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## Metal–insulator transition tuned by oxygen vacancy migration across TiO<sub>2</sub>/VO<sub>2</sub> interface

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Oxygen defects are essential building blocks for designing functional oxides with remarkable properties, ranging from electrical and ionic conductivity to magnetism and ferroelectricity. Oxygen defects, despite being spatially localized, can profoundly alter global properties such as the crystal symmetry and electronic structure, thereby enabling emergent phenomena. In this work, we achieved tunable metal–insulator transitions (MIT) in oxide heterostructures by inducing interfacial oxygen vacancy migration. We chose the non-stoichiometric VO<sub>2-δ</sub> as a model system due to its near room temperature MIT temperature. We found that depositing a TiO<sub>2</sub> capping layer on an epitaxial VO<sub>2</sub> thin film can effectively reduce the resistance of the insulating phase in VO<sub>2</sub>, yielding a significantly reduced R<sub>OFF</sub>/R<sub>ON</sub> ratio. We systematically studied the TiO<sub>2</sub>/VO<sub>2</sub> heterostructures by structural and transport measurements, X-ray photoelectron spectroscopy, and ab initio calculations and found that oxygen vacancy migration from TiO<sub>2</sub> to VO<sub>2</sub> is responsible for the suppression of the MIT. Our findings underscore the importance of the interfacial oxygen vacancy migration and redistribution in controlling the electronic structure and emergent functionality of the heterostructure, thereby providing a new approach to designing oxide heterostructures for novel ionotronics and neuromorphic-computing devices.

The importance of oxygen point defects in dictating physical properties has been more and more widely recognized by the functional oxide community<sup>1–4</sup>. Oxygen defects, disguised by the name, can be actually used to advantageously enhance functionalities and device performances, ranging from electronic<sup>5–7</sup>, magnetic<sup>8–10</sup> and multiferroic properties<sup>11</sup> to energy storage and conversion applications<sup>2,12,13</sup>. Especially, there has been an increasing interest in utilizing oxygen point defects for tailoring electronic structures of oxides, due to the designability and reversibility of this approach<sup>14</sup>. Electrical switching enabled by oxygen defects has been proven promising for applications in neuromorphic computing due to the fact that oxygen defects allow actively tuning electrical conductivity on demand<sup>14,15</sup>. In the pursuit of a defect-tuning functionality in oxides, it was found that the effects of oxygen defects can go beyond what can be explained within the simple rigid band model and band-filling picture. In correlated oxide systems, changes in oxygen content can profoundly alter electronic structure and even trigger a metal–insulator transition (MIT). VO<sub>2-δ</sub> (δ denotes oxygen non-stoichiometry) is such a material system, wherein a small change in composition can lead to a large modulation in correlation effects<sup>16–20</sup>. Near-stoichiometric VO<sub>2</sub> has 3d<sup>1</sup> electron configuration and shows a MIT with a transition temperature T<sub>c</sub> ≈ 340 K, accompanied by a structural transition from low-temperature M1 (monoclinic) phase to high-temperature R (rutile) phase. The MIT transition temperature can be lowered by 60 K using epitaxial strain imposed by substrates<sup>21,22</sup>. Interestingly, the MIT has been shown to be completely suppressed by inducing oxygen vacancy formation, either chemically<sup>17,23</sup> or electrochemically<sup>16,24</sup>. Oxygen-deficient VO<sub>2-δ</sub> was shown to remain in the metallic R phase when cooled down to below the MIT transition temperature. This makes oxygen stoichiometry a knob for reversibly controlling the MIT in VO<sub>2</sub>.

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Oxygen non-stoichiometries in functional oxide thin films are most commonly manipulated by changing the oxygen electrochemical potential via annealing in a certain oxygen partial pressure ( $pO_2$ ) or by applying electrical bias<sup>25</sup>. In contrast, a novel strategy based on interfacial oxygen defect migration induced by the mismatch of defect formation energy of two dissimilar oxides, is much less studied. This “oxygen diode” effect essentially utilizes the oxygen chemical potential gradient from the difference in defect formation energy ( $E_f$ ) across oxide interfaces. In order to balance the oxygen chemical potential, a unidirectional flow of oxygen defects can be induced during the fabrication process of oxide heterostructures. Recently, this approach has been successfully applied to tune the charge carrier density of  $LaNiO_{3-\delta}$  (LNO) by using oxide capping layers with different oxygen vacancy formation energies<sup>26</sup>, and also to transform thin films of  $La_{0.67}Sr_{0.33}CoO_3$  (LSCO) from its perovskite form to the brownmillerite form  $La_{0.67}Sr_{0.33}CoO_{2.5}$  by capping thin film with Gd<sup>27</sup>. Since the underlying mechanism of this effect is not material specific, it should be feasible to apply this approach to a broader spectrum of oxide material systems.

