In-plane orientation-dependent metal-insulator transition in vanadium dioxide induced by sublattice strain engineering

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SELECTIVELY MODULATING THE SUBLATTICES IN 3D TRANSITION METAL OXIDES VIA STRAINS COULD TAILOR THE ELECTRONIC CONFIGURATIONS WITH EMERGING ANOMALOUS PROPERTIES, WHICH PROVIDES NEW PLATFORMS FOR FUNDAMENTAL RESEARCHES AS WELL AS DESIGNS OF DEVICES. HERein, WE REPORT TAILORING THE OXYGEN OCTAHEDRAL SUBLATTICES IN VANADIUM DIOXIDE (VO2) THIN FILMS BY ANISOTROPIC IN-PLANE STRAINS, AND THE OBSERVATION OF IN-PLANE ORIENTATION-DEPENDENT METAL–INSULATOR TRANSITION. THROUGH MULTIMODAL CHARACTERIZATIONS BASED ON HIGH-RESOLUTION X-RAY DIFFRACTION, ELECTRICAL TRANSPORT MEASUREMENTS, AND POLARIZATION-DEPENDENT X-RAY ABSORPTION SPECTROSCOPY AT DIFFERENT TEMPERATURES, WE DEMONSTRATE THAT NONEQUAL STRAINS WERE SUCCESSFULLY INDUCED ALONG A AND B OXYGEN OCTAHEDRAL CHAINS IN VO2 FILMS VIA A SPECIAL DESIGN OF EPITAXIAL GROWTH ON VICINAL SUBSTRATES. THE V 3d0 ORBITAL CONFIGURATIONS ARE MODULATED IN THE TWO OXYGEN OCTAHEDRAL CHAINS, RESULTING IN IN-PLANE ORIENTATION-DEPENDENT METAL–INSULATOR TRANSITION BEHAVIORS SUCH AS REDUCED Hysteresis width and anisotropic phase transition temperature. THIS WORK PROVIDES NEW FUNDAMENTAL INSIGHTS ON METAL–INSULATOR TRANSITIONS, AND MORE IMPORTANTLY, OPENS UP NEW OPPORTUNITIES FOR MATERIAL AND DEVICE DEVELOPMENTS.
redistribution of \( V \) 3D electrons is very sensitive to the energy levels of \( d_{\pi} \) and \( \pi^* \) orbitals, which are strongly influenced by the apical V–O bond length.\(^3\) If we observe along the \( c_R \) direction, the \( d_{xy}, d_{xz}, \) and \( d_{yz} \) orbitals extend to different directions in VO\(_2\) (001) plane (as shown in Fig. 1f–h).\(^4,5\) The A octahedral chain and the B octahedral chain have a relative 90° rotation around \( c_R \) axis, so their apical V–O bond and orbitals also rotate. Since the energy level of \( \pi^* \) is sensitive to the apical V–O bond length, the energy levels of \( \pi^* \) of 3d\(^{5}\) electrons in A octahedral chain and the B octahedral chain would be influenced by strains with a relative 90° rotation, respectively. When isotropic biaxial strains are loaded along VO\(_2\) [110]\(_L\) and [1\( \bar{1} \)0]\(_L\) directions (as the case of Fig. 1d), the apical V–O bond lengths of both the A octahedral chain and B octahedral chain would be tuned to the same degree simultaneously, as reported by Aetukuri et al.\(^3\) The isotropic biaxial strains loaded along VO\(_2\) [110]\(_L\) and [1\( \bar{1} \)0]\(_L\) directions can modulate the electronic configurations of \( V \) 3D electrons, consequently significantly tune the MIT temperature. Since the strains along VO\(_2\) [110]\(_L\) and [1\( \bar{1} \)0]\(_L\) directions can selectively influence the apical V–O bond lengths of the A octahedral chain and B octahedral chain, their sublattices could be tuned separately with nonequal strains along VO\(_2\) [110]\(_L\) and [1\( \bar{1} \)0]\(_L\) directions. In other words, the orbital configurations of the A octahedral chain and the B octahedral chain can be tailored separately by the anisotropic strains (as the case of Fig. 1e). High-quality works on tailoring the MIT properties of VO\(_2\) in virtue of thickness effects on the epitaxial strain,\(^11,12\) thermal strain,\(^13\) and interface facet effect\(^14\) were reported. However, researches on the effect of anisotropic strains are still rare. Although the experiments of loading uniaxial strain along the [110]\(_L\) direction have been demonstrated in VO\(_2\) nanowire system,\(^10,15\) the impact of the applied strain on the physical properties was hardly determined due to the dimension limitation. Furthermore, there is few data available on the anisotropic electron transport properties and the electronic

