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## Epitaxial stabilization and phase instability of VO<sub>2</sub> polymorphs

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The VO<sub>2</sub> polymorphs, i.e., VO<sub>2</sub>(A), VO<sub>2</sub>(B), VO<sub>2</sub>(M1) and VO<sub>2</sub>(R), have a wide spectrum of functionalities useful for many potential applications in information and energy technologies. However, synthesis of phase pure materials, especially in thin film forms, has been a challenging task due to the fact that the VO<sub>2</sub> polymorphs are closely related to each other in a thermodynamic framework. Here, we report epitaxial stabilization of the VO<sub>2</sub> polymorphs to synthesize high quality single crystalline thin films and study the phase stability of these metastable materials. We selectively deposit all the phases on various perovskite substrates with different crystallographic orientations. By investigating the phase instability, phonon modes and transport behaviours, not only do we find distinctively contrasting physical properties of the VO<sub>2</sub> polymorphs, but that the polymorphs can be on the verge of phase transitions when heated as low as ~400 °C. Our successful epitaxy of both VO<sub>2</sub>(A) and VO<sub>2</sub>(B) phases, which are rarely studied due to the lack of phase pure materials, will open the door to the fundamental studies of VO<sub>2</sub> polymorphs for potential applications in advanced electronic and energy devices.

Vanadium dioxides (VO<sub>2</sub>) are strongly correlated *d*<sup>1</sup> electron systems and are known to have several polymorphs, which include VO<sub>2</sub>(A), VO<sub>2</sub>(B), VO<sub>2</sub>(M1) and VO<sub>2</sub>(R). While the chemical formula is the same, their crystalline and electronic structures are completely different and highly complex, exhibiting many interesting electrical, optical and chemical properties owing to the strong electron correlation<sup>1–3</sup>. Among the aforementioned VO<sub>2</sub> polymorphs, the rutile VO<sub>2</sub>(R) and the monoclinic VO<sub>2</sub>(M1) have been the most widely studied phases due primarily to their metal-to-insulator transition (MIT) temperature close to room temperature (68 °C)<sup>1–3</sup>. Since this phase transition is accompanied by a huge change in resistivity by three orders of magnitude, VO<sub>2</sub>(R) and VO<sub>2</sub>(M1) have attracted tremendous attention for the electronic and optical applications, such as smart windows<sup>4</sup>, frequency-agile metamaterials<sup>5,6</sup> and electrical switches<sup>7–9</sup>.

The monoclinic VO<sub>2</sub>(B) phase has also been explored. However, the focus has been on utilization of the open framework, which originates from the edge-sharing VO<sub>6</sub> octahedra<sup>10–12</sup>. Such open framework makes VO<sub>2</sub>(B) a promising energy material, which can be used as electrodes in Li-ion batteries<sup>13</sup>. Chen *et al.* first reported the growth of textured VO<sub>2</sub>(B) films on (001)-oriented SrTiO<sub>3</sub> substrates<sup>14</sup>, but pure phase could be stabilized only at thin (<25 nm) films. It is known that the growth of single crystalline VO<sub>2</sub>(B) is very challenging due to the complex crystal structure<sup>14,15</sup>. Similarly, the study of the tetragonal VO<sub>2</sub>(A) has so far been very limited<sup>15–17</sup> as compared to other VO<sub>2</sub> polymorphs, due to the difficulty in synthesizing phase pure crystals. Thus, their physical properties and potential for technical applications have not been much explored.

One of the main reasons for the difficulty in preparing phase pure VO<sub>2</sub> polymorphs is the narrow range of phase diagram<sup>3</sup> and, more importantly, the VO<sub>2</sub> polymorphs are closely related to each other in a thermodynamic framework<sup>10,12,16</sup>. For example, it has been shown that the VO<sub>2</sub>(A) and VO<sub>2</sub>(B) phases are metastable in bulk and undergo an irreversible phase change into VO<sub>2</sub>(R) upon heating<sup>10,12,16</sup>, resulting in a mixture of VO<sub>2</sub> polymorphs. The formation of such mixed phases hinders the accurate understanding of the physical properties of the VO<sub>2</sub> polymorphs. Hence, preparation of phase pure and high quality crystalline materials has been one of the major challenges in VO<sub>2</sub> research.