In this work, we use a  $TiO_2$  capping layer to construct “oxygen diodes” of  $TiO_2/VO_2$  heterostructures, in order to tune the MIT behavior of  $VO_2$ . Interfacial oxygen vacancy migration from rutile  $TiO_2$  to  $VO_2$  is induced by the much higher oxygen vacancy formation energy ( $E_f$ ) of  $TiO_2$  compared with  $VO_2$ , as predicted by our ab initio many body diffusion Monte Carlo (DMC) as well as DMC-benchmarked density function theory (DFT + U) based calculations of  $E_f$  across this heterostructure. The formation of oxygen vacancies in  $VO_2$  induced by a  $TiO_2$  capping layer was also confirmed by an observed *c*-axis lattice expansion using X-ray diffraction (XRD), as well as by electron microscopy and X-ray photoelectron spectroscopy characterization, in agreement with our computational predictions. The MIT behavior in  $VO_2$  was drastically altered by the incorporation of oxygen vacancies. While a  $VO_2$  thin film without a  $TiO_2$  capping layer showed a sharp transition in resistivity vs. temperature, the transition was shown to be suppressed in  $VO_2$  with  $TiO_2$  capping layers. Our combined experimental and computational investigation on the  $TiO_2/VO_2$  system underscores the effects of oxygen defect redistribution in oxide heterostructures on altering electronic structure and demonstrates how to use the ‘oxygen diode’ effect to control a MIT.

## Methods

**Thin film deposition.**  $VO_2$  and  $TiO_2/VO_2$  thin films were grown by using pulsed laser epitaxy (PLE) on  $TiO_2$  (001) single crystals (CrysTec, Germany). Growth temperature was fixed at 300 °C, and  $VO_2$  layer was grown in oxygen partial pressure ( $pO_2$ ) of 15 mTorr, while the  $TiO_2$  capping layers were grown in three different  $pO_2$ , i.e. 10 mTorr, 15 mTorr and 20 mTorr. X-ray diffraction (XRD) was performed on the grown thin films by using a four-circle X-ray diffractometer (Panalytical X’Pert MRD).

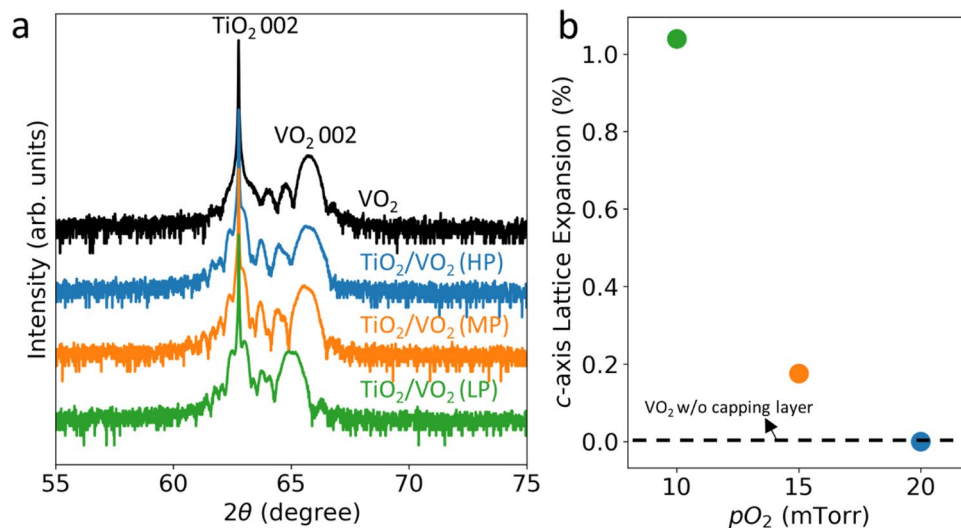
**Transport measurement.** Electrical contacts to thin film samples were made by using ultrasonic Al wire bonding. A Physical Property Measurement System (PPMS, Quantum Design) was used for measuring resistivity as a function of temperature by performing a warming up and cooling down cycle.

