly correlated VO<sub>2</sub> and its heterostructures establishes a correlation between inclusions, defect dynamics and the stabilization of monoclinic versus tetragonal phases. However, a comprehensive atomic-level understanding of these processes remains insufficient to elucidate the underlying multiple defect-phase relationship mechanisms. Herein, we uncover the atomic-scale inter-layer defect transfer mechanism in VO<sub>2</sub>-based Fabry-Pérot resonant cavity heterostructures under vacuum-ultraviolet (VUV) irradiation. The irradiation induces cleavage of In–O and Sn–O bonds within the indium-tin-oxide (ITO) layer, triggering the concerted diffusive migration of In, Sn, and oxygen vacancies with VO<sub>2</sub>. This migration elevates electron occupancy in the hybridized energy levels of the d<sub>||</sub>-bond orbital and In/Sn-d orbitals within V–V dimers. The enhanced d<sub>||</sub> electron density strengthens orbital overlap with π\* antibonding orbitals, driving the VO<sub>2</sub> phase transition from insulating monoclinic to metallic rutile. These results offer important theoretical and experimental insights into defect-mediated phase engineering in strongly correlated oxides and hold promise for advancing applications in quantum optoelectronic information and adaptive optics.

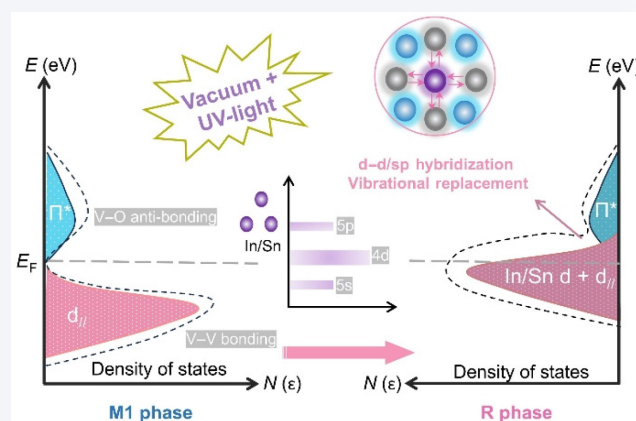
**KEYWORDS:** VO<sub>2</sub> phase transition, strongly correlated oxide, defect migration, vacuum ultraviolet, heterostructure

## 1 Introduction

The precise control of multiple functionalities in strongly correlated oxide vanadium dioxide (VO<sub>2</sub>) and its heterostructures remains a central challenge, owing to their extreme sensitivity to external stimuli. By navigating neighboring minima in the free energy landscape—governed by parameters such as temperature, magnetic field, doping, and high-energy light irradiation—it becomes possible to induce atomic rearrangements, driving phase transitions between the insulating and metallic phases [1–3]. A defining feature of correlated electron systems is the profound influence of intrinsic

and extrinsic atomic defects on d-band filling under various stimuli [4]. Strong electronic correlations, coupled with structural transitions, lead to dramatic modifications in the electronic structure, manifesting in emergent electronic, ferroelectric, optical, and magnetic properties [5]. These tunable functional properties have enabled diverse applications, including neuromorphic computing [6], thermochromic smart windows [7], memristors [8], dynamic thermal management systems [9], and deformation-toughened materials [10].

As a prototypical strongly correlated oxide, VO<sub>2</sub> exhibits defect-dependent phase stability that is critical for property engineering. Intrinsic defects, particularly oxygen vacancies, dramatically influence electronic performance through redox-mediated conductivity modulation, where vacancy concentrations directly govern charge transport characteristics [11]. Extrinsic doping provides an additional degree of control, enabling tailored insulator-to-metal transitions that can be either reversible or irreversible at



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temperatures below the characteristic 68 °C transition threshold [12]. For example, tungsten substitution in the vanadium sublattice demonstrates particularly pronounced effects: its large ionic radius induces substantial anisotropic strain while its hexavalent state drives electron doping, collectively destabilizing the low-temperature M1 phase relative to the metallic state [13]. Alternative dopants produce distinct structural consequences—Cr and Al preferentially stabilize the M2 phase through either substitutional doping or epitaxial strain [14, 15], interstitial hydrogen induces orthorhombic phase formation while enabling room-temperature stabilization of the metallic rutile phase [16], and boron interstitials selectively promote the R phase over M1 [17]. Although these empirical observations establish a clear correlation between inclusion-related defect dynamics and phase stabilization (monoclinic versus tetragonal phases), a comprehensive atomic-level understanding of these processes that elucidates the underlying multiple defect-phase relationship mechanisms remains insufficient.

Herein, we elucidate the mechanism by which the evolution of interlayer oxide defects affects the phase transition of VO<sub>2</sub> in Fabry-Perot resonant cavity (V-FPRC) structure under vacuum UV irradiation. This mechanism at the atomic scale is clearly evidenced by a combination of techniques, including high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS), selected area electron diffraction (SAED), deep-etching X-ray photoelectron spectroscopy, and photo-induced force microscopy (PiFM). The phase transition from monoclinic (M) to rutile (R) in VO<sub>2</sub> is attributed to the interlayer diffusion of indium (In), tin (Sn), and V<sub>O</sub> within the V-FPRC structure. The hybridization-induced energy level alignment between the d-orbitals of In/Sn and the bonding d<sub>||</sub> orbitals of V-V dimers leads to vibrational replacement. Consequently, this process induces a distinct shift from the d<sub>||</sub> bonding orbital to the  $\pi^*$  antibonding orbital in VO<sub>2</sub>. These findings offer substantial theoretical and experimental insights that advance the rational design of defect-engineered strongly correlated oxides for quantum optoelectronic information science applications.

