Effects of charge fluctuation and charge regulation on the phase transitions in stoichiometric VO₂

Siddharth Joshi¹,³, Nicholas Smieszek¹,³ & Vidhya Chakrapani¹,²

Detailed electrical and photoemission studies were carried out to probe the chemical nature of the insulating ground state of VO₂, whose properties have been an issue for accurate prediction by common theoretical probes. The effects of a systematic modulation of oxygen over-stoichiometry of VO₂ from 1.86 to 2.44 on the band structure and insulator–metal transitions are presented for the first time. Results offer a different perspective on the temperature- and doping-induced IMT process. They suggest that charge fluctuation in the metallic phase of intrinsic VO₂ results in the formation of e⁻ and h⁺ pairs that lead to delocalized polaronic V³⁺ and V⁵⁺ cation states. The metal-to-insulator transition is linked to the cooperative effects of changes in the V–O bond length, localization of V³⁺ electrons at V⁵⁺ sites, which results in the formation of V⁴⁺–V⁴⁺ dimers, and removal of π* screening electrons. It is shown that the nature of phase transitions is linked to the lattice V³⁺/V⁵⁺ concentrations of stoichiometric VO₂ and that electronic transitions are regulated by the interplay between charge fluctuation, charge redistribution, and structural transition.

Despite many intensive investigations, the fundamental nature of the non-magnetic insulating ground state of VO₂ is not well-understood. During a temperature-induced transition that occurs at 340 K, the non-magnetic monoclinic (M₁) ground state undergoes a phase transition to a paramagnetic rutile (R) lattice that is metallic¹. The prominent theories attribute the insulator-to-metal transition (IMT) process to the structure-driven Peierls-distortion², Mott–Hubbard e⁻ correlation effects³, or a combination of both these mechanisms⁴–⁶. Dopants and time-resolved diffraction studies⁷ lend support to the Peierls-distortion theory, while more recent time-resolved results⁸–¹⁰ support the Mott–Hubbard e⁻ correlation. Common theoretical probes like local density approximation (LDA) and generalized gradient approximation (GGA) correctly predict the metallic state of the R phase, but fail to reproduce the insulating state of the M₁ phase¹¹. In contrast, the LDA + U method predicts insulating states with finite band gaps for both M₁ and R phases¹²,¹³. The dynamical mean-field theory (DMFT) and its variants accurately predict the metallic and insulating states of the R and M₁ phases¹⁴,¹⁵, respectively, however, they are based on adjustable parameters. Similarly, the hybrid Heyd–Scuseria–Ernzerhof (HSE) method correctly predicts electrical phases¹⁶ but not their magnetic properties¹⁷. More recently, calculations using modified Becke–Johnson exchange potential (mBJLDA) of DFT have successfully reproduced all the structural, electronic, and magnetic features of the IMT process¹⁸. However, the failures of common theoretical probes to accurately describe the ground state of VO₂ raises the question if its chemical nature has been correctly captured in the experimental studies. Interestingly, in a prior study, Boyarsky et al.¹⁹ noted that the asymmetric ⁵¹V nuclear magnetic resonance (NMR) spectral line of insulating VO₂ can be accurately fitted with the superposition of symmetrical lines of V³⁺ and V⁵⁺, and therefore suggested that the transition from metallic to insulating ground state involves the transition 2V⁴⁺ → V³⁺ + V⁵⁺ with the ground state composed of V³⁺ and V⁵⁺ ions. However, a subsequent study by Neilsen et al.²⁰ disputed the analysis of Boyarsky et al. by employing both higher and lower-field NMR measurements, and noted that the insulating phase consists of only V⁵⁺ cations. In an unrelated study, Chen and Fan²¹ found that charge localization and segregation in the form of V⁵⁺ can occur at the surface due to subtle fluctuations of deposition conditions which can induce acceptor doping in otherwise n-type VO₂. One way to elucidate the true chemical nature of stoichiometric VO₂ is by studying the electronic structure and the related phase transitions in carefully prepared under- and over-stoichiometric phases close to the stoichiometric

¹Howard P. Isermann Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA. ²Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180, USA. ³These authors contributed equally: Siddharth Joshi and Nicholas Smieszek. *email: chakrv@rpi.edu
point without inducing phase change to other vanadium oxide compounds. It is well known that introduction of oxygen vacancy ($V_{O}$) defects in the lattice results in a decrease in the transition temperature, $T_{IMT}$, to room temperature, or below\textsuperscript{22}. In this study, we carried out detailed transport and photoemission studies on compositionally-modulated VO$_2$ lattices, from VO$_{1.6}$ to VO$_{2.44}$ by systematically introducing oxygen interstitial (O$_i$) defects into VO$_2$ to understand the effects on oxygen over-stoichiometry on the valence band (VB) structure, electrical resistivity, and structural transitions. Our results shed a new light on the IMT process. They indicate that stoichiometric VO$_2$ in the metallic state is multi-valent with co-existing V$^{4+}$ and V$^{3+}$ ions that are a result of charge fluctuation of lattice V$^{4+}$ cations. Localization of charge carriers at the disproportionated cationic sites, likely due to strong correlation effects, together with lattice distortions, lead to the nucleation of an insulating phase. Similar multivalence of the stoichiometric lattice have previously been noted in other correlated-systems. A striking example of this occurs in stoichiometric CrO$_2$, a 3d$^5$ system with Cr in the +4 state, which is expected to be a Mott insulator. However, results show that CrO$_2$ is a half-metallic ferromagnet due to its mixed valent lattice composed of Cr$^{3+}$ and Cr$^{4+}$ ions\textsuperscript{23-25}.

**Results**

Measurements were performed with two-dimensional (2D) single crystalline platelets of VO$_2$ synthesized from the phase transformation of V$_2$O$_5$, 2D platelets that were grown using hot filament chemical vapor deposition technique (see “Methods”\textsuperscript{26,27}). Scanning electron micrographs (Fig. S1A in the supporting information, SI) showed the platelets to be 1–2 microns in length and 20–50 nm in thickness. X-ray diffraction patterns (Fig. S1B) showed a characteristic 2θ angle at 26.9° corresponding to (111) monoclinic VO$_2$. The as-produced platelets were metallic due to lattice oxygen-deficiency (VO$_{2-x}$) and were converted to semiconducting, stoichiometric VO$_2$ by annealing in air at 220 °C for 72 h or until they showed a characteristic IMT at 67 °C (Fig. S1C). The stoichiometry of this sample, as determined from the ICP-MS analysis, was VO$_{1.97}$ (referred henceforth as VO$_2$).