Epitaxial stabilization of crystalline materials by formation of low energy interface is a well-known approach to creating pure phase materials<sup>18–22</sup>. Because the stability of these non-equilibrium materials is affected by both thermodynamic and kinetic factors, the highly non-equilibrium film growth conditions offered by pulsed laser epitaxy (PLE) provide a unique opportunity to discover a wide range of materials with unprecedented functionalities.

Here, we report comparatively the physical properties of four VO<sub>2</sub> polymorphs (i.e., R, M1, A and B phases) epitaxially stabilized by PLE on various perovskite substrates with different crystallographic orientations, i.e.,

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VO <sub>2</sub> polymorphs	Crystal structure (space group)	Lattice constants in bulk				Substrates for epitaxial growth	Critical growth condition
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)		
VO <sub>2</sub> (A)	Tetragonal (P4 <sub>2</sub> /ncm (138))	8.43	8.43	7.68		STO(011), LAO(011)	$T_s < 430$ °C
VO <sub>2</sub> (B)	Monoclinic (C2/m (12))	12.03	3.69	6.42	106.6	pc-TSO(001), STO(001), LSAT(001), LAO(001), pc-YAO(001)	$T_s < 430$ °C
VO <sub>2</sub> (M1)	Monoclinic (P2 <sub>1</sub> /c (14))	5.38	4.52	5.74	122.6	STO(111), LSAT(111), LAO(111)	Not critical to $T_s$
VO <sub>2</sub> (R)	Tetragonal (P4 <sub>2</sub> /mnm (136))	4.55	4.55	2.86		Thermal heating of VO <sub>2</sub> (M1) above 68 °C	

**Table 1.** Crystal structure, lattice parameters and growth conditions for VO<sub>2</sub> polymorphs.

ABO<sub>3</sub>(001), ABO<sub>3</sub>(011) and ABO<sub>3</sub>(111). Distinctively contrasting phase stability, lattice motions and transport properties reported here will provide useful information to develop VO<sub>2</sub>-based electronic devices and energy materials.

## Results and Discussion

In order to selectively grow VO<sub>2</sub> polymorphs, commercially-available perovskite-oxide substrates, including TbScO<sub>3</sub> (TSO), SrTiO<sub>3</sub> (STO), (LaAlO<sub>3</sub>)<sub>0.3</sub>(SrAl<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub>)<sub>0.7</sub> (LSAT), LaAlO<sub>3</sub> (LAO) and YAlO<sub>3</sub> (YAO), were used. As summarized in Table 1, we were able to epitaxially grow (1) the tetragonal VO<sub>2</sub>(A) phase on (011)-oriented STO and LAO substrates; (2) the monoclinic VO<sub>2</sub>(B) phase on a wide selection of (001)-oriented substrates, including pseudo-cubic TSO, STO, LSAT, LAO and pseudo-cubic YAO; and (3) the monoclinic VO<sub>2</sub>(M1) phase on (111)-oriented STO, LSAT and LAO substrates, which commonly have a 3*m* surface symmetry.

The selective growth occurs due to preferential in-plane lattice matching of perovskite-oxide substrates with the VO<sub>2</sub> polymorphs. VO<sub>2</sub>(B) has a low-symmetry monoclinic structure (space group of C2/m (12)) with lattice constants of  $a = 12.03$  Å,  $b = 3.69$  Å,  $c = 6.42$  Å and  $\beta = 106.6^\circ$ , as summarized in Table 1 and as schematically shown in Fig. 1a. Various X-ray diffraction (XRD) scans, including  $\theta - 2\theta$  scans shown in Fig. 2a and  $\phi$  scans shown in Fig. 2d, for VO<sub>2</sub>(B) films on (001)STO ( $a_{\text{STO}} = 3.905$  Å) confirmed the following epitaxy relationship: (001)VO<sub>2</sub>(B) || (001)STO and [100]VO<sub>2</sub>(B) || [100]STO (see Fig. 2g). The lattice mismatch ( $(a_{\text{sub}} - a_{\text{film}})/a_{\text{sub}} \times 100$ ) was  $-2.6\%$  for [010]VO<sub>2</sub>(B) || [010]STO and  $+5.8\%$  for [100]VO<sub>2</sub>(B) || [100]STO, where the negative and positive signs indicate compressive and tensile strain, respectively.