## 2 Results and discussion

### 2.1 Observation of V-FPRC macroscopic infrared (IR) optical response under UV-irradiation

In this study, the V-FPRC sample before vacuum-UV irradiation was designated as the pristine sample, while the sample after irradiation was termed the irradiated sample. To efficiently assess the optical response behaviour of the VO<sub>2</sub> phase structure, the layered structure of the V-FPRC is illustrated in Fig. 1(a), where the Fabry-Pérot (F-P) cavity, with a layered structure of Al/HfO<sub>2</sub>/VO<sub>2</sub>/indium-tin-oxide (ITO) (high-resistance and infrared-transmittance), functions as a thermally infrared regulator [18]. This design facilitates tunable infrared emission (2.5–25  $\mu$ m), enabling dynamic control of radiative heat transfer. Below the phase transition temperature ( $T_c$ ), VO<sub>2</sub> exists in an insulating state, wherein the resonant cavity is absent. In this regime, incident IR light transmits through the ITO/VO<sub>2</sub>/HfO<sub>2</sub> multilayer stack and undergoes high reflection (low emissivity) at the Al interface. Upon exceeding the phase transition temperature, VO<sub>2</sub> undergoes a reversible transition to a metallic state, forming a F-P resonant cavity composed of ITO/VO<sub>2</sub>/HfO<sub>2</sub>/Al. This structural

configuration facilitates multiple reflections and constructive interference of IR light within the cavity, resulting in strong absorption (high emissivity). Correspondingly, PiFM provides nanoscale optical imaging capabilities surpassing the diffraction limit (Fig. 1(a)). This technique employs wavelength-tuned infrared laser illumination of an atomic force microscope's (AFM) metallized tip, generating a strongly confined evanescent field at the tip apex. Analysis of the resulting near-field interactions enables direct mapping of local compositional variations at the nanoscale [19].

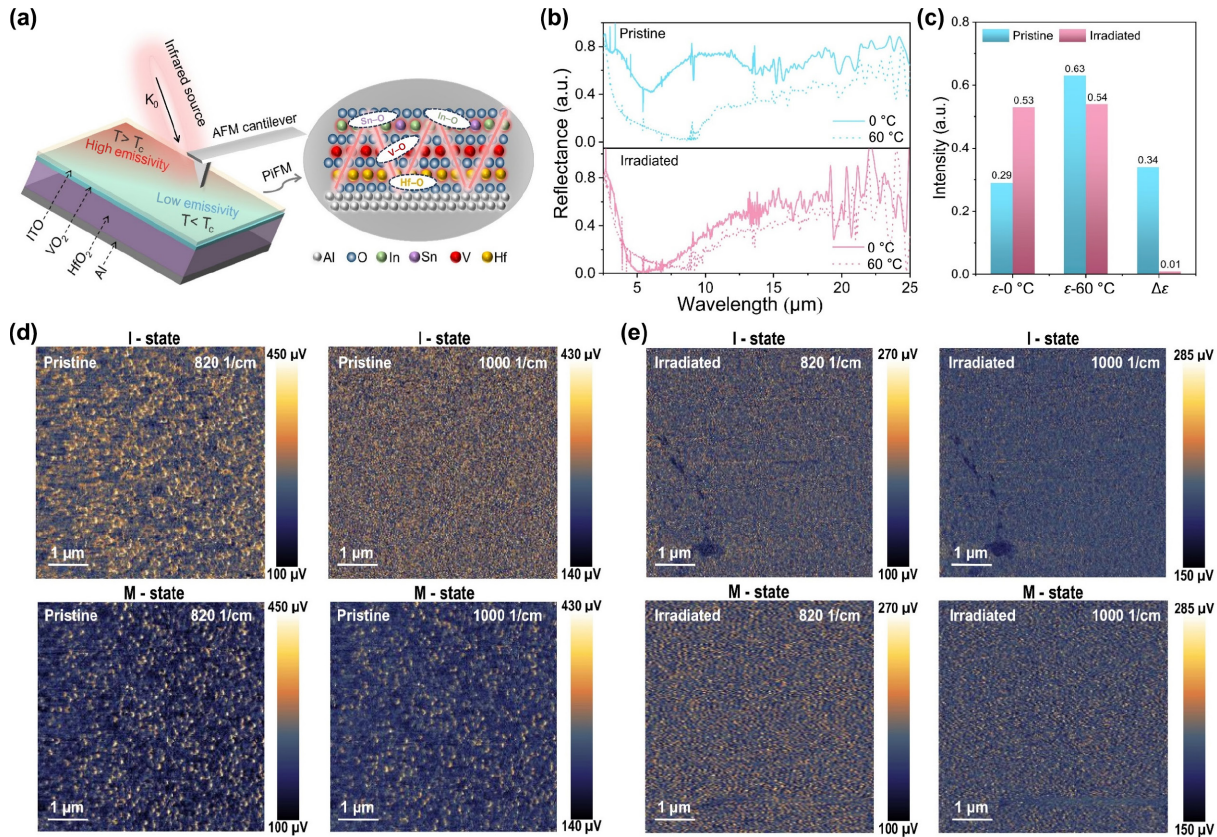
The cross-sectional transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) mapping images of the V-FPRC reveal that the thicknesses of the Al, HfO<sub>2</sub>, VO<sub>2</sub>, and ITO layers are 150, 600, 50, and 30 nm, respectively (Fig. S1 in the Electronic Supplementary Material (ESM)). To assess the regulation of thermal infrared optics of the V-FPRC samples before and after irradiation, the Fourier transform infrared reflectance spectra (FTIR) were obtained. As in Fig. 1(b), the pristine V-FPRC in its two states exhibits notable variations across the 2.5–25  $\mu$ m range, by contrast, the irradiated V-FPRC infrared radiation modulation capability disappears. Subsequently, the emissivity of irradiated V-FPRC increases from 0.29 to 0.53 at 0 °C, and the IR-emissivity regulation ( $\Delta\epsilon$ ) decreases from 0.34 to 0.01 (Fig. 1(c)). Nano-IR amplitude PiFM data were acquired at a detection frequency of  $\omega \approx 820$  and 1000 cm<sup>-1</sup> (10  $\mu$ m), corresponding to the photophonon (OPhs) modes of the M1-phase VO<sub>2</sub> and F-P modes [20, 21]. As shown in Figs. 1(d) and 1(e), the PiFM signal imaging of the irradiated sample revealed no significant changes between the insulating (I) and metallic (M) states, along with the disappearance of the M1-phase V-V dimer phonon vibration. These observations further support the optical nature of the degradation in dynamic IR-regulation.