Prior studies have shown that non-native dopants, such as W, Nb, Cr, etc. strongly affect the $T_{IMT}$\textsuperscript{28,29}. However, their presence introduces additional structural distortion due to lattice strain\textsuperscript{30,31}, and gives rise to overlapping chemical and magnetic signatures, thus complicating the study of phase transition behavior. These issues can be avoided if methods exist for the controlled introduction of native defects (V and O) that would then enable the study of resulting band structure changes and its corresponding influence on IMT. While O deficiency can be easily engineered during the growth process because of the propensity of VO$_2$ for O vacancies, introducing excess O into the lattice without nucleation of secondary phases such as V$_2$O$_5$ is challenging, and has not been demonstrated. Initial attempts at controlled increase in the oxygen stoichiometry of VO$_2$ through thermal annealing without causing the nucleation of a V$_2$O$_5$ phase were unsuccessful. Prolonged annealing of VO$_2$ samples in air at 220 °C did not increase the O stoichiometry or the room-temperature resistance value, while oxidation at a slightly higher temperature of 250 °C, even for a short duration, resulted in the nucleation of V$_2$O$_5$ phase within the VO$_2$ phase. A faint characteristic Raman peak at 993 cm$^{-1}$ (Fig. S1D) along with the observation of a faint yellow tint of the surface post-oxidation provided confirmation for the incorporation of excess O as a V$_2$O$_5$ phase instead of uniform bulk doping to give VO$_{2+y}$. Therefore, an electrochemical approach was pursued to modulate the O stoichiometry. The advantage of electrochemical doping is that a controlled number of O dopants can be introduced uniformly across the lattice by simply controlling the total number of injected charge carriers. Prior studies have demonstrated the synthesis of superconducting oxide with a wide range of oxygen over-stoichiometry through electrochemical doping in KOH electrolyte, which was not achievable through oxidative thermal annealing\textsuperscript{32-35}. We note that electrochemical doping is distinct from the electrochemical gating process in that the doping is irreversible, (or quasi-reversible) involving oxygen incorporation into the lattice, which is stable even after emersion from the electrolyte and subsequent heat treatment. The key advantage of electrochemical doping over thermal treatment is its ability to charge thick films of nanostructures due to their nanoporous nature, which allows percolation of ions within the film and reduces the time needed to achieve uniform bulk doping.

Given the instability of VO$_2$ in KOH electrolyte, oxidation was performed in air-saturated propylene carbonate (PC) electrolyte containing peroxomonosulfate (H$SO_5^-$) ions with 1.6% active oxygen (tradename OXONE). OXONE has a higher redox potential (+1.81 V) than KOH (+1.23 V), and, therefore, is a more powerful oxidant than KOH. As a result, a wide concentration range of O stoichiometry from 2 (VO$_2$) to 2.44 (V$_2$O$_5$) was achievable. Figure 1A shows the measured electrochemical response of an oxygen-deficient VO$_{2-x}$ film during anodic oxidation in OXONE electrolyte. The oxygen doping process was confirmed via simultaneous in-situ measurement of sample resistance (inset of Fig. 1A) during polarization. Data showed that the oxygen insertion occurred at potentials between 0.2 and 1.0 V versus the standard hydrogen electrode (SHE). At potentials greater than 1.0 V, large faradaic currents were observed due to gas evolution that led to a decrease in the amount of inserted oxygen. All doping experiments were done within the stable potential window between 0.4 and 1 V (Supplementary Fig. S2).

The structural phase transitions resulting from the doping process were monitored through Raman measurements\textsuperscript{36-38}. Samples after polarization were removed from the electrolyte, washed in PC, and dried under vacuum before measurements. Figure 1B shows the Raman spectrum of the VO$_2$ film before and after oxidative doping at 0.4 V and 1.0 V. Spectra of pristine samples showed sharp peaks at 140, 189, 221, 307, 496 and 611 cm$^{-1}$ that are characteristic of the pure monoclinic M1 phase\textsuperscript{36}. A shift in the $A_{1g}$ mode of the V–O bond from 611 to 634 cm$^{-1}$ along with a peak at 589 cm$^{-1}$ confirmed a phase change from M1 phase to a triclinic T phase\textsuperscript{36} for electrodes polarized at 0.4 V. Further polarization at 1 V resulted in the disappearance of the small peak at 589 cm$^{-1}$ and a further shift of the $A_{1g}$ mode to 639 cm$^{-1}$, which is indicative of the formation of the insulating M2 monoclinic phase. The lack of the vanadyl mode at 993 cm$^{-1}$, as well as of the most intense lattice mode at 147 cm$^{-1}$ (Fig. S1D) confirmed uniform doping and the absence of VO$_2$ phase in the oxidized samples.
Figure 1C shows the resistance changes of VO$_2$ and VO$_{2-x}$ electrodes as a function of temperature measured after oxidation at +1 V bias for 20 min without emersion from the electrolyte. Oxidation led to a complete suppression of IMT up to 90 °C in both VO$_2$ and VO$_{2-x}$. Metallic VO$_2$ also showed two-orders of magnitude increase in resistance after 20 min polarization at 1 V bias along with a phase transition from M1 to M2 with no IMT transition up to 90 °C. Measurements in an extended temperature range done on emersed dried films in air showed an IMT at 118 °C (Fig. 1D). This increase in TIMT from 67 to 118 °C with O doping is similar to trends seen with Cr-doping.