![Fig. 1](image-url)

Fig. 1 The schematic of lattice and electronic structures for VO\(_2\): \( a \) the VO\(_2\) lattice constructed with A and B oxygen octahedral chains which are edge-shared oxygen octahedral chains with \( V \) ions located inside the oxygen octahedral; \( b \) the details of A and B octahedral chains of VO\(_2\); \( c \) the definition of V–O apical bonds and equatorial bonds of oxygen octahedral in VO\(_2\); \( d \) the lattice of VO\(_2\) grown on a normal TiO\(_2\) (001) substrate, which undergoes symmetric biaxial strains along VO\(_2\) [110]\(_L\) and [1\( \bar{1} \)0]\(_L\) directions; \( e \) the lattice of VO\(_2\) grown on a vicinal TiO\(_2\) (001) substrate with asymmetric biaxial strains along VO\(_2\) [110]\(_L\) and [1\( \bar{1} \)0]\(_L\) directions, in which the VO\(_2\) [110]\(_L\) direction is the vicinal direction and bares a smaller strain compared with VO\(_2\) [1\( \bar{1} \)0]\(_L\) direction; \( f–h \) the schematic of the \( d_{xy}, d_{xz}, \) and \( d_{yz} \) molecular orbitals of VO\(_2\) observed from VO\(_2\) (001)\(_L\) direction, respectively.
configurations under the anisotropic strains. On the other hand, it has been demonstrated that substrates with small miscutting angles can induce designable strains in the films by virtue of the mismatching between the surface–step–terrace of the substrate and lattice unit cells of the films.\textsuperscript{16–19} For the substrates with miscutting angles, the surface–step–terrace can be formed after being annealed at a high temperature and its width can be adjusted by tuning the miscutting angles. When the films are grown on such substrates, the lattice unit cells of the films have to accommodate the width of surface–step–terrace, consequently strain is induced. (more details can be accessed in Supplementary Figs. S3 and S4). Herein, we induce nonequal strains in a VO\textsubscript{2} film via high-quality epitaxial growth on a designed vicinal TiO\textsubscript{2} (001) substrate with a small miscutting angle along VO\textsubscript{2} [110\textsubscript{R}] direction.\textsuperscript{20} More details can be accessed in our previous reports.\textsuperscript{21,22} The epitaxial relationship between the substrates is VO\textsubscript{2} (001)R∥TiO\textsubscript{2}(001) and VO\textsubscript{2} [110\textsubscript{R}]∥TiO\textsubscript{2}[110] (Supplementary Fig. S5). And the thickness of the films is about 17 nm. An ordinary TiO\textsubscript{2} (001) substrate with no intentional miscut and a vicinal TiO\textsubscript{2} (001) substrate with a 1° miscutting angle along TiO\textsubscript{2} [110] direction were used for comparative study. The anisotropic in-plane strains were successfully induced in the VO\textsubscript{2} film on the vicinal TiO\textsubscript{2}(001) substrate as manifested by the high-resolution reciprocal space mapping (RSM) (Fig. 2). For the film grown on the normal TiO\textsubscript{2} (001) substrate, equal strain of \(\sigma_a\) was found along both VO\textsubscript{2} [110\textsubscript{R}] and [110\textsubscript{R}] directions in the VO\textsubscript{2} film (Fig. 1d). However, the case was found to be different for the VO\textsubscript{2} film grown on the vicinal TiO\textsubscript{2} (001) substrate. We denoted the strain in the film grown on the vicinal substrate along the VO\textsubscript{2} [110\textsubscript{R}] direction as \(\sigma_a\) and along the VO\textsubscript{2} [110\textsubscript{R}] direction as \(\sigma_b\) (Fig. 1e). It was found that the strain \(\sigma_b\) is very close to \(\sigma_a\) but the strain \(\sigma_a\) is different from the strain \(\sigma_{ab}\). Obviously, the strain along the VO\textsubscript{2} [110\textsubscript{R}] direction was modulated by the surface–step–terrace on the vicinal substrate, as what it can be expected.