To further investigate the degradation of IR modulation performance in V-FPRC after vacuum UV irradiation, a series of material phase characterizations were conducted. The grazing-incidence X-ray diffraction (GIXRD) patterns of irradiated V-FPRC reveal VO<sub>2</sub>'s R-phase (27.6°, (110)), in contrast to the M1-phase (27.8°, (110)) dominant in the pristine sample (Figs. S2(a) and S2(b) in the ESM) [22, 23]. Using the HfO<sub>2</sub>(200) peak area in each V-FPRC sample as a benchmark, we observed a 3.5-fold increase in the ITO(222) peak area for irradiated V-FPRC (Fig. S2(c) in the ESM), alongside a 2.4-fold enhancement in the VO<sub>2</sub> R-phase (110) peak area (Fig. S2(e) in the ESM), while the HfO<sub>2</sub>(011) peak area remained unchanged (Fig. S2(d) in the ESM) [24, 25]. This is further confirmed by SAED and cross-sectional TEM images, where the HfO<sub>2</sub> layer for irradiated V-FPRC shows distinct diffraction spots at the ( $\bar{1}11$ ) crystal planes, confirming results consistent with the pristine V-FPRC crystallinity (Fig. S3 in the ESM). These results indicate that UV irradiation enhances the crystallinity of both the ITO and VO<sub>2</sub> layers in V-FPRC. In contrast, the loss of IR modulation capability in V-FPRC is primarily attributed to phase alterations in the ITO and VO<sub>2</sub> layers.

### 2.2 UV-irradiation effect on ITO/VO<sub>2</sub> heterojunction interface of V-FPRC

Cross-sectional STEM was performed to gain deeper insight into the ITO/VO<sub>2</sub> morphology and crystal structure of the pristine and irradiated V-FPRC. Figures 2(a) and 2(b) depict STEM images of a cross section of the V-FPRC, the representative selected area in the cross section consists of the ITO on top of the VO<sub>2</sub> layer also including the interface, and the blue and red regions correspond to





**Figure 1** Infrared optics testing of V-FPRC thermal radiation before and after irradiation. (a) Schematic of the experiment PFM and the structure of the V-FPRC. (b) Infrared reflectance spectra of the pristine and irradiated V-FPRC at 0 and 60 °C. (c) Emittance values of pristine and irradiated V-FPRC. (d) and (e) Experimental PFM signal imaging mapping of the near-field amplitude of the pristine and irradiated V-FPRC, PFM data collected in the I-state (20 °C) and M-state (60 °C) at the frequency  $\omega \approx 820 \text{ cm}^{-1}$  and  $\omega \approx 1000 \text{ cm}^{-1}$  (10  $\mu\text{m}$ ), representing M1-phase  $\text{VO}_2$  optical phonons and F-P modes.

the pristine and irradiated samples, respectively. The irradiated V-FPRC displays a rougher heterointerface than the pristine sample, indicative of aging-induced interfacial degradation, presumably caused by ion-migration and compositional loss [26]. The EDX elemental profiles along the indicated arrows in Figs. 2(a) and 2(b) are shown in Figs. 2(c) and 2(d), the vacuum ultraviolet irradiation significantly enhances the accumulation of  $\text{In}^+$  and  $\text{Sn}^+$  at the ITO/ $\text{VO}_2$  interface, as well as their subsequent migration into the  $\text{VO}_2$  layers. The elemental distributions were compared by EDX mappings in STEM (Figs. 2(e)–2(h)). On close inspection, large accumulations of both indium and tin can be seen for the irradiated V-FPRC along the interface ITO/ $\text{VO}_2$  region, and oxygen partitioning (white arrows) between the layers is more significant. These findings are strongly corroborated by quantitative elemental distribution analysis. Next, we performed temperature-dependent conductivity measurement and used the Nernst–Einstein equation (Eq. (1)) to evaluate the ion migration behavior [27]

$$\sigma T = \sigma_0 e^{-E_a / k_B T} \quad (1)$$

where  $E_a$  is the activation energy of ion migration,  $\sigma$  is the conductivity,  $k_B$  represents the Boltzmann constant, and  $T$  is the temperature, respectively. The  $E_a$  values are 1.04 and 0.56 eV for the pristine and irradiated V-FPRC, respectively (Fig. S4 and Table S4 in the ESM). The attenuated  $E_a$  indicates that the ion migration is significantly enhanced for the irradiated V-FPRC.