Valence band density of states. The changes in the electronic structure occurring as a result of O doping were studied through X-ray photoemission spectroscopy (XPS) measurements. Both stoichiometric and non-stoichiometric samples likely have some V$_2$O$_5$ on the surface that results from over-oxidation, as noted by Chen and Fan. Therefore, all samples for photoemission studies were prepared by gently sputtering with an Ar$^+$ beam for 2 min to remove any over-oxidized surface layer, as monitored via V$^{5+}$ signal in the V 2p core-level peak, and followed by annealing in ultrahigh vacuum (UHV) at 220 °C for 3 h to desorb physisorbed electrolyte or other contaminants and recover any damage induced by the ion bombardment. Both core-level and valence band (VB) spectra (Figs. 2, 3) were recorded on these UHV-prepared samples at various temperatures. To observe any systematic trend in the changes in the VB structure resulting from O doping, we compared the room-temperature VB spectra of VO$_2$ with increasing O stoichiometry with the spectrum of V$_2$O$_5$. To enable comparison, the spectra from various samples were normalized to the intensity of the O 2p band centered at a binding energy (BE) of 6 eV, and are shown in Fig. 2. The VB signal comprises of signal from the V 3d band ($E_F$ to 2.5 eV) and the O 2p band (2.5–10 eV). The lower energy spectral function seen above $E_F$ is generally referred to as the
Figure 2. (A) Valence band XPS spectrum of VO₂ of various oxygen stoichiometry in comparison to spectrum of V₂O₅ measured at room temperatures; and (B) schematic showing the observed changes in the VB spectrum with varying O stoichiometry.

...incoherent feature, which arises mainly from the lower Hubbard band (LHB) of V 3d∥ orbitals. Cluster model calculations of Mossanek and Abbate indicate that this incoherent feature is due to screening of 3d¹ electrons by the O 2p ligand. The small signal seen at Eₐ in VO₁.₈₆ represents the delocalized d-band states and represents the coherent part of the spectral function. These signals from V 3d states are nearly absent in the spectrum of V₂O₅. The dominant V⁵⁺ ions of V₂O₅ have a 3d⁰ electronic configuration and therefore do not contribute to the photoemission signal in this energy range. The residual signal seen between Eₐ and 2 eV arises from the small amount of V⁴⁺ ions (Fig. 3B) with 3d¹ configurations that are formed due to the VO defects in the lattice, as noted...
in a previous study\textsuperscript{26}. With increasing O content of the VO\textsubscript{2} lattice, three trends become noticeable in the room temperature VB spectra (Fig. 2A): (1) The O 2p band progressively shifts to lower BE; (2) The rising edge of the VB curve shifts to higher BE, and (3) The width of the V 3d\parallel band decreases dramatically with increasing O stoichiometry, indicating a lower density of occupied 3d states (DOS). The observed trends are shown schematically as a band diagram in Fig. 2B. An electrostatics model of the ionic lattice suggests that an increase in the oxygen interstitial (O\textsubscript{i}) defects will lead to an increase in the hole concentration in accordance with the defect reaction in Kröger–Vink notation:\[{\frac{1}{2}}O_2(g) ⇔ O\textsubscript{i} + 2h^+\]. The trapping of these holes at the nearest-neighbor V\textsuperscript{4+} sites in VO\textsubscript{2} would create V\textsuperscript{5+} sites with corresponding acceptor-type defect states above the VB of VO\textsubscript{2}. In contrast, donor-type V\textsuperscript{3+} defect states are created from V\textsubscript{O} defects through the reaction \[{O_2^\circ} \leftrightarrow V\textsubscript{O} + 2e^- + \frac{1}{2}O_2(g)\] and e\textsuperscript{-} trapping at the V\textsuperscript{4+} sites. Here, O\textsubscript{2} represents the lattice oxygen. Therefore, it can be concluded that an overall higher DOS and the observed finite number of states at \(E_F\) (metallic phase) in oxygen-deficient VO\textsubscript{1.86} is due to the presence of V\textsuperscript{3+}-related occupied states (Fig. 2B). This leads to an increase in the \(E_F\), which manifests as an increased energy separation (5.7 eV) between the \(E_F\) and O 2p band center in the XPS spectrum. On the other hand, increasing holes in the O 2p band with increasing O\textsubscript{i} defects result in a lower V 3d band width due to the interconversion of part of V\textsuperscript{4+} to V\textsuperscript{5+} with 3d\textsuperscript{0} electronic configuration that does not contribute to the XPS signal. In an n-type lattice, the increasing hole concentration will result in a lower free electron concentration due to e\textsuperscript{-} trapping which will lead to a decrease in the \(E_F\) value. In the XPS spectrum, this results in a decrease in the...
energy gap between the $E_g$ and O 2p band center (5.1 eV). All samples except VO$_{1.86}$ exhibit insulating (semiconducting) behavior at room temperature. We note that there have been important prior XPS studies in phase transitions in the other various phases of vanadium oxides such as V$_2$O$_5$, V$_2$O$_3$, V$_2$O$_2$, and V$_2$O$_{13}$, and has also been reviewed by Surewicz et al. These oxides belong to Wadsley ($V_2O_{35-\delta}$) or Magnéli ($V_2O_{3n-1}$) phases with increasing O/V ratios. The results of the present study are however distinct from the results of these prior studies in that they represent oxygen composition that are in between the above stoichiometric phases, and thus aid in understanding phase behavior slightly above and below the stoichiometric point of a given crystallographic phase. Additionally, while we observe an increase in the $T_{\text{IMT}}$ of VO$_2$ with an increase in the O stoichiometry, this trend is not necessarily followed among the various stoichiometric phases of vanadium oxides. For instance, V$_2$O$_{13}$, which has a higher O/V ratio (2.167) than that of VO$_2$ (2), has a lower $T_{\text{IMT}}$ (145 K) than that of VO$_2$ (340 K). The only undoped vanadium oxide that shows a true electronic phase transition at $T_{\text{IMT}}$ greater than that of VO$_2$ is V$_2$O$_3$, a lower O/V oxide (1.67), with a $T_{\text{IMT}}$ of 425 K.

The variations in $T_{\text{IMT}}$ with O stoichiometry seen with temperature-dependent resistance measurements was confirmed using VB spectra obtained at different temperatures (Fig. 3A). In stoichiometric VO$_2$, the V 3d DOS show a clear shift towards the $E_g$ at 100 °C, which is higher than $T_{\text{IMT}}$ of 67 °C, and thus confirming the formation of a metallic state. During phase transition, the signal of lower-BE V 3d states (coherent states) is seen to increase at the expense of higher-BE V 3d states. In over-stoichiometric VO$_{2+x}$, only a small shift is seen at 100 °C, which is below the $T_{\text{IMT}}$ of 118 °C. However, a larger DOS shift to lower BE is seen at 150 °C, which is indicative of the metallic state, and is consistent with the bulk transport measurements. The spectra of VO$_{2-x}$ showed finite number of states at $E_g$ both at RT and at 100 °C that is consistent with their metallic nature.