**STEM and EELS.** Cross-sectional STEM specimens were prepared to see along the [100] $TiO_2$  substrate direction using mechanical thinning and precision polishing followed by ion milling. High-angle annular dark-field (HAADF) imaging and STEM-EELS analysis were carried out in Nion UltraSTEM200 operated at 200 keV. For HAADF imaging, inner detector angle of 65 mrad was used, and the convergence semi-angle for the electron probe was set to 30 mrad.

**X-ray photoelectron spectroscopy (XPS).** XPS measurements were performed on a  $VO_2$  thin film sample and a  $VO_2$  thin film with a very thin  $TiO_2$  capping layer (~2 nm). The thin  $TiO_2$  capping layer was deposited by using the same condition as the LP sample (i.e., 10 mTorr  $pO_2$ ). The reason for choosing a thin thickness for the  $TiO_2$  capping layer is due to the shallow probing depth of XPS (estimated ~5 nm for V 2*p* spectra). XPS spectra of O 1*s* and V 2*p* were collected by using a system equipped with a monochromated Al K $\alpha$  X-ray source ( $h\nu = 1486.7$  eV) and a multi-channel detector (Sigma Surface Science, Germany). XPS data collection, as well as XRD and STEM characterizations, were performed at room temperature.

**DFT calculations.** Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP<sup>28</sup>). Electron exchange correlation was represented by the functional of Perdew, Burke, and Ernzerhof (PBE) of generalized gradient approximation (GGA<sup>29</sup>). The correlation effects were considered by using the DFT + U method<sup>30</sup> with U values of ( $U_V, U_{Ti}$ ) = (4.0, 5.0) eV as determined by scanning the two-parameter space using many-body quantum Monte Carlo (QMC) calculations (further details available in SI and “QMC calculation” section below). The ion–electron interaction was described with the projector augmented wave (PAW) method<sup>31</sup>. A cutoff energy of 400 eV was used for the plane-wave basis set. The internal coordinates were relaxed until the forces were lower than 0.01 eV/Å. The calculations were performed with spin polarization, and a ferromagnetic (FM) ordering was applied to the V sites.

DFT calculations were performed on 48-atom and 96-atom  $TiO_2/VO_2$  supercells. The 48-atom supercell contains four  $VO_2$  layers and four  $TiO_2$  layers stacked along the rutile *c* axis ( $a = 6.4966$  Å,  $b = 6.4966$  Å,  $c = 11.5892$  Å), while the 96-atom supercell contains eight  $VO_2$  layers and eight  $TiO_2$  layers ( $c = 23.1784$  Å). Monkhorst–Pack *k*-point meshes of  $6 \times 6 \times 3$  and  $6 \times 6 \times 2$  were used for the 48-atom and 96-atom supercells, respectively. The O vacancy formation energy  $E_f^O$  was calculated using the equation:  $E_f^O = E^{tot}[Vo] - E^{tot}[perf] + \mu_O$ , where  $E^{tot}[Vo]$  is the total energy of the supercell with one oxygen vacancy,  $E^{tot}[perf]$  is the total energy of the pristine supercell, and  $\mu_O$  is the chemical potential of oxygen. We use a definition of  $\mu_O$  common in the literature<sup>32</sup> as



**Figure 1.** Lattice expansion in  $\text{VO}_2$  induced by interfacial oxygen vacancy migration. **(a)** X-ray diffraction (XRD) results on a  $\text{VO}_2$  thin film (deposited in 15 mTorr  $p\text{O}_2$ ) and  $\text{VO}_2$  thin films (deposited in 15 mTorr  $p\text{O}_2$ ) with  $\text{TiO}_2$  capping layers deposited under different  $p\text{O}_2$  of 10, 15, and 20 mTorr (denoted as LP, MP and HP, respectively). **(b)**  $c$ -axis lattice expansion, compared with a  $\text{VO}_2$  sample without capping layer indicated by the black dashline, as a function of deposition  $p\text{O}_2$  for the  $\text{TiO}_2$  capping layer.