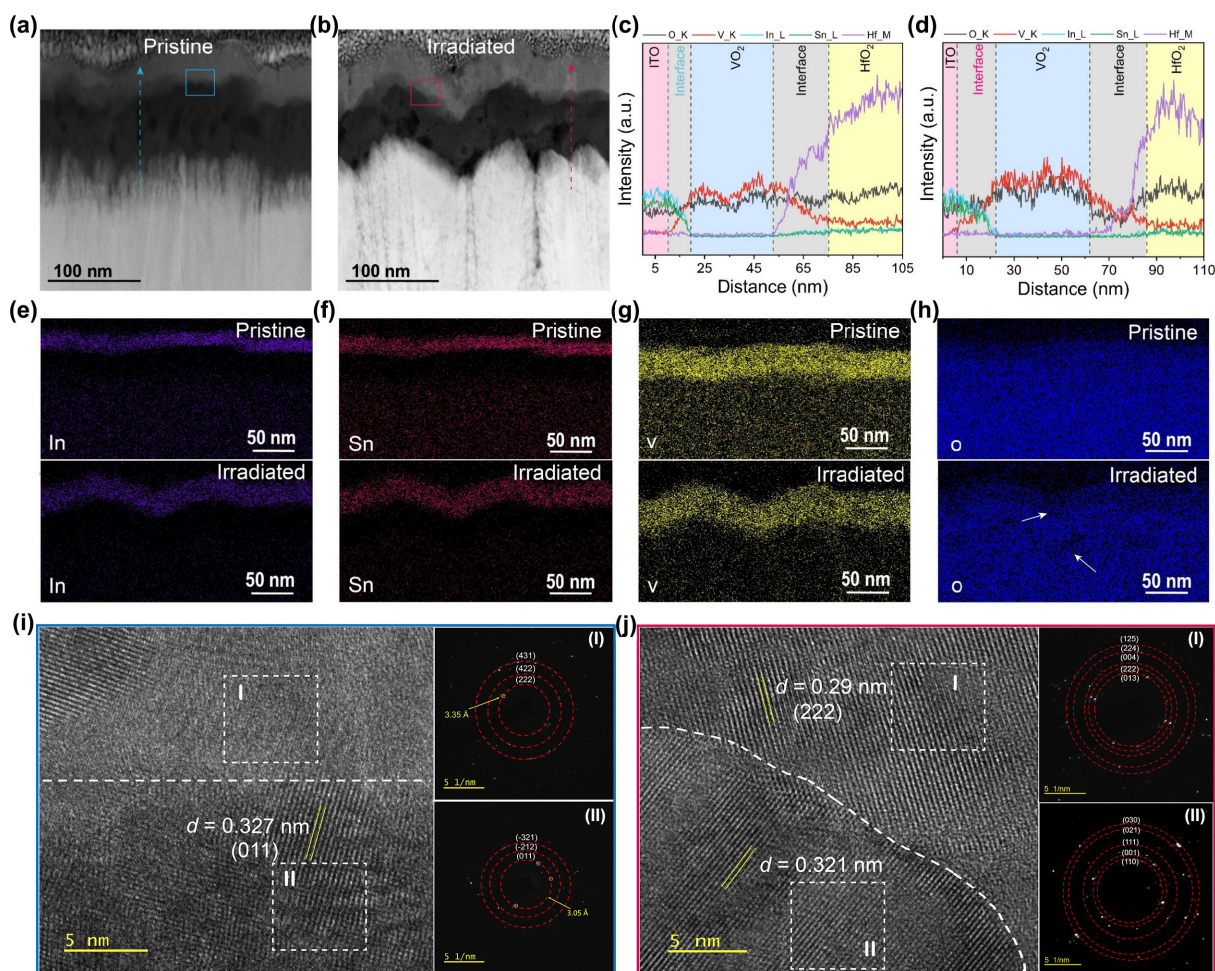
HAADF-STEM and SAED measurements were used to analyze the effect of elemental migration on the crystal structure of ITO and  $\text{VO}_2$  interface (Figs. 2(i) and 2(j)). In stark contrast to the pristine

sample, a more pronounced nanoscale lattice fringe ordering is observed in the irradiated ITO and  $\text{VO}_2$  interface. The (222) crystal surface of  $\text{In}_2\text{O}_3$  is exposed [25], with a surface spacing of 0.29 nm, which corresponds to the SAED result (Figs. 2(i) and 2(j)(I)). Furthermore, compared to the pristine sample, the irradiated ITO surface exhibited reduced grain size and roughness (Figs. S5 and S6 in the ESM), which correlated with decreased sheet resistance and increased carrier concentration and mobility (Fig. S7 in the ESM). The results reveal that irradiation alters the crystallinity of ITO, concomitantly affecting its electrical properties. Then, the  $\text{VO}_2$  interplanar spacing evolves from 0.327 nm (M1-phase, (011)) to 0.321 nm (R-phase, (110)) following irradiation. This observation is further corroborated by SAED analysis (Figs. 2(i) and 2(j)(II)), where the pristine  $\text{VO}_2$  exhibits distinct diffraction spots corresponding to the (011), ( $\bar{2}$ 12), and ( $\bar{3}$ 21) planes of the M1-phase, while the irradiated  $\text{VO}_2$  displays diffraction patterns assignable to the (110), (001), (111), and (021) planes of the R-phase. These structural changes correlate well with the GIXRD results.