Figure 2 show the RSMs for the nonvicinal and vicinal samples in both the metallic and insulating states, measured at 298 and 373 K, respectively. Lattice parameters of the VO\textsubscript{2} thin films are calculated based on the RSM data and listed in Table 1. It is clearly indicated that the anisotropic in-plane biaxial strains (\(\sigma_a\) and \(\sigma_b\)) have been induced along [110\textsubscript{R}] and [110\textsubscript{R}] directions in the VO\textsubscript{2} film on the vicinal substrate. The most profound influence of the anisotropic in-plane strains on the VO\textsubscript{2} lattice is the ability of tailoring the apical V–O bond length of the sublattices in the different octahedral chains separately. The A octahedral chain bares the \(\sigma_a\) strain while the B octahedral chain bares the \(\sigma_b\) strain along the apical V–O bond direction. The anisotropic in-plane biaxial strains will result in different apical V–O bond lengths in the A and B octahedral chains. From the measured lattice parameter in Table 1, we can estimate the apical V–O bond lengths for both samples in the metallic states.

### RESULTS

The VO\textsubscript{2} films were grown using a polymer-assisted deposition technique.\textsuperscript{20} More details can be accessed in our previous reports.\textsuperscript{21,22} The epitaxial relationship between the films and the substrates is VO\textsubscript{2} (001)∥TiO\textsubscript{2}(001) and VO\textsubscript{2} [110\textsubscript{R}]∥TiO\textsubscript{2}[110] (Supplementary Fig. S5). And the thickness of the films is about 17 nm. An ordinary TiO\textsubscript{2} (001) substrate with no intentional miscut.

![Fig. 2](image-url) The high-resolution reciprocal space maps (RSMs). (a–f) (002), (112) and (1T2) diffractions of the nonvicinal and vicinal samples at 298 K, respectively. (g–l) (002), (112) and (1T2) diffractions of the nonvicinal and vicinal samples at 373 K, respectively.
obviously, the apical V – O bond lengths can be considered as the same for both A octahedral chain and B octahedral chain, which are determined to be 1.9331 Å in the metallic state. However, for the vicinal sample, they become 1.9538 Å and 1.9208 Å for the A octahedral chain and the B octahedral chain in the metallic state, respectively. The nonequal apical V – O bonds in the A octahedral chain and the B octahedral chain for the vicinal sample are resulted from the nonequal biaxial strains.

The change of the apical V – O bond length by strain would affect the overlap of V 3d and O 2p orbitals. A shorter apical V – O bond length increases the overlap of V 3d and O 2p orbitals, which would increase the energy level of π* orbitals relative to those of the dπ orbitals, hence decrease the electron occupancy of π* orbitals. Since the dπ and π* orbitals are both partially occupied in the metallic state, as shown in Fig. S2, the electron occupancy of dπ orbitals will increase correspondingly. In other words, the nonequal strains in the VO2 film along VO2 [110]R and [1T0]R directions result in nonequal apical V – O bond lengths in A and B octahedral chains, leading to different energy levels of π* orbitals and different electronic configurations of the A and B octahedral chains.

To verify the electronic state configurations described above, synchrotron-based linear-polarization-dependent X-ray absorption spectroscopy (XAS) was tested at the V L2,3 edges of both VO2 thin films epitaxially grown on non-vicinal and vicinal substrates. The experiments were performed using total electron yield (TEY) detection with a typical probe depth of about 10 nm. Linearly polarized X-rays with the electric-field orientation parallel (E ∥ cR) and perpendicular (E ⊥ cR) to the rutile VO2 c-axis are measured to probe the vacant dπ and π* valence-electron states, respectively.

To investigate the anisotropic in-plane strain effect, the measurements perpendicular to the rutile c-axis (E ⊥ cR) were performed along VO2 [110]R and [1T0]R directions, respectively. Based on previous studies on the valence-electron states, we particularly focus on the excitonic features of the XAS spectra with 512–516 eV photon energies.