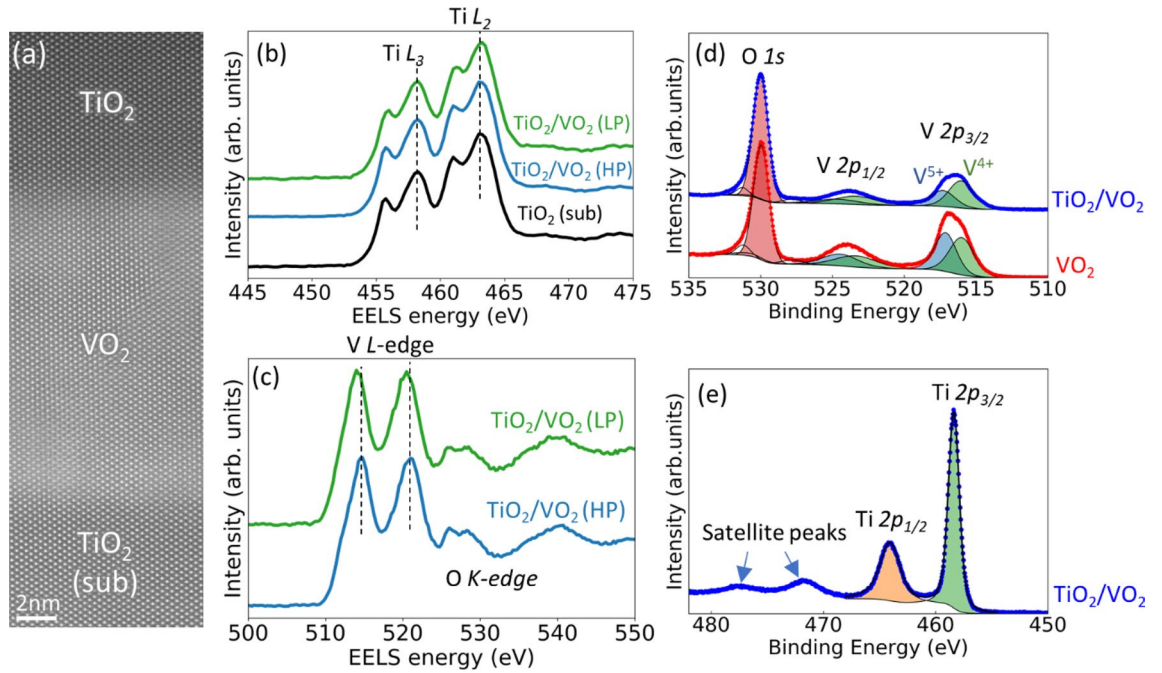
$\mu_{\text{O}} = \frac{1}{2}(2 E^{\text{tot}}[\text{O}] + \varepsilon_{\text{O}_2}^{\text{coh}})$  where  $E^{\text{tot}}[\text{O}]$  is the energy of an oxygen atom, and  $\varepsilon_{\text{O}_2}^{\text{coh}}$  is the cohesive energy of oxygen molecule. From experimental data, we determined  $\varepsilon_{\text{O}_2}^{\text{coh}}$  to be  $-5.21$  eV<sup>33</sup>.

**QMC calculations.** Calculations using the Diffusion Monte Carlo (DMC)<sup>34</sup> flavor of QMC were performed on 48 atom rutile  $\text{TiO}_2/\text{VO}_2$  interfacial cells containing a neutral oxygen vacancy for all inequivalent sites. The V site magnetic moments were constrained to a ferromagnetic configuration. High quality pseudopotentials<sup>35</sup> were used to represent the V, Ti, and O species. Fixed node errors were minimized by optimizing LDA + U<sup>36</sup> parameters for both the V and Ti species separately. All other parameters of the trial wavefunction were optimized via the linear method<sup>37</sup>. All supercell results were averaged over a  $2 \times 2 \times 2$  Gamma centered supercell twist grid. The calculations were performed with the QMCPACK simulation code<sup>38</sup> at the Argonne Leadership Computing Facility and all simulation workflows were driven with the Nexus workflow automation system<sup>39</sup>.