### 2.3 Analysis of ITO/ $\text{VO}_2$ heterojunction internal phase characteristics

Figures 3(a) and 3(e) further analyze the regions distal to the interface, with yellow and green dotted lines denoting the ITO and  $\text{VO}_2$  layers, respectively. HAADF-STEM reveals well-defined lattice fringes in both pristine and irradiated ITO, showing no significant structural alteration (Figs. 3(b) and 3(f)). The irradiated ITO layer





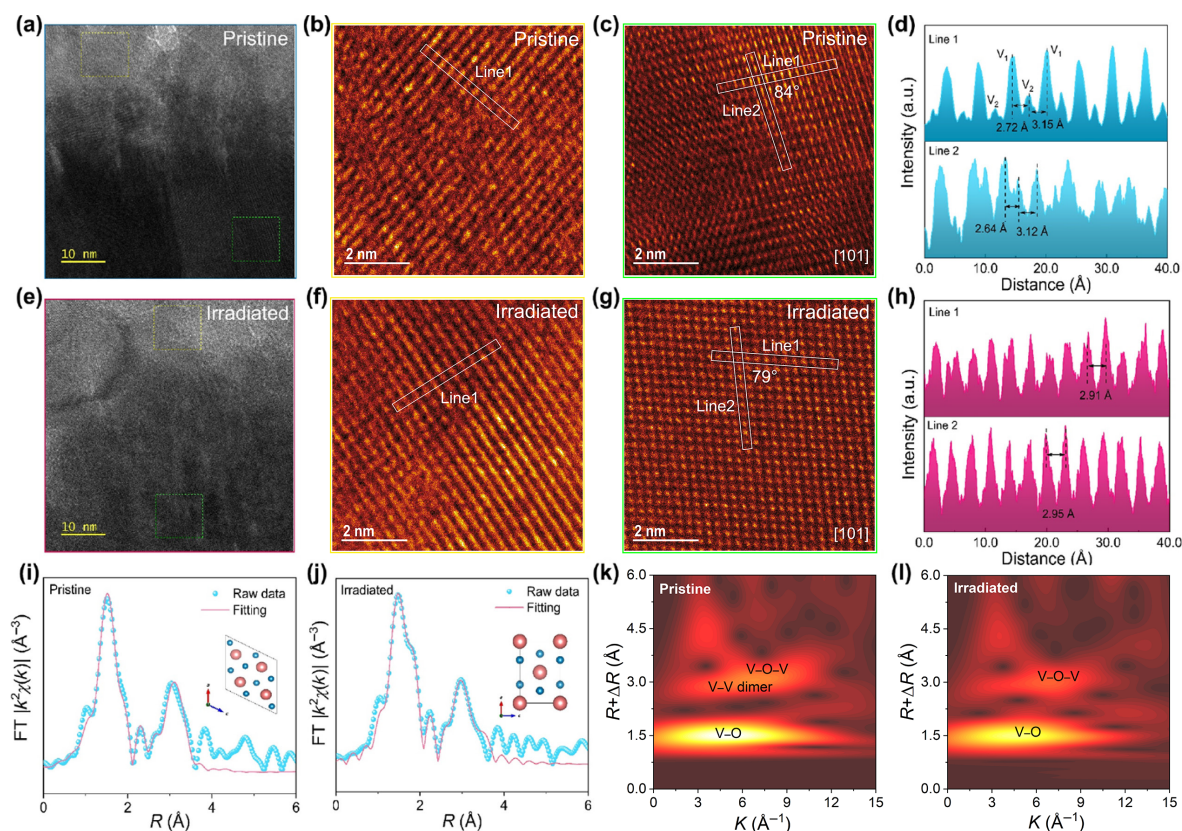
**Figure 2** Characterization of ITO/ $\text{VO}_2$  interface morphology and crystal structure of the pristine and irradiated V-FPRC. (a) and (b) Cross-sectional STEM images of the pristine and irradiated V-FPRC. (c) and (d) EDX elemental profiles along the indicated arrows in panels (a) and (b), respectively. (e)–(h) EDX elemental maps of indium (e), tin (f), vanadium (g), and oxygen (h) for pristine and irradiated V-FPRC cross-sectional STEM samples. (i) HAADF-STEM and SAED images of the domains of the pristine ITO/ $\text{VO}_2$  interface. (j) HAADF-STEM and SAED images of the domains of the irradiated ITO/ $\text{VO}_2$  interface.