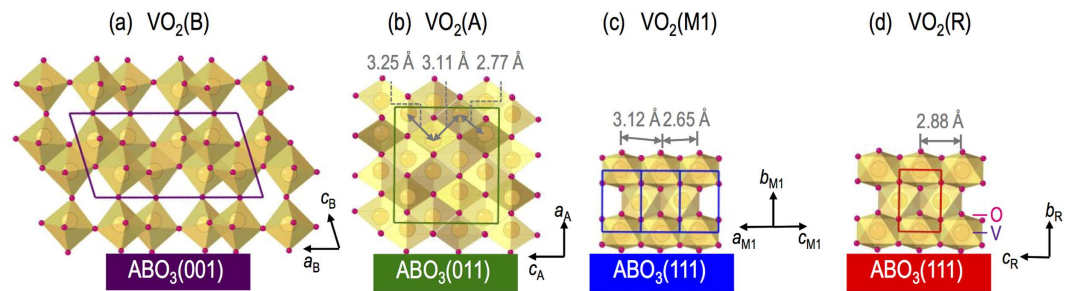
VO<sub>2</sub>(A) has a tetragonal structure (space group of P4<sub>2</sub>/ncm (138)) with lattice constants of  $a = b = 8.43$  Å and  $c = 7.68$  Å, as schematically shown in Fig. 1b. We found that the single crystalline VO<sub>2</sub>(A) phase could be grown best on (011)STO with the following epitaxy relationship: (100)VO<sub>2</sub>(A) || (011)STO and [010]VO<sub>2</sub>(A) || [011]STO (see Fig. 2h), as confirmed by XRD  $\theta - 2\theta$  scans (see Fig. 2b) and  $\phi$  scans (see Fig. 2e). The mismatches along the two orthogonal directions, i.e., [010]VO<sub>2</sub>(A) || [011]STO and [001]VO<sub>2</sub>(A) || [100]STO are  $-1.7$  and  $+1.7\%$ , respectively.

The VO<sub>2</sub>(M1) phase has a low-symmetry monoclinic structure (space group of P2<sub>1</sub>/c (14)) with lattice constant of  $a = 5.38$  Å,  $b = 4.52$  Å,  $c = 5.74$  Å and  $\beta = 122.6^\circ$ , as schematically shown in Fig. 1c. There have been several reports on the successful growth of VO<sub>2</sub>(M1) films on substrates with a 3*m* surface symmetry<sup>23</sup> such as (0001) Al<sub>2</sub>O<sub>3</sub>, (111)MgAl<sub>2</sub>O<sub>4</sub>, (111)MgO and (0001)ZnO. In our study, we mainly attempted to grow epitaxial films on (111)STO substrates to unify the substrates for VO<sub>2</sub> polymorph films. Since the XRD peak positions of VO<sub>2</sub>(M1) are very close to those of the STO substrate, the film peaks are hardly observed in Fig. 2c. Nevertheless, as confirmed by XRD  $\phi$  scans (see Fig. 2f), VO<sub>2</sub>(M1) could be grown on (111)STO with the following epitaxy relationship: (010)VO<sub>2</sub>(M1) || (111)STO and [001]VO<sub>2</sub>(M1) ||  $[\bar{2}11]$ STO, as illustrated in Fig. 2i (see the left portion). The lattice mismatch is  $-3.8\%$  along the [001]VO<sub>2</sub>(M1) ||  $[\bar{2}11]$ STO and  $+2.6\%$  along the [100]VO<sub>2</sub>(M1) ||  $[\bar{1}\bar{2}1]$ STO.