Broadening of V 2p core-level spectra: localized and delocalized ground states. Analysis of the core-level V 2p$_{3/2}$ envelope was performed between samples of different oxygen stoichiometry to identify valent states involved in phase transitions, as shown in Fig. 3B. All spectra were corrected for the background signal using Shirley analysis and the peak position and area were optimized by a weighted least-square fitting method using Gaussian line shapes.

No contribution from adsorbed water or other ambient adsorbates, which are seen at BEs of 532.5–533 eV, was observed on UHV-annealed samples. The V 2p$_{3/2}$ spectrum of V$_2$O$_3$ shows a sharp peak at 517.2 eV that corresponds to the V$^{3+}$ oxidation state. A set of V$_2$O$_5$ samples were intentionally grown under reducing conditions to generate increasing lattice V$_2$O defects in the material. The V 2p$_{3/2}$ spectrum of one such V$_2$O$_{5-x}$ sample, also shown in Fig. 3B, shows the presence of an additional peak at a BE of 515.8 eV, corresponding to V$^{4+}$ cations. The full-width-at-half-maximum (FWHM) of the V$^{4+}$ defect-related peak ranged from 1.1 to 1.3 eV when present in low and high concentrations, respectively. On the other hand, the V 2p$_{3/2}$ spectrum of stoichiometric VO$_2$ shows a broad peak at 516.1 eV, also corresponding to V$^{4+}$, which can be fitted with a single Gaussian peak of FWHM of 2.8 eV, which is within the reported values of 2.0–3.2 eV. We note that the reported V 2p$_{3/2}$ spectrum of both insitu cleaved or UHV-prepared (similar to current study) single crystalline and polycrystalline VO$_2$ are in general broad, as seen from the reported values summarized in Table S1 in SI, and in general much broader than V$_2$O$_3$ or VO phases. Interestingly, the spectra of mixed-valent vanadium oxides such as (V$_2$O$_{13}$, V$_2$O$_3$, V$_2$O$_2$, and V$_2$O$_3$) that exhibit IMT at varying temperatures are similarly broad. In general, peak broadening occurs due to both intrinsic and extrinsic mechanisms. Apart from the known effects of the instruments limitations or core–hole lifetime changes, important broadening mechanisms of core-level peaks, especially in open-shell systems like VO$_2$ can be attributed to (1) multiplet features arising due to the angular momentum coupling between the core–hole created due to photoionization and open-shell valence d electrons, and (2) phonon broadening. However, the multiplet splitting expected to be present in VO$_2$ cannot explain the magnitude of observed broadening because of the band width (W). Typical values of $Q$ in vanadium oxides are 0.8–1.2 eV, which are obtained by comparing the band gap, d–d separation, and the band width are 0.6 eV, ~1.0 eV and 1.5 eV, respectively. Therefore, electron excitation from the filled band to conduction band (CB) states in order to screen the influence of photoionized core-holes can result in bound e$^-$ (V$^{3+}$) and h$^+$ (V$^{5+}$) pairs that would correspond to instantaneous mixed-valent final states. Correspondingly, the single broad Gaussian peak in VO$_2$ can be resolved to three Gaussian peaks corresponding to V$^{3+}$ (515.0 eV as in V$_2$O$_3$) V$^{4+}$ (516.1 eV), and V$^{5+}$ (517.2 eV as in V$_2$O$_3$) final states. The ratio of V$^{3+}$ to V$^{5+}$ is ~1. It is important to note that such states are not representative of chemical shifts occurring in the sample (initial state), which remains in the V$^{4+}$ state. This is consistent with the average vanadium oxidation state of 4.39 determined from ICP-MS analysis (Supplementary Table S3).

In non-stoichiometric VO$_2$, a further broadening of the 2p peak is observed. An increase in O stoichiometry gives rise to an increase in the signal at the BE corresponding to V$^{3+}$, as seen from the difference spectrum (ΔI versus BE curve), and is as expected because hole doping should increase the number of V$^{3+}$ cations in the lattice. In contrast, the spectrum of VO$_{1.86}$ shows an increase in the signal at a lower BE corresponding to the signal of V$^{3+}$, which is consistent with the chemical shift expected from the presence of V$^{3+}$ in the lattice due to the formation of V$_2$O defects. Here, the 2p$_{3/2}$ peak broadening represents both initial (chemical shift) and final (photoionized) mixed-valent states. This is further confirmed by comparing the average oxidation state estimated through this XPS analysis of the relative area contribution of the individual peak to the overall spectrum to the
average vanadium oxidation state calculated from ICP-MS data. For VO$_2$$_{-x}$, the analysis gives the average oxidation state of +3.76, which is relatively close to the value of +3.72 from ICP-MS analysis (Supplementary Table S3).

In addition, a strong increase in the peak broadening can be seen in stoichiometric VO$_2$ due to temperature-induced phase transition from insulating to the metallic phase at temperatures higher than TIMT (Fig. 4). An increase in the signal at both low and high BE can be seen, indicating the formation of V$^{3+}$ and V$^{5+}$ cations. Localization of itinerant electrons at the V$^{4+}$ site in the metallic state would lead to V$^{3+}$ cation (polaron) formation. Therefore, this broadening seen is likely due to changes in the initial state. An explanation for the formation of V$^{5+}$ is given in "Discussion" section. Supplementary Tables S1 and S2 summarizes the various fitting parameters along with the values reported in the literature for single crystalline and polycrystalline samples.

**Discussion**

A cooperative structural and electronic phase transition model. The combined results of electrical resistivity and photoemission measurements show that the doping-induced IMT process is controlled by the lattice V$^{3+}$/V$^{5+}$ ratio. An increase in V$^{3+}$ concentration in the lattice relative to the stoichiometric lattice decreases T$_{\text{IMT}}$, while an increase in V$^{5+}$ leads to an increase in T$_{\text{IMT}}$. Further, if the increased peak broadening seen in the XPS is due to initial state effects, then the results show that the temperature-induced IMT process in stoichiometric VO$_2$ results in the formation of V$^{3+}$ and V$^{5+}$ cations in the metallic phase. While this is not conclusive evidence, we show below that other evidence exists in the literature that substantiates this assertion. Thus, any proposed model must account for both doping- and temperature-induced IMT and structural transitions.