presents an enhanced (222) plane spacing of 0.306 nm than that of the pristine sample (0.302 nm) (Fig. S8 in the ESM), which corresponds to the lattice expansion of 1.3%. In the  $\text{VO}_2$  layer, atomic-resolution HAADF images in Figs. 3(c) and 3(g) reveal the well-ordered arrangement of V atoms, both before and after irradiation. The observed structural modifications V–V spacings evolving from 2.72/3.15 to 2.91/2.95 Å (Figs. 3(d) and 3(h)) and interatomic angle reduction ( $84^\circ$  to  $79^\circ$ ) quantitatively match the characteristic structural signature of the  $\text{VO}_2$  M1-R phase transition, demonstrating irradiation-induced phase transformation [28, 29]. To elucidate the influence of ITO crystal structure modifications on the local strain and lattice distortion in  $\text{VO}_2$ , we conducted geometric phase analysis (GPA) on the HAADF-STEM images. Color mapping of the strain distribution identifies red regions as tensile-strained and blue regions as compressive-strained. Figure S9 in the ESM shows the in-plane strain ( $E_{xx}$ ) and out-of-plane strain ( $E_{yy}$ ) along the direction of [111] of  $\text{In}_2\text{O}_3$ , respectively. The local strain evolution reveals that irradiation induces compressive lattice distortion along the in-plane direction ( $E_{xx}$ ), tensile distortion along the out-plane direction ( $E_{yy}$ ), and enhanced strain inhomogeneity ( $E_{yy}$ ). Correspondingly in the  $\text{VO}_2$  layer, the GPA shows that the tensile strain  $E_{xx}$  in the direction of [101] increased after irradiation, while the  $E_{yy}$  strain fluctuation decreased,

and the overall uniformity became better (Fig. S10 in the ESM). Thus, the migration of In, Sn, and oxygen vacancies alters the local bonding environment and induces lattice distortion in  $\text{VO}_2$ . This structural perturbation modifies the M1-to-R transformation, which arises not from strain or defect doping alone, but from their combined effect.

To explore the variation in vanadium's coordination structure before and after UV-irradiation, the  $k^2$ -weighted Fourier transforms of the V K-edge EXAFS and the corresponding fitting curves without phase correction in  $R$ -space were employed. As shown in Figs. 3(i) and 3(j) and Fig. S11 in the ESM, the V–O bond length (2.05 Å) becomes longer and the V–V bond length becomes 3.01 Å after irradiation compared to the peaks at 1.84 Å (V–O), 2.43 Å (V–V, dimer), 3.14 Å (V–V, adjacent V atoms in the chain), and 3.45 Å (V–O–V) of the pristine, and the parameters are detailed in Table S3 in the ESM. Similarly, the EXAFS of the wavelet transform (Figs. 3(k) and 3(l)) further reveals the evolution of the intensity of the V–O, V–V dimer, and V–O–V regions in the  $K$ -space. After irradiation, the disappearance of the V–V dimer signal (intra-chain sub-neighbor V) bond at about  $6 \text{ \AA}^{-1}$  further confirmed the emergence of the vanadium coordination structure of R phase  $\text{VO}_2$ . Notably, the V K-edge absorption edge remains unchanged (Fig. S12 in the ESM), indicating that the vanadium oxidation state





**Figure 3** Atomic-level analysis of ITO and VO<sub>2</sub> layers of the pristine and irradiated V-FPRC. (a) and (e) Cross-sectional STEM images of the pristine and irradiated ITO and VO<sub>2</sub> layers. (b) and (f) HAADF-STEM images of the pristine and irradiated ITO layer. (c) and (g) HAADF-STEM images along [101] direction of the pristine and irradiated VO<sub>2</sub> layer. (d) The line intensity profiles, taken from (c), correspond to lines observed in HAADF-STEM image of VO<sub>2</sub>. (h) The line intensity profiles, taken from (g), correspond to lines observed in HAADF-STEM image of VO<sub>2</sub>. (i) and (j) Fitting curves of V K-edge FT-EXAFS spectra of the pristine and irradiated VO<sub>2</sub> layer at R space. (k) and (l)  $k^2$ -weighted WT EXAFS signals of the pristine and irradiated VO<sub>2</sub> layer at V K-edges.