## Results and discussion

$\text{VO}_2$  thin films and  $\text{TiO}_2/\text{VO}_2$  heterostructures were grown on  $\text{TiO}_2(001)$  substrates by pulsed laser epitaxy (PLE) in different oxygen partial pressures ( $p\text{O}_2$ ). The deposition conditions for the  $\text{VO}_2$  layers were fixed to a substrate temperature of 300 °C and 15 mTorr  $p\text{O}_2$ , while the growth  $p\text{O}_2$  of the  $\text{TiO}_2$  capping layers was varied between 10 mTorr, 15 mTorr and 20 mTorr. Both the  $\text{VO}_2$  thin films and the  $\text{TiO}_2$  capping layers were  $\sim 15$  nm thick. We refer to the three  $\text{TiO}_2/\text{VO}_2$  heterostructures grown in different  $p\text{O}_2$  as LP, MP and HP (i.e., low, medium and high pressure). The different growth  $p\text{O}_2$  of the  $\text{TiO}_2$  capping layer effectively changes the concentration of formed oxygen vacancy in  $\text{TiO}_2$  during deposition. Figure 1 shows XRD scans on  $\text{VO}_2$  and  $\text{TiO}_2/\text{VO}_2$  samples. The clearly resolved thickness fringes indicate the high sample quality. We observed a clear trend of  $c$ -axis lattice expansion following the direction of decreasing growth  $p\text{O}_2$  of  $\text{TiO}_2$  capping layer (i.e. HP < MP < LP). This “chemical expansion”<sup>40</sup> indicates an increased oxygen vacancy concentration in LP and MP samples compared with bare  $\text{VO}_2$  and HP samples. Therefore, the XRD data is a strong proof of interfacial migration of formed oxygen vacancies in the  $\text{TiO}_2$  capping layer to the  $\text{VO}_2$  layer underneath. A lower growth  $p\text{O}_2$  introduces more oxygen vacancies into  $\text{VO}_2$  layer, which results a larger  $c$ -axis lattice spacing.

We also performed detailed structural and chemical analysis to verify the reduction of  $\text{VO}_2$  induced by  $\text{TiO}_2$  capping layers, as shown in Fig. 2. Figure 2a shows a Z-contrast (where Z refers to atomic number) high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image of a  $\text{TiO}_2/\text{VO}_2$  heterostructure grown on a  $\text{TiO}_2$  substrate. Clearly resolved atom columns and coherent interface again indicate the high sample quality. Figures 2b,c show electron energy loss spectra (EELS) of the Ti  $L_{2,3}$ -edge of the  $\text{TiO}_2$  substrate and capping layer, as well as V  $L_{2,3}$ -edge of LP and HP samples. The identical line shapes and peak positions in Ti  $L_{2,3}$ -edge show the nearly indistinguishable chemical states between  $\text{TiO}_2$  substrate and capping layer. The well-resolved  $t_{2g}$  and  $e_g$  peaks indicate that Ti cations in the  $\text{TiO}_2$  capping layer have 4+ oxidation state with no appreciable reduction to 3+, and do not change valence with decreasing deposition  $p\text{O}_2$ . In contrast, a clear peak shift towards lower energy was observed in V  $L_{2,3}$ -edge spectra comparing LP and HP sample, indicating a lower V oxidation state (high oxygen vacancy concentration) in the LP sample. EELS spectroscopic results on  $\text{TiO}_2$  capping layer and  $\text{VO}_2$  layer evidently reveal that the oxygen vacancies introduced by lowering growth  $p\text{O}_2$  of  $\text{TiO}_2$  capping layer migrates to the  $\text{VO}_2$  layer, resulting in the reduced V oxidation state. We believe the atomic-scale



**Figure 2.** Structure and chemical states of  $\text{TiO}_2/\text{VO}_2$  thin films. **(a)** HAADF-STEM image of  $\text{TiO}_2/\text{VO}_2$  (LP) along the [100] axis of  $\text{TiO}_2$  substrate, which shows high crystal quality without observable extended defects. **(b,c)** Background subtracted EELS spectra of Ti  $L$ -edge **(b)** and V  $L$ -edge **(c)**. While there are no appreciable differences between Ti  $L$ -edge spectra measured on the  $\text{TiO}_2$  capping layers of LP and HP samples, as well as the  $\text{TiO}_2$  substrate, a clear peak shift towards lower energy is observed in V  $L$ -edge spectrum of LP sample, compared with HP sample. **(d,e)** XPS spectra in V  $2p$  **(d)** and Ti  $2p$  **(e)** regions, which provides surface sensitive chemical information. While the Ti  $2p$  peaks can be fitted with purely  $4+$  oxidation state, two components representing  $4+$  and  $5+$  oxidation states were needed to fit V  $2p$  peaks.  $\text{TiO}_2/\text{VO}_2$  sample showed higher  $V^{4+}/V^{5+}$  relative concentration compared with pure  $\text{VO}_2$  sample, which indicates an increased oxygen vacancy concentration induced by the  $\text{TiO}_2$  capping layer.