Based on the XPS results, we propose that in stoichiometric VO$_2$, strong charge fluctuation occurs in the metallic phase, which leads to the creation of e$^-$ and h$^+$ pairs that correspond to the formation of V$^{3+}$ and V$^{5+}$ cations between the V–V dimers seen in the insulating ground state. This implies that in the metallic phase, the LHB $d_{\|}$ band corresponds to a V$^{5+}$ hole band (3d$^0$ configuration) that lacks the 3d$^1$ electron of the V$^{4+}$ cations. The antibonding $d_{\parallel}$ band ($d_f^\ast$) corresponds to a filled V$^{3+}$ band of 3d$^2$ configuration. In the metallic phase of stoichiometric VO$_2$, charge fluctuation would lead to a V$^{3+}$/V$^{5+}$ ratio of 1. The conduction occurs through hopping of e$^-$ in V$^{3+}$ to the next site and so on through the lattice (polaronic hopping). Similarly, h$^+$ in V$^{5+}$ can also hop to the neighboring sites and move through the lattice, thus leading to hole conductivity. Since V$^{3+}$ and V$^{5+}$ cations can be considered as donors and acceptors, respectively, in a stoichiometric lattice, the metallic phase consists of both e$^-$ and h$^+$ and therefore, both contribute to the conductivity. This is supported by the results of transport studies and arguments presented by some earlier researchers. While both hall-effect and thermopower measurements indicate dominant conduction by electrons in both phases, the measured electron mobility in both phases is low (~ μ ~ 0.5 cm$^2$V$^{-1}$s$^{-1}$) and the measured Hall coefficient is nearly three-times lower than that expected for a simple metal with one electron per atom. Both theoretical and experimental results show very large electron effective mass with values of m* between 2 and 65 times the free carrier mass (m$^0$). These results together with the observed low Hall constant and short mean free path of ~ 20% of V–V distance led to the suggestion by Ladd of a two-band conduction model where both the e$^-$ and h$^+$ contribute to conductivity, but their nearly equal but opposite polarity contributes to the lower calculated values of Hall constant and mobility. He suggested that true mobility may be higher than the calculated values. Kabashima et al. indicated that both band and hopping conductivity is present in the metallic phase, and therefore models with a single type of charge carrier are inappropriate to explain the changes. Similarly, theoretical calculations of Caruthers and Kleinman indicate that the metallic phase of VO$_2$ is to be intrinsic with the presence of both e$^-$ and h$^+$ in the lattice.

![Figure 4](https://example.com/vo2_xps.jpg)
Yeo et al. calculations performed using three-band Hubbard model showed that the only necessary parameter for inducing leads to the localization of a majority of e− from V3+ sites at hole fields (V5+ sites), which would convert the sites from $V^{3+} \rightarrow V^{4+}$ and $V^{5+} \rightarrow V^{4+}$. Thus, we attribute the observed formation of V–V dimers in the insulating state to the charge localization between the fluctuating states to create V4+–V4+ dimers. Therefore, one can view the insulating ground state of VO2 as a self-compensated semiconductor, where most donors are neutralized by the acceptors to create a low-conducting state consisting of predominantly V4+ lattice sites and a small number of uncompensated V3+ and V5+ cations. This is shown schematically in Fig. 5A. Upon thermal excitation at the transition temperature, e− transition from the lower lying filled acceptor states ($V^{4+} \rightarrow V^{5+}$) to the empty dσ and π* donor states ($V^{4+} \rightarrow V^{3+}$) should result in an increased filling of higher energy states (lower BE states in VB spectrum), an increase in the DOS of both V3+ and V5+ states, and a corresponding decrease in the DOS of V4+. This would explain the spectral weight transfer of the V 3d3 VB spectra towards Ef. Further, fast e− hopping between two polaronic V4+ and V5+ sites in the metallic phase should result in a more symmetric structure (equally spaced vanadium chains), while carrier trapping in the low-temperature phase leads to structural distortion. The above picture represents the possible electronic aspect of the IMT process. However, there are other important aspects of the transition that must be considered. For instance, in the metallic state, there would be a strong Coulomb interaction between the e− and h+ pairs created by the fluctuation which would result in a bound state and not contribute to the conductivity. Combined XAS and XPS studies indicate a closing of 0.6 eV gap upon transition to the metallic phase, which is much larger than the energy scale of the $T_{\text{IMT}}$ ($kT = 0.03$ eV).

Further, in a simple donor–acceptor band model, one would expect a transition temperature instead of the sharp transition at a critical temperature with a large latent heat of phase change (1020 cal/mole°C). The contribution of electronic entropy of large density of states of the metallic phase alone cannot account for the measured latent heat, as pointed out by Ladd. These discrepancies can be resolved if one considers a co-operative structural and electronic transition process. In our model, the metallic state with co-existing e− and h+ charges are stabilized by screening of the Coulomb field of the d∥ hole band by electron in a comparatively wider π* band, a concept proposed previously by Mott et al.3, 58. The nucleation of an insulating state occurs as a result of displacement of V atoms perpendicular to the c-axis that specifically raises the energy of the π* band, thereby increasing the energetic gap between the π* band and d∥ band. This removes the necessary screening between the V3+ dσ electrons and V5+ d∥ hole band and causes localization of e− in the Coulomb field of holes. This assertion is compatible with the results of Tanaka et al., whose calculations performed using three-band Hubbard model showed that the only necessary parameter for inducing phase transition is energy separation (D) between the dσ and π∗. Therefore, we believe that IMT is a cooperative process between temperature-induced lattice distortion, the resulting modulation of the energy of the π* band and its influence on the efficacy of screening of dσ electrons against the hole field.