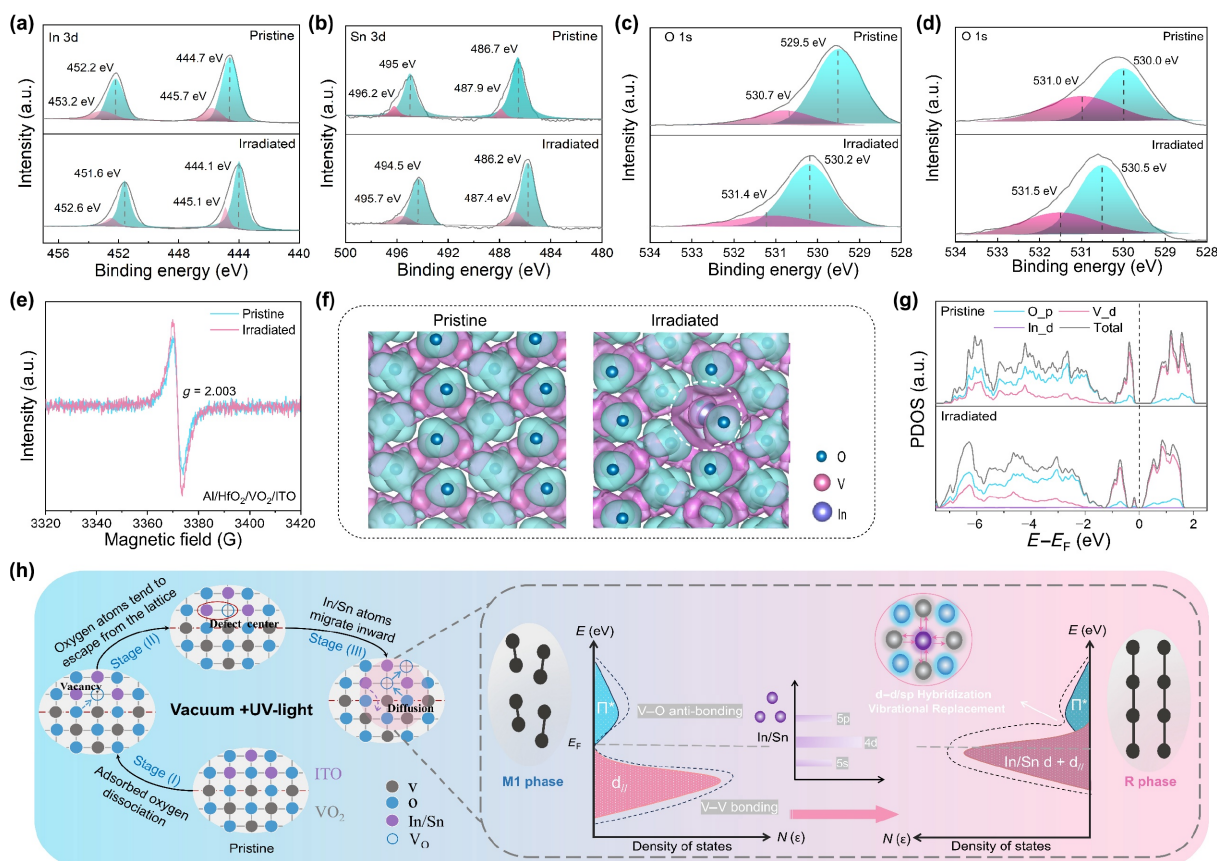
persists as V<sup>4+</sup> before and after irradiation (Fig. S12 in the ESM). These observations suggest that the bulk VO<sub>2</sub> phase transition is likely induced by lattice strain resulting from interfacial element diffusion [30]. The above evidence demonstrates that the irradiation-induced modification of ITO's crystallographic and elemental migration properties drives a VO<sub>2</sub> phase transition from M1 to R, occurring not only at the ITO/VO<sub>2</sub> interface but also throughout the bulk VO<sub>2</sub> layer.

## 2.4 Mechanism of UV-induced VO<sub>2</sub> heterojunction phase transition

Deep etching X-ray photoelectron spectroscopy (XPS) characterizations were carried out to investigate the interaction between ITO and VO<sub>2</sub> layers after irradiation. The signal mappings of In, Sn, O, V, and W exhibit depth-dependent variations, as illustrated in Fig. S13 in the ESM, In and Sn signals attenuated beyond 40–50 nm, whereas V and W signals appeared at ~ 30 nm, with all four elements showing pronounced interdiffusion in the irradiated specimen. To probe irradiation-induced effects, we analyzed the binding energy shifts of In, Sn, and O (ITO layer, 20 nm depth) before and after irradiation, along with those of V, W, and O (VO<sub>2</sub> layer, 80 nm depth). The In 3d peak and Sn 3d peak of irradiated sample exhibit a downward shift to lower binding energies by 0.5–0.6 eV (Figs. 4(a) and 4(b)). The O 1s of ITO peaks shift to higher binding energies by 0.7 eV (Fig. 4(c)). Correspondingly, the O 1s of VO<sub>2</sub> peaks shift to higher binding energy by 0.5 eV (Fig. 4(d)), and both the V 2p peak and the W 4f peak exhibit a

notable decrease of 0.3–0.5 eV in the low binding energy region (Fig. S14 in the ESM). Additionally, electron paramagnetic resonance (EPR) spectroscopy results revealed a 13% increase in the sharp signal peak at a  $g$ -value of 2.003 in the irradiated sample (Fig. 4(e)). This peak is characteristic of oxygen vacancies (V<sub>o</sub><sup>•</sup>) and serves as a definitive signature of oxygen deficiency. The O K-edge XANES spectra analysis, showing a shift of the absorption edge of binding energy towards the low-energy region, further corroborates this finding (Fig. S15 in the ESM). These results indicate that the chemical orbital environment of the ITO and VO<sub>2</sub> layers is altered by the interlayer migration of In<sup>3+</sup>, Sn<sup>4+</sup>, and V<sub>o</sub><sup>•</sup> ions subsequent to irradiation.