While the three VO<sub>2</sub> phases listed above are accessible at room temperature from as grown films, we also tried to access to the VO<sub>2</sub>(R) phase via a structural phase transition by heating a VO<sub>2</sub>(M1) film above the  $T_c$  (68 °C). The VO<sub>2</sub>(R) has a tetragonal structure (space group of P4<sub>2</sub>/mnm (136)) with lattice constants of  $a = b = 4.55$  Å and  $c = 2.86$  Å, as schematically shown in Fig. 1d. As shown in the inset of Fig. 2c, we were able to confirm the phase transition into the VO<sub>2</sub>(R) phase by performing an XRD  $\theta - 2\theta$  scans at 100 °C, which is higher than the  $T_c$ . Both VO<sub>2</sub>(R) and VO<sub>2</sub>(M1) phases on (111)STO are (010)-oriented. The epitaxial relationship for VO<sub>2</sub>(R) on (111)STO is illustrated in Fig. 2i (see the right portion) as follows: (010)VO<sub>2</sub>(R) || (111)STO and [100]VO<sub>2</sub>(R) ||  $[\bar{2}11]$ STO with the lattice mismatch of  $+4.9\%$  along the [100]VO<sub>2</sub>(R) ||  $[\bar{2}11]$ STO direction and  $-3.6\%$  along the [001]VO<sub>2</sub>(R) ||  $[0\bar{1}\bar{1}]$ STO direction.

Among the growth parameters, we found that a proper choice of the substrate temperature,  $T_s$ , is critical, in particular for VO<sub>2</sub>(A) and VO<sub>2</sub>(B) phases on perovskite substrates. As shown in Table 1, we could reproducibly grow VO<sub>2</sub>(A) and VO<sub>2</sub>(B) phases when  $T_s$  was lower than 430 °C. On the other hand, the growth of VO<sub>2</sub>(M1) phase was quite insensitive to  $T_s$ , as we confirmed the growth of high quality films in a wide temperature window ( $400 \leq T_s \leq 600$  °C).

To evaluate the thermal stability of VO<sub>2</sub> polymorphs, epitaxial films of VO<sub>2</sub>(A), VO<sub>2</sub>(B) and VO<sub>2</sub>(M1) phases were heated up to 600 °C. We kept the samples in vacuum ( $\sim 0.37$  Torr) to avoid spontaneous oxidation into the V<sub>2</sub>O<sub>5</sub> phase<sup>24</sup>. Fig. 3a,b show the phase evolution of VO<sub>2</sub>(B)/STO(001) and VO<sub>2</sub>(A)/STO(011), respectively, characterized by XRD  $\theta - 2\theta$  scans as a function of temperature. In case of VO<sub>2</sub>(B) on STO(001), upon heating, XRD peaks corresponding to (00*l*) VO<sub>2</sub>(B) disappeared above 430 °C and then the (330) VO<sub>2</sub>(A) peak subsequently appeared above 440 °C, indicating the formation of polycrystalline VO<sub>2</sub>(A). When we further increased  $T_s$ , the VO<sub>2</sub>(A) phase disappeared above 470 °C, and the polycrystalline VO<sub>2</sub>(R) phase appeared above 520 °C. This transformation, i.e., VO<sub>2</sub>(B)  $\rightarrow$  VO<sub>2</sub>(A)  $\rightarrow$  VO<sub>2</sub>(R), indicates that the structural frameworks are similar among the



**Figure 1.** Schematics of (a)  $\text{VO}_2(\text{B})$ , (b)  $\text{VO}_2(\text{A})$ , (c)  $\text{VO}_2(\text{M1})$  and (d)  $\text{VO}_2(\text{R})$  phases grown on various perovskite substrates with different crystallographic orientations, i.e.,  $\text{ABO}_3(001)$ ,  $\text{ABO}_3(011)$  and  $\text{ABO}_3(111)$ , respectively.