In our two-band picture shown in the Fig. 5A, there is no collapse of the gap between the dσ and d∥ band, rather metallicity is induced by the downward shift of the π* band and consequent overlap with the d∥ band. Optical measurements on high-quality VO2 show a low energy peak at ~1.1 eV due to $dσ \rightarrow dσ$ transitions, and a peak around 3.1 eV due to O 2p–d band electronic transitions. Our temperature-dependent measurement of the optical spectrum of VO2, shown in Supplementary Fig. S3, shows no significant difference in the spectral shape of the transmission curve between the metallic and insulating phases in the 300–1700 nm spectral range, and only changes in the transmittance values are observed. Both the π–d and d–d peaks occur at the same energy in both the insulating and metallic phases, which indicates there is no shift in the O 2p and d bands between the two phases. In addition, we note that if our assertion of the presence of V3+ hole band in the metallic state is correct, then the interpretation of the X-ray absorption spectroscopy (XAS) data needs to be reevaluated with theoretical calculations. For instance, the rising portion of the O K edge spectral curve is taken to be due to transitions to the unoccupied π* band. However, this transition could also be due to electron transitions from core-level to the unoccupied states of V5+ hole band. This is supported by the observation that the intensity of this peak is higher in the metallic phase than in the insulating phase, as reported in the literature, and points to the lower occupancy of this band in the metallic, which is opposite to conventional understanding of partly-filled π* bands in the metallic state. Further, oxygen-stoichiometry-dependent XAS measurements of Yeo et al. do show an increased spectral weight of this band with increasing O stoichiometry, which is consistent with our picture of a larger unoccupied V3+ hole band in the metallic and insulating phases of O-excess samples compared to that of O-deficient VO2.

The high-temperature phase of the VO2 is considered to be a bad metal because of its high relative resistivity. According to the Drude model of metallic conduction, electrical conductivity should decrease with an increase in temperature because of the increased carrier scattering from the thermally-excited lattice vibrations. Transport measurements of the metallic phase, however, show that carrier mobility increases, albeit slowly, as the temperature is increased from $T_{\text{IMT}}$. As thermal excitation facilitates polaronic hopping between neighboring sites, the trend in the carrier mobility supports our polaronic model of the metallic phase.

By accurately fitting the observed asymmetric 51V NMR spectral line of insulating VO2 with superposition of symmetrical lines of V3+ and V5+, Boyarsky et al. suggested that the low temperature phase of VO2 consists of V3+ and V5+. In our model, it is the high-temperature phase that consists of co-existing V3+ and V5+ cations. Our model, in some sense, is consistent with the donor–acceptor (D–A) pair model proposed by Berglund and Guggenheim. While asserting that correlation effects are not important, the authors attributed the insulating phase at room temperature to a heavily compensated n-type semiconductor due to the presence of a high density of both “donor-like” and “acceptor-like” unidentified states within the band gap of VO2. Their argument for the
existence of co-existing donor and acceptor states within the band gap stems from the observations that: (1) no clear abrupt optical absorption threshold has been observed in VO₂ at the photon energy corresponding to the energy gap in the semiconducting state; (2) absence of any observable photoconductivity in VO₂, and (3) absence of rectifying behavior at the metal–semiconductor (VO₂) contact with high work function metals such as Pt, Au, Al or Cu. They argued that all of the above could be explained by the presence of a high density of trap (acceptor) states within the band gap. Though the model proposed in this study differs from that of Berglund and

Figure 5. (A) Schematic showing the electronic aspects of the charge fluctuation and charge localization processes in the metallic and insulating phases of VO₂, respectively. Also shown is the charge regulation occurring in doped VO₂ as a result of charge injection and its effect on the IMT process; and (B) phase diagram of structural evolution of VO₂ as a function of doping and oxygen stoichiometry of the lattice. Doping with acceptor-type impurities or defects lead to the stabilization of V⁵⁺ defect states, which then stabilizes the various insulating monoclinic phases. In contrast, doping with donor-type defects induce metallic phase transitions due to stabilization of V³⁺ defect states.
Guggenheim\textsuperscript{57} in several aspects, it fits with their concept of co-existing $e^-$ and $h^+$ states and the experimental observations stated above underlying their model.

Finally, we show that both doping-induced and stress-induced IMTs can be rationalized easily within the proposed mixed-valent (D-A) lattice framework. The schematic of the atomic arrangement, as shown by Pouget et al.\textsuperscript{29} of the two interpenetrating sublattices of vanadium atom chains, A and B, in different VO\textsubscript{2} phases is shown, Fig.\textsuperscript{5B} for illustrating the process of structural transitions. The oxygen octahedron, whose principle axis points in the [110] direction, surrounding each V atom of the sublattices are not shown for clarity. Starting from the stoichiometric monoclinic M1 phase of VO\textsubscript{2}, which is characterized by alternating shorter and longer V–V bond lengths and twisted V–V chains, we first show the effects of hole doping. Introduction of O\textsuperscript{2−} defects or substitutional trivalent dopants such as Cr, Al, and Fe into the M1 lattice will lead to the formation of O 2p holes or V\textsuperscript{5+} cations to maintain charge neutrality\textsuperscript{29,64}. Electronically, the width of the V\textsuperscript{5+} hole band will increase causing greater localization of any uncompensated $e^-$ of the M1 phase, resulting in increased resistance of the lattice and a lower density of V\textsuperscript{4+} states in the $d_1$ LHB due to its partial conversion to V\textsuperscript{5+} states. This is consistent with the lower DOS observed in the VB spectra with increasing O stoichiometry (Fig. 2A). Structurally, the presence of V\textsuperscript{5+} would lead to a reduction in V–O bond length between the V\textsuperscript{5+} and the O\textsuperscript{2−} as well as the apical O\textsuperscript{2−}–O\textsuperscript{2−} distance in the surrounding oxygen octahedron. This contraction in the [110] direction would lead to an increase in the V–V distance in the [100]\textsubscript{\textipa{h}} direction, which causes a straightening of the tilted V–V pairs in the A sublattice, which in turn induces the depairing of V–V dimers in B sublattice to produce zig-zag chains, an arrangement defined as the M2 phase. Application of uniaxial stress in the [110]\textsubscript{\textipa{h}} direction of M1 phase in undoped VO\textsubscript{2} has the same effect of compressing the O–O bond distance as the hole-induced O–O shortening, thus both induce and stabilize insulating M2 and T\textsubscript{\textipa{h}} phases\textsuperscript{65}. The resultant increase in the V–V distance leads to a decrease in the band width of V\textsuperscript{5+} donor band and V\textsuperscript{2+} acceptor band and an increase in the energy separation between them, which would necessitate a greater thermal and phonon coupling, an increase in T\textsubscript{IMT} is observed. The results of Villenauve et al.\textsuperscript{64} who showed that stability of the M2 phase is closely linked to the oxygen stoichiometry of VO\textsubscript{2+x} lattice. The M2 phase disappears for $y \leq -0.01$, i.e. it is unstable in the presence of V\textsuperscript{4+} defects. In contrast, its stability domain increases when O stoichiometry is greater than 2. In other words, the M2 phase is stabilized by V\textsuperscript{5+} defects, a result which is consistent with our proposed V\textsuperscript{3+}–V\textsuperscript{5+} model.