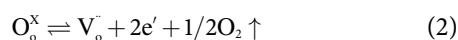
Density functional theory (DFT) calculations were performed to gain further insights into the charge density and atom orbitals variations. The reduced crystal formation energy in oxygen-deficient M-phase VO<sub>2</sub> implies that oxygen vacancies lower the energy barrier for interfacial In diffusion (Fig. S16 in the ESM). The pristine VO<sub>2</sub> (M1 phase) exhibits an intrinsic band gap of 0.71 eV [31], introduction of In dopants and oxygen vacancies (irradiated) induce a downward shift in the bands near the Fermi level, reducing the band gap to 0.32 eV and enhancing the VO<sub>2</sub>'s metallic properties (Fig. S17 in the ESM). Charge density difference analysis reveals an enhanced electron density accumulation on the O atoms, resulting from electron donation by the V atoms in pristine VO<sub>2</sub>. Visualization of the charge transfer process exhibits a pink equivalence surface near the In atom of the irradiated VO<sub>2</sub>, while the O side displayed cyan equivalence surfaces, indicating the more



**Figure 4** Mechanism of vacuum-UV induced M1-VO<sub>2</sub> phase degradation. XPS spectra of (a) In 3d, (b) Sn 3d, and (c) O 1s of the pristine and irradiated ITO layer. (d) XPS spectra of O 1s of the pristine and irradiated VO<sub>2</sub> layer. (e) EPR spectra of the pristine and irradiated V-FPRC. (f) Surface charge density difference, the cyan and pink regions correspond to an accumulation and depletion of electron density, respectively. (g) Projected density of states (PDOS) of O atom p-orbital, and V, In, Sn atoms d-orbitals of the pristine and irradiated VO<sub>2</sub>. (h) Schematic illustration of vacuum-UV induced VO<sub>2</sub> M1-phase to R-phase conversion in the V-FPRC.

electron transfer from In to O (Fig. 4(f)). Figure 4(g) shows the atoms orbital diagram and projected density of states (PDOS) calculations. There are distinct shifts in the density of states in the p-orbitals of O and the d-orbitals of V atoms toward the top of the valence band. Specifically, with respect to the Fermi level, the maximum valence bands of O atomic density of states shifted from 0.49 to 0.13 eV, and V atomic density of states shifted from 0.42 to 0.10 eV, respectively (Fig. S18 in the ESM). After irradiation, the electrons first occupy the lower  $t_{2g}$  levels, including the  $d_{||}$  and  $d_{||}^*/\pi^*$  orbitals, resulting in the Fermi level upshift as well as producing the new defect energy level (Fig. S19 in the ESM).

Based on the evidence of experimental and theoretical calculations, we propose the VO<sub>2</sub> phase transition mechanism in Fig. 4(h). Under vacuum ultraviolet (VUV) irradiation, the oxygen vacancies in the ITO layer initially contain a substantial amount of adsorbed oxygen [32]. Upon irradiation, the adsorbed oxygen atoms acquire sufficient energy to desorb from the surface, leading to ultraviolet-induced outgassing and an increase in surface oxygen vacancy concentration. With prolonged irradiation, some lattice oxygen ions ( $O^{2-}$ ) in In<sub>2</sub>O<sub>3</sub> are released, generating additional oxygen vacancies, while a lower O<sub>2</sub> partial pressure further promotes the formation of doubly ionized oxygen vacancies ( $V_o^{\bullet\bullet}$ ) and defect centers (In- $V_o^{\bullet\bullet}$ /Sn- $V_o^{\bullet\bullet}$ /V- $V_o^{\bullet\bullet}$ ). This shift in the reaction equilibrium (Eq. (2)) facilitates interfacial oxygen migration and the formation of oxygen vacancies in the VO<sub>2</sub> layer (Eq. (3)) [33, 34]



Prolonged high-energy UV irradiation further promotes the cleavage of In-O and Sn-O bonds in the ITO layer, which facilitates the interdiffusion and migration of In and Sn. This migration enhances the electron occupancy of the hybridized energy level formed by the  $d_{||}$ -bond orbital and In/Sn-d orbitals in the V-V dimer. The increased electron density in the  $d_{||}$  state strengthens orbital overlap with hybridized  $\pi^*$  antibonding orbitals, ultimately driving the phase transition of VO<sub>2</sub> from the insulating monoclinic (M1) phase to the metallic rutile (R) phase.

### 3 Conclusion

In summary, our findings reveal, at the atomic scale, the phase-transition mechanism of VO<sub>2</sub> driven by the interlayer diffusion of In, Sn, and V<sub>o</sub> under vacuum ultraviolet irradiation in V-FPRC. The interlayer diffusion of elements induces a vibrational displacement of the  $d_{||}$  bonding orbital in the V-V dimer. This displacement facilitates orbital overlap with the hybridized  $\pi$  antibonding orbital, ultimately triggering the phase transition of VO<sub>2</sub> from the M1 to the R phase. To further corroborate our experimental findings, DFT calculations were performed, yielding results that consistently validated the experimental observations. These theoretical results provide crucial mechanistic insights into the defects induced VO<sub>2</sub> phase stabilization, while simultaneously establishing a robust foundation for both the rational design of



strongly correlated oxides and future investigations in optoelectronic information science.

**Electronic Supplementary Material:** Supplementary material (experimental section, experimental and characterization details, density functional theory methodology, and supporting experimental results such as Figs. S1–S20, Table S1–S4) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908919>.

## Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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## Declaration of competing interest

All the contributing authors report no conflicts of interest in this work.

## Author contribution statement

Y. L. and T. Z. conceived the idea and designed the experiments. T. Z. was involved in all the experimental parts. Y. Y. C., X. Q. G., Q. Q. Z., J. R. L., and C. L. contributed to the fabrication of the high-performance passive dynamic thermal radiator. Y. F. Y., J. X. G., and S. L. D. helped to optimize the experiments and conduct the characterizations. H. Y. O. Y. carried out the theoretical calculation of the DFT. Y. L., J. P. Z., and T. Z. wrote and revised the manuscript. All authors were involved in the discussion for data analysis and commented on the manuscript.

## Use of AI statement

None.

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