Figure 3 shows the polarization-dependent V L-edge XAS spectra in the metallic and insulating states of the nonvicinal and vicinal samples. The intensity differences ΔI∥ – ΔI⊥, which are respectively defined as ΔIcR – ΔI110 and ΔIcR – ΔI1T0 along the VO2 [110]R and [1T0]R directions, are also plotted. In the insulating state, the dichroic signals ΔIcR – ΔI110 and ΔIcR – ΔI1T0 (Fig. 3a, b) of both nonvicinal and vicinal samples show negligible difference. That is expected and consistent with the previous report, because the 3dπ electron occupies the dπ orbitals while the π* orbitals located above the Fermi level are empty in the insulating state. However, the orbital occupancy in the metallic state, which is believed to set the energy scale for the MIT of VO2, shows remarkable distinctions between the two samples, as reflected by the XAS data. It is found that the XAS dichroic signals ΔIcR – ΔI110 and ΔIcR – ΔI1T0 of the nonvicinal sample in the energy region of 512–516 eV show negligible difference in the metallic state (Fig. 3c), which is as expected due to the equal strains along VO2 [110]R and [1T0]R directions. On the other hand, the XAS dichroic signals ΔIcR – ΔI110 and ΔIcR – ΔI1T0 of the vicinal sample in the metallic state (Fig. 3d), show obvious difference in this energy region, which should be attributed to the nonequal strains along VO2 [110]R and [1T0]R directions. For the vicinal sample, the apical V – O bond length of the B octahedral chain (1.9208 Å) was shorter than the A octahedral chain (1.9538 Å), suggesting that the difference in the XAS dichroic signals ΔIcR – ΔI110 and ΔIcR – ΔI1T0 is due to the redistribution of the orbital occupation. As mentioned above, the shorter apical V – O bond length increases the p–d overlap, hence raises the energy level of π* orbital and consequently reduces their orbital occupancy, resulting in the increase of the orbital occupancy of dπ orbitals. Since the XAS data correspond to the unoccupied states of the orbitals, the increase of the occupancy of dπ orbitals will reduce the signal ΔIcR. For the π* orbitals, the dxz orbitals extend along [110]R direction (Fig. 1g) while the dyz orbitals of B octahedral chain extend along [110]R direction (Fig. 1g) and decrease the orbital occupancy of the dxz orbitals in the B octahedral chain, compared with those in the A octahedral chain. Such an effect is directly shown in the XAS raw data plot in Fig. 3d, with stronger ΔI100 signals comparing with ΔI1R signals on the vicinal substrate, it can significantly modulate the MIT behaviors of the film. Temperature-dependent resistances of both the nonvicinal and the vicinal samples were tested. In-plane orientation-dependent MIT behavior attributed to the anisotropic in-plane strains were observed in the vicinal sample. The nonvicinal sample exhibits a normal MIT behavior (Fig. 4a, c). The resistance-temperature (R – T) curves tested along VO2 [110]R and [1T0]R directions show weak directional dependency, as shown in the direction-dependent resistance in metallic state is shown in Fig. 4e. Its phase transition temperature (Tc) for heating was determined to be 324 K in both VO2 [110]R and [1T0]R directions (derived from the dR/dT curves in Fig. 4c), and the hysteresis width (∆Tc, defined as the difference of Tc for heating and cooling) is about 3.5 K. These results are very similar to previous reports. However, for the vicinal sample, the MIT behavior has been obviously altered (Fig. 4b, d). The R – T curves tested along VO2 [110]R and [1T0]R directions show obvious directional dependency. The film in the metallic state has a much larger resistance along the VO2 [110]R direction (vicinal direction) than along the VO2 [1T0]R direction. The direction-dependent resistance in metallic state is shown in Fig. 4f, which can be fitted by:

\[ R(\theta) = R_{110R} \sin^2(\theta) + R_{1T0R} \cos^2(\theta) \] (1)

where \( R_{110R}/R_{1T0R} = 17.3 \). The phase transition temperature exhibits anisotropy as well. The \( T_c \) values measured along [110]R and [1T0]R directions are determined to be 333 and 326 K, respectively. From Table 1, we observe that the vicinal sample