Conversely, an increase in the O–O bond length and the resulting decrease in V–V bond distance would correspond to the case of increased band width (higher DOS) or lower energy gap between V\textsuperscript{3+} $d_{\|}$ band and V\textsuperscript{2+} $d_{\perp}$ band, which should decrease T\textsubscript{IMT}. This is seen in epitaxial strained films\textsuperscript{63}, where strong reduction in T\textsubscript{IMT} has been shown with the application of stress in the [001] direction. This is also the case when $V_{0}$ defects (through hydrogenation and electrochemical gating\textsuperscript{66}) or pentavalent or hexavalent substitutional impurities such as Nb, Mo, W, and Re are introduced in the lattice which leads to an increase in the V\textsuperscript{5+} states\textsuperscript{68}. In all the above cases, the V\textsuperscript{3+} band stabilizes the rutile phase of VO\textsubscript{2}.

The above explanation for doping-induced IMT shows that T\textsubscript{IMT} is regulated in the VO\textsubscript{2} lattice through combined effects of charge redistribution between the V\textsuperscript{3+}, V\textsuperscript{4+} and V\textsuperscript{5+} cations, and corresponding changes in the V–O and V–V bond lengths.

**Charge disproportionation in ternary vanadates: similarities and differences.** Charge disproportionation has been noted in other correlated systems like ternary and quaternary alloys of vanadates involving substitution with lanthanides (LaVO\textsubscript{3}) or alkaline earth elements (La\textsubscript{1−x}Ca\textsubscript{x}VO\textsubscript{3}, Sr\textsubscript{1−x}Ca\textsubscript{x}VO\textsubscript{3}). In these systems substitution of trivalent La with divalent elements such as Ca or Sr leads to paramagnetic metallic hole doping of LaVO\textsubscript{3} for $x \approx 0.2$, which is otherwise an antiferromagnetic Mott insulator for $0 < x < 0.2$. Photomission studies\textsuperscript{67,68} with different excitation energies have shown that the measured electronic properties strongly depend on the escape depth with the surface region exhibiting charge localization or insulating behavior while the bulk of the film corresponding to the metallic phase, as noted by the absence/presence of coherent signal near $E_F$. Maiti et al.\textsuperscript{67,68} attributed this to the enhanced correlation effect at the surface compared to the bulk which causes spontaneous disproportionation of lattice V\textsuperscript{4+} ions according to the reaction $2V^{4+} \rightarrow V^{3+} + V^{5+}$. Consistent with this reaction, all members of the series show three distinct peaks in the V 2p\textsubscript{3/2} core-level spectra corresponding to V\textsuperscript{3+}, V\textsuperscript{4+}, and V\textsuperscript{5+} species. Further, the observation of 1:1 ratio of V\textsuperscript{3+} to V\textsuperscript{5+} peak intensities in these compounds together with an observed increase in their signal when probed with lower energy excitation (more surface sensitive) provided strong evidence for spontaneous electronic phase segregation into metallic bulk consisting of V\textsuperscript{4+} cations and a more insulating surface with V\textsuperscript{3+} and V\textsuperscript{5+} cations. Therefore, such vanadates serve as an important reference for understanding the effects of charge disproportionation reactions in pure VO\textsubscript{2} discussed in the present study. While the two systems may appear to be similar, they, however, differ in several aspects. The major difference between the two systems is the condition under which charge disproportionation occurs. Surface charge disproportionation into V\textsuperscript{3+} and V\textsuperscript{5+} has been attributed to be the cause for the formation of insulating phase in doped vanadates. In contrast, we attribute charge disproportionation (or fluctuation) into V\textsuperscript{3+} and V\textsuperscript{5+} in the bulk of the metallic phase of stoichiometric VO\textsubscript{2}, while the localization of $e^-$ at the V\textsuperscript{5+} sites in the bulk as the cause for the formation of insulating phase with V\textsuperscript{4+} cations. In vanadates, disproportionation gives rise to localized, non-interacting mixed valent states. In contrast, in stoichiometric VO\textsubscript{2}, the mixed valent states correspond to delocalized states and therefore contribute to conductivity. Further, our results across stoichiometrically-modulated VO\textsubscript{2}, indicate that the ratio of V\textsuperscript{3+}/V\textsuperscript{5+} dictates T\textsubscript{IMT}, i.e. an increase in V\textsuperscript{3+}/V\textsuperscript{5+} ratio decreases T\textsubscript{IMT} and vice versa. The underlying mechanism giving rise to these differences in not clear. Although both VO\textsubscript{2} and SrVO\textsubscript{3} represent d\textsuperscript{1} configuration, according to Fujimori et al.\textsuperscript{38} the ratio of the effective Hubbard parameter ($U_{eq}$) to band width (W) of VO\textsubscript{2} is expected to be smaller than that of SrVO\textsubscript{3}, as W is larger for VO\textsubscript{2} due to much shorter V–V distances. Therefore, correlation effects are expected to be stronger in SrVO\textsubscript{3} than in VO\textsubscript{2}, thus leading to strong charge localization. Another interesting feature is that the V 2p\textsubscript{3/2} peaks of doped
vanadates show distinct peaks across the entire compositionally-modulated series that are clearly resolvable into Gaussian peaks corresponding to $V^{3+}$, $V^{4+}$, and $V^{5+}$ signals. In contrast, the spectrum of stoichiometric VO$_2$, in both metallic and insulating states shows a single broad peak that can be easily fitted by a single Gaussian peak albeit with different FWHM between the two phases. This indicates that the nature of the ground state, whether it is localized or delocalized valence states, between the two systems is different. Secondly, charge disproportionation in vanadates is restricted to the surface, as seen from the differences in the measured density of states between He-I, He-II and Al $K\alpha$ excitation signal. In all compositionally tuned VO$_2$ samples, the measured VB with respect to the standard hydrogen electrode (SHE) that has a work function of $\sim -4.44$ eV with respect to the vacuum level.