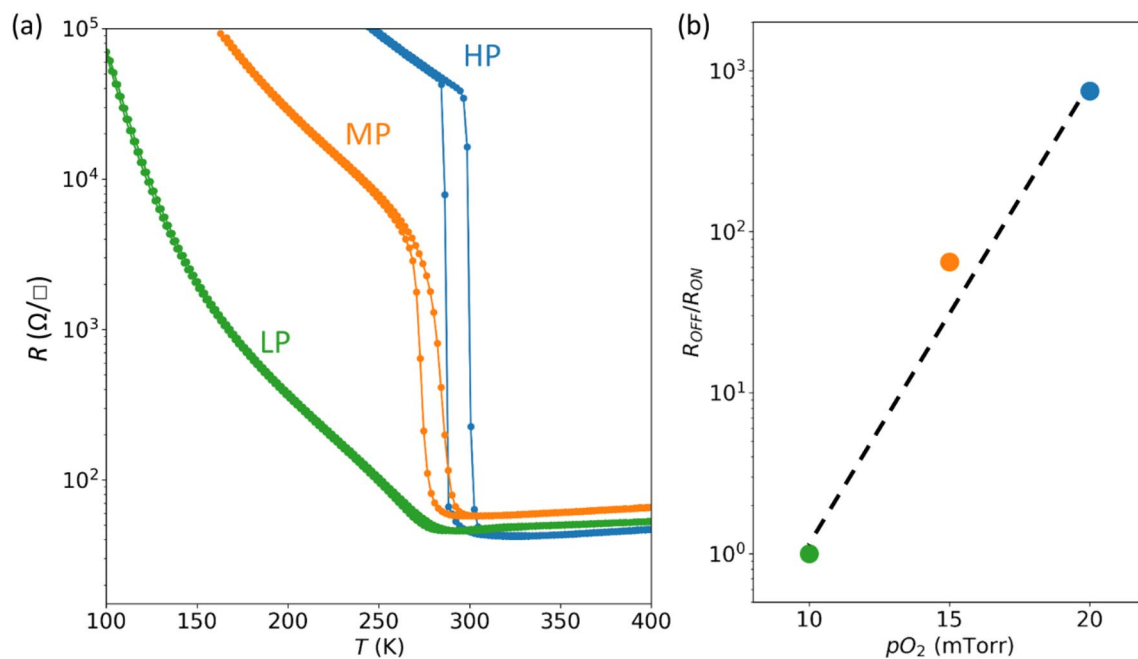
oxygen vacancy redistribution in  $\text{VO}_2$  could be affected and non-uniform along the thickness direction due to the vicinity effects associated with the surface and interface. Further investigation to determine both the quantity and spatial nonuniformity of oxygen vacancies would provide useful information to accurately understand the ion transport in  $\text{VO}_2/\text{TiO}_2$  heterostructures.

The unidirectional oxygen vacancy migration from  $\text{TiO}_2$  to  $\text{VO}_2$  was also probed by using X-ray photoelectron spectroscopy (XPS), shown in Fig. 2d,e. Due to the shallow probing depth of XPS ( $\sim 5$  nm), we decreased the thickness of the  $\text{TiO}_2$  capping layer down to  $\sim 2$  nm, while interestingly the oxygen diode effect was still apparent.  $\text{VO}_2$  is known to have overoxidized surface layers, therefore a  $V^{5+}$  oxidation state was present in the V  $2p$  spectra<sup>41,42</sup>. Due to the existence of  $V^{5+}$  oxidation state, we used the average V oxidation state, represented by the intensity ratio of  $V^{4+}$  and  $V^{5+}$  (i.e.,  $I(V^{4+})/I(V^{5+})$ ), as a measure of oxygen vacancy concentration in the  $\text{VO}_2$  layer. As shown in Fig. 2d, the  $\text{TiO}_2$  capping lowered the average oxidation state of V, as indicated by a higher relative intensity of  $V^{4+}$  peak (higher  $I(V^{4+})/I(V^{5+})$ ). On the other hand, the Ti  $2p$  spectrum collected on  $\text{TiO}_2$  capping layer (Fig. 2e) can be fitted with only one single component of  $\text{Ti}^{4+}$ , which is consistent with EELS results showing the near absence of oxygen deficiency in  $\text{TiO}_2$  capping layer. We would like to point out that, since the quantitative analysis of oxygen vacancies based on the local EELS data and surface sensitive XPS is challenging, we remain our conclusion be only qualitative.