| Sample     | Temperature | \( d_{[002]} \) | \( \sigma_{[002]} \) | \( d_{[110]} \) | \( \sigma_{[110]} \) | \( d_{[1T0]} \) | \( \sigma_{[1T0]} \) |
|------------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Nonvicinal  | 298 K       | 1.4329         | 0.238          | 3.288          | 0.202          | 3.2300         | 0.248          |
| Nonvicinal  | 373 K       | 1.4251         | −0.308         | 3.2234         | 0.043          | 3.2204         | −0.050         |
| Vicinal     | 298 K       | 1.4423         | 0.895          | 3.2187         | −0.102         | 3.2543         | 1.003          |
| Vicinal     | 373 K       | 1.4365         | 0.490          | 3.2013         | −0.642         | 3.2564         | 1.068          |
undergoes a tensile strain along the \([\frac{1}{2}1\overline{1}0]_{\text{C138}}\) direction, while it undergoes a compressive strain along the \([110]_{\text{R}}\) direction. The higher value of \(T_c\) along the \([110]_{\text{R}}\) direction should be attributed to the compressive strain along that direction.

**DISCUSSION**

A possible mechanism for the conductivity anisotropy is the strip-like phase domain structure generated by the phase separation during the phase transition in the film.25 Clearly, mixture of the
metallic and insulating phases would occur in the temperature range near the phase transition temperature. This mixing phase domains would form anisotropic percolation hence lead to anisotropic carrier transport behavior. Anisotropy of the conductivity induced by this mechanism will disappear beyond the phase transition temperature range, since the phase transition has completed and the metallic and insulating domains no longer coexist. However, our vicinal sample shows obvious anisotropic conductivity even at a high (373 K) and a low (298 K) temperature beyond the phase transition temperature. Other mechanisms need to be proposed to understand the phenomenon. We suggest that the anisotropic in-plane strains play a key role. The shorter apical V–O bond in the B octahedral chain compared with the A octahedral chain increases the $p$–$d$ overlap and the $d_{xz}$ energy level. Since the $d_{yz}$ orbitals of the B octahedral chain extend to $[110]_A$ direction while those of the A octahedral chain extend to $[1\bar{1}0]_B$ direction, if we assume that the $d_{z^2}$ orbital levels are the same in the A and B octahedral chains, the electron hopping would be harder along $[110]_A$ than $[1\bar{1}0]_B$. As a result, the resistance along $[110]_A$ is larger than that along $[1\bar{1}0]_B$.

Moreover, the nonequal apical V–O bonds change the electronic configurations of the A octahedral chain and the B

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**Fig. 4** The electrical properties. a Temperature-dependent resistance and c $\ln R/dT-T$ curves of the nonvicinal sample, respectively; b temperature-dependent resistance and d $\ln R/dT-T$ curves of the vicinal sample, respectively; e, f the experimental and fitting results of direction-dependent resistance for the nonvicinal and vicinal sample in metallic state, respectively.
where $\eta$ is the domain shape parameter, $G$ is the shear modulus, $\gamma$ is the shear strain, and $S$ is entropy change of the phase transition. The asymmetrical in-plane strains in the film may alter the shear strain $\gamma$ hence narrow the hysteresis loop.

By epitaxial growth of a high-quality VO$_2$ thin film on a designed vicinal TiO$_2$ substrate, we deliberately tailored the sublattices of VO$_2$ crystal utilizing the nonequal biaxial in-plane strains. The anisotropic in-plane strain leads to different apical V–O bond lengths in A and B octahedral chains of the VO$_2$ film, which modulates the orbital configurations of V 3d$^2$ and induces in-plane orientation-dependent MIT behaviors in the VO$_2$ film. Specifically, direction-dependent conductivity and phase transition temperature $T_c$ as well as the significant reduction of the hysteresis width $\Delta T_c$ have been observed. Our experimental results demonstrate the feasibility of tailoring the sublattices in the 3D transition metal oxides for modulating their electronic configure using anisotropic strains. This demonstration presents a unique platform in the material genetic design for exploring both fundamental physical properties and practical applications.

**METHODS**

The vicinal TiO$_2$ (001) substrate and the normal TiO$_2$ (001) substrate were both ultrasonically cleaned in acetone and deionized water, then immersed in 5 vol% HCl solution for 5 min to remove the metal contamination on the surfaces of the substrates before being washed in deionized water. After that, the substrates were etched in 20 vol% HF solution for 2 min, and then ultrasonically cleaned in deionized water. Finally, the substrates were annealed in oxygen at 750 °C for 2 h to form a solution for 2 min, and then ultrasonically cleaned in deionized water.

**DATA AVAILABILITY**

All data supporting the findings of this study are available from the corresponding authors Y.L. and M.G. upon request.
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