In conclusion, the results of oxygen stoichiometry-dependent phase transitions presented here offer a new perspective on the mechanism of temperature- and doping-induced IMT processes. Results and their interpretations suggest that charge fluctuation in the metallic phase of intrinsic VO$_2$ results in the formation of $e^-$ and $h^+$ pairs that lead to polaronic $V^{3+}$ and $V^{5+}$ cation states. The $d_{||}$ lower Hubbard band consists of the $V^{5+}$ hole band while the upper $d_{\perp}$ and $\pi^*$ bands form the $V^{3+}$ bands. The metal-to-insulator transition is linked to the cooperative effects of changes in the $V$–O bond length, localization of $V^{5+}$ electron at $V^{3+}$ sites that results in the formation of $V^{4+}$–$V^{4+}$ dimers, and removal of $\pi^*$ screening electrons. Our results on the doping-induced process suggests these co-operative changes are linked to the lattice $V^{3+}/V^{5+}$ concentrations of VO$_2$, wherein an increase in $V^{5+}$ concentration relative to $V^{3+}$ suppresses the metallic phase (increases $T_{\text{IMT}}$), while an increase in $V^{5+}/V^{3+}$ ratio suppresses the insulating phase (decreases $T_{\text{IMT}}$). Lastly, the analysis indicates that cooperative effects of structural and electronic phase transitions are needed to fully explain the IMT process.

**Methods**

**Synthesis of VO$_2$.** Bulk thin films of VO$_2$ were synthesized by reactive vapor transport by annealing commercial VO$_2$ powder (Sigma Aldrich) at 650 °C in a quartz boat. Stoichiometric VO$_2$ was deposited directly on a Si substrate kept on top of the boat. Two-dimensional VO$_2$ platelets were synthesized using a two-step process involving reductive phase transformation of $V_2O_5$ platelet films. Single crystalline $V_2O_5$ platelets were synthesized on fluorinated tin oxide (FTO)-coated glass slides by hot filament chemical vapor deposition, as reported previously. Briefly, the technique consists of resistively heating a vanadium wire in the presence of oxygen at a pressure of 800 mTorr at a substrate temperature between 450 and 500 °C. As-prepared films were then annealed in a $H_2/Ar$ (1:4 vol ratio) atmosphere at a temperature of 540 °C for 4–8 h to enable conversion to VO$_2$. The VO$_2$ formed by this procedure was observed to be oxygen deficient and metallic. These films are referred to as “VO$_{2-x}$” in the text. Metallic VO$_{2-x}$ was converted to semiconducting VO$_2$ by further annealing in air at 220 °C for 24–72 h to convert to the stoichiometric VO$_2$ phase. X-ray diffraction patterns of both phases were indexed to a pure VO$_2$ phase.

**Inductively coupled plasma mass spectroscopy (ICP-MS) analysis.** The stoichiometry of vanadium oxide samples was determined using combined thermogravimetric analysis (TGA) and ICP-MS analysis. A known amount of oxide sample was weighed in the TGA balance. The sample was then heated up to a temperature of 220 °C under nitrogen and the mass loss due to physisorbed water was recorded, which was generally 3–5% of the sample weight. The powder was then dissolved in concentrated HCl solution and then diluted by a factor of 1:20. The vanadium concentration in this solution was then determined using a Bruker 820 ICP-MS spectrometer by comparison with standard solutions having vanadium concentrations of 0.3 ppm, 1 ppm and 3 ppm, respectively. The oxygen content of the powder was determined from the relative mass difference between the total weight corrected for ambient adsorbates from the TGA analysis and the weight of vanadium determined from ICP-MS analysis.

**Electrochemical doping.** Electrochemical doping of the oxide was performed using a three electrode setup with platinum as the counter electrode and silver foil as the reference electrode in a 0.1 M solution of tetrabutylammonium triple salt of hydrogen monopersulfate (2H$\text{HSO}_5^-$), peroxomonomosulfate ($\text{H}_3\text{SO}_5^-$), and persulfate ($\text{SO}_5^{2-}$) (tradename OXONE) in propylene carbonate (PC) under ambient conditions. For all measurements, charging was performed by applying a potential step using a potentiostat (660E, CH Instruments) for a fixed time period or until ionic equilibrium throughout the bulk of the film was reached, which was indicated when the charging current reached low values ($\sim 10^{-8}$ to $10^{-7}$ A). Electrical resistance of the VO$_2$ film was then measured using two molybdenum clips pressed onto the sample and a Keithley 2400 SourceMeter. The nature of dominant carriers in some of the samples was determined using Hall Effect measurements (Silicon Valley Science Labs) at a magnetic field of 8000 Gauss.

**Calibration of reference scale.** The potential of the Ag pseudo-reference electrode was calibrated using ferrocene/ferrocenium redox couple under working conditions using a polished Pt disk as the working electrode, Pt wire as the counter electrode and Ag foil as the reference electrode. All potentials are referenced with respect to the standard hydrogen electrode (SHE) that has a work function of $\sim -4.44$ eV with respect to the vacuum level.

**Optical studies.** Raman spectrum of VO$_2$ films was recorded using a HORIBA Scientific LabRAM HR Evolution spectrometer at an excitation wavelength of 633 nm (He–Ne laser). Raman spectra of electrochemically-doped electrodes were collected ex-situ from the emmersed electrodes after drying under vacuum.
**Photoemission studies.** XPS measurements were done using a Physical Electronics PHI 5000 Versa Probe system using a monochromatic Al (Kα) (1486.7 eV) X-ray source and detected using a 150 mm radius hemispherical electron energy analyzer. All samples were gently sputtered with an Ar⁺ beam for 2 min to remove any over-oxidized surface layer, and then annealed in ultrahigh vacuum at 220 °C for 3 h to desorb physisorbed electrolyte or other contaminants. Calibration of the spectrometer was performed using silver and gold standards. During XPS measurements with VO₂, the Fermi edge of the spectrum was calibrated against the signal from a polycrystalline Ag foil that was cleaned in vacuum using Ar⁺ sputtering. Survey scans were collected over the range from 1100 to 0 eV with a pass energy of 117.4 eV for a collection duration of ~ 10 min. Higher-resolution scans were collected over a range of 10 eV around the peak of interest for ~ 30 min.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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V.C. designed the project and wrote the manuscript. S.J and N.S. carried out the experiments. All authors contributed towards analysis of the data and preparation of the manuscript.

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Correspondence and requests for materials should be addressed to V.C.