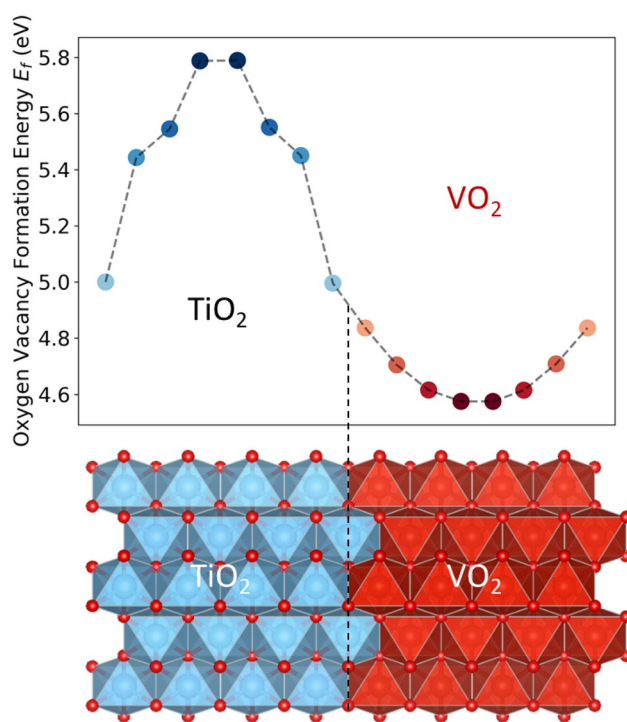
We hypothesize that the increased oxygen deficiency is due to the oxygen diode effect, and results in strongly affecting the MIT of  $\text{VO}_2$ , as shown by transport (resistivity  $\sim$  temperature plot) data in Fig. 3. We observed a clear MIT in the  $\text{TiO}_2/\text{VO}_2$  HP sample with a sharp change in the resistivity at  $T_c$  of  $\sim 300$  K. This is consistent with the XRD data showing that there is no difference between the  $c$ -axis lattice spacing of HP and bare  $\text{VO}_2$ , indicating a nearly identical oxygen stoichiometry between these two samples. Contrarily, the sharp MIT was gradually suppressed with decreasing deposition  $p\text{O}_2$ . While the MP sample showed a much lower ON/OFF ratio ( $R_{\text{OFF}}/R_{\text{ON}}$ , defined as the ratio of resistance measured during warming up and cooling down experiments at  $T_c$ , see Fig. 3b) compared with the HP sample, the resistivity hysteresis was completely suppressed in the LP sample. The observed suppression of the MIT is consistent with a previous report on oxygen deficient  $\text{VO}_{2-\delta}$  thin films<sup>17</sup>. We also note that our finding is consistent with a recent report on  $\text{VO}_2/\text{TiO}_2$  heterostructures<sup>43</sup>. By utilizing the proposed “oxygen diode effect” we could tune the MIT and thereby change the ON/OFF ratio by three orders of magnitudes. This therefore provides a novel route of controlling oxide electronic properties.

We further explored the mechanism of the unidirectional oxygen vacancy migration in  $\text{TiO}_2/\text{VO}_2$  by performing ab initio many body diffusion Monte Carlo (DMC) as well as DMC-benchmarked density function theory (DFT + U) calculations. Because of two different 3d metal atoms, we used a hybrid U value of  $(U_{\text{V}}, U_{\text{Ti}}) = (4.0, 5.0)$





**Figure 3.** Metal–insulator transition (MIT) tuned by interfacial oxygen vacancy migration. **(a)** Sheet resistance of  $TiO_2/VO_2$  LP, MP and HP samples. **(b)** ON/OFF ratio (ratio of resistivity measured during cooling down and warming up cycle at  $T_c$ , i.e., 278, 287, and 295 K for LP, MP and HP samples, respectively) as a function of deposition  $pO_2$  of the  $TiO_2$  capping layers.  $T_c$  for each sample is defined by taking the average of transition temperatures for cooling down and warming up cycle.



**Figure 4.** Oxygen vacancy formation energy ( $E_f$ ) landscape.  $E_f$  is mapped at different positions of a 96-atom supercell consisting of  $TiO_2/VO_2$  bilayer. Oxygen vacancy formation energy was shown significantly lower in the  $VO_2$  layer compared with the  $TiO_2$  layer. The dash line indicates the position of  $TiO_2/VO_2$  interface.

eV as benchmarked by surveying the two-dimensional parameter space using total-energies from many-body quantum Monte Carlo (QMC) calculations (further details about the calculations as well as benchmarking can be found in the SI). A 96-atom supercell consisting of TiO<sub>2</sub>/VO<sub>2</sub> bilayers with an atomically ‘sharp’ interface was used in the DFT calculations to evaluate the (neutral) oxygen vacancy formation energy ( $E_f$ ) in each oxygen atomic layer, as shown in Fig. 4. A gradient of  $E_f$  across the TiO<sub>2</sub>/VO<sub>2</sub> interface was observed, with  $E_f$  decreasing from the TiO<sub>2</sub> layer to the VO<sub>2</sub> layer.  $E_f$  at oxygen layers away from the interfaces approaches the bulk  $E_f$  value of TiO<sub>2</sub> (~ 5.8 eV) and VO<sub>2</sub> (~ 4.6 eV). In spite of quantitative differences (Fig. S2, discussion in SI), that can be rationalized by comparing the underlying electronic-structure changes (Fig S3), the considerably lower (~ 1 eV) formation energy of oxygen vacancies in VO<sub>2</sub> compared to TiO<sub>2</sub> is further supported by benchmark DMC calculations performed in a smaller 48-atom supercell. These DMC calculations provide further support for a solid theoretical justification for the hypothesis that the TiO<sub>2</sub>/VO<sub>2</sub> heterostructure behaves as an “oxide diode”, similar to the perovskite heterostructures<sup>26</sup>. Allowing effects of cation intermixing to model more realistic interface geometries, at the otherwise ‘sharp’ interface model, does not change this conclusion (Fig. S4). This implies that there is a strong chemical driving force for oxygen vacancy migration from TiO<sub>2</sub> layer to VO<sub>2</sub> layer, which is responsible for tuning the oxygen non-stoichiometry, and thereby achieving the suppression of the MIT, that we achieved by using TiO<sub>2</sub> capping layers grown at different pO<sub>2</sub> conditions. Even though we did not model the dynamic process of oxygen migration from TiO<sub>2</sub> to VO<sub>2</sub>, we would like to point out that the growth pO<sub>2</sub> of the TiO<sub>2</sub> capping layer is the only parameter we altered. Since oxygen vacancies can be readily introduced into grown TiO<sub>2</sub> by lowering growth pO<sub>2</sub> (See Figure S5 in SI), the only feasible mechanism that responsible for the observed suppressed MIT is the oxygen vacancy migration we discussed above.

## Conclusions

In summary, by utilizing the “oxygen diode effect” in TiO<sub>2</sub>/VO<sub>2</sub> heterostructure we have demonstrated tunability of the MIT and thereby changes in the ON/OFF resistivity ratio by three orders of magnitudes. This, therefore provides a novel route of controlling oxide electronic properties. Electronic-structure calculations as well as multiple characterization methods including XRD, STEM-EELS and XPS were used to prove the unidirectional oxygen vacancy migration across the interface from TiO<sub>2</sub> to VO<sub>2</sub>. Our results highlight the importance of oxygen defect redistribution by design in oxide heterostructures on determining physical properties and functionalities.

## Data availability

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

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## Author contributions

Q.L. and C.S. performed thin film growth, XRD, XPS and transport characterizations. X.G. and M.C. performed STEM characterizations. G.H. did DFT calculations. I.K. and J.T.K. did QMC and DMC calculations. P.C., O.H., P.G. and H.L. supervised the whole project. All authors contributed to discussions and manuscript writing.

## Competing interests

The authors declare no competing interests.

## Additional information

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