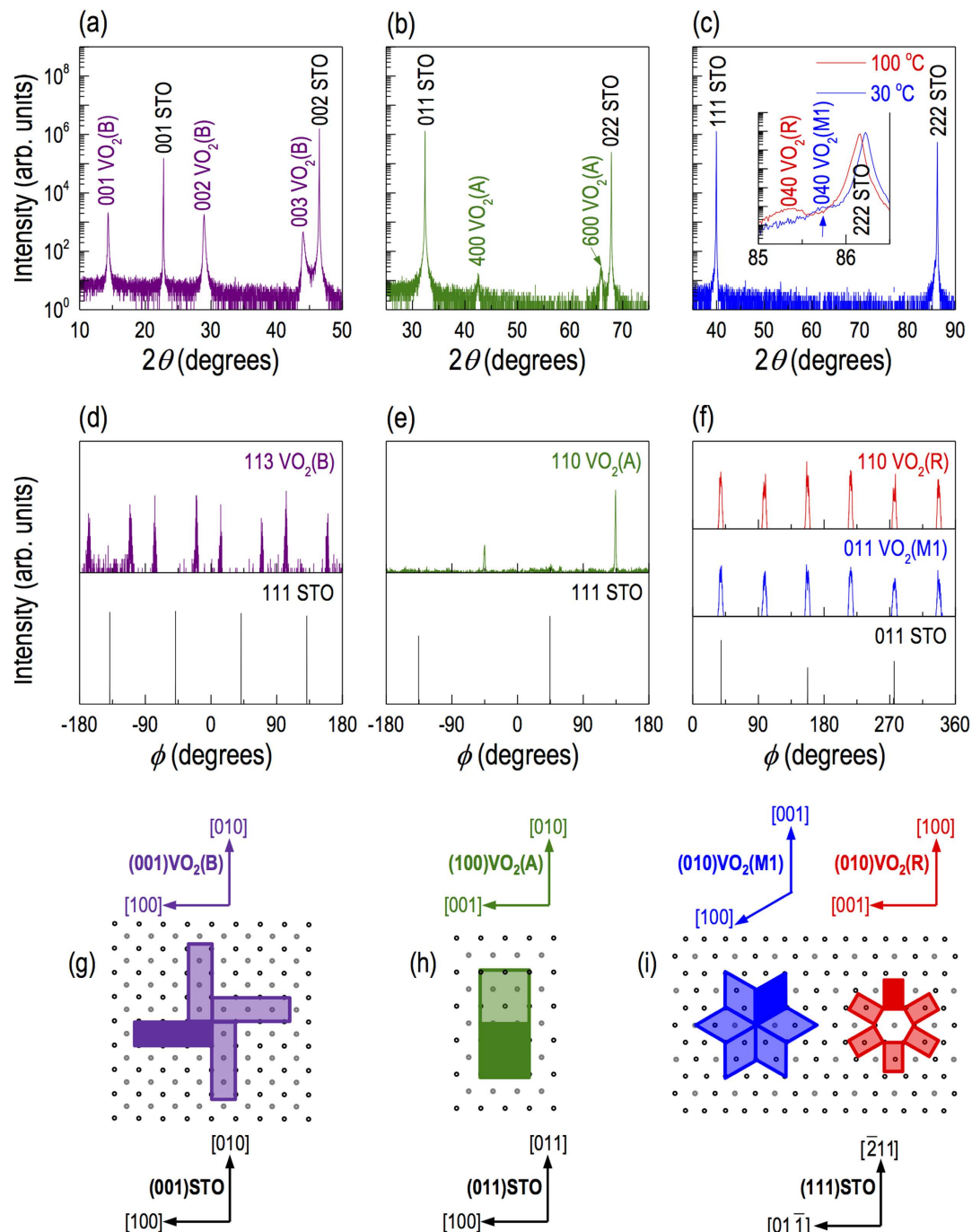
phases. The first transition to A-phase is known to associate with the realignment of  $\text{VO}_6$  octahedra from edge shared to face shared<sup>10</sup> and, the second transition to the R-phase is attributed to the reorientation of the half of the  $\text{VO}_6$  octahedra<sup>10</sup>.

As shown in Fig. 3b, the  $\text{VO}_2(\text{A})/\text{STO}(011)$  also revealed similar thermal stability. The peaks corresponding to (100)  $\text{VO}_2(\text{A})$  disappeared above 430 °C and polycrystalline  $\text{VO}_2(\text{R})$  was subsequently formed above 470 °C. The phase transitions of both  $\text{VO}_2(\text{B})$  and  $\text{VO}_2(\text{A})$  were irreversible upon cooling. The irreversible phase transformation of  $\text{VO}_2$  polymorphs is similar to what was observed in other binary oxide polymorphs. For example,  $\text{TiO}_2$  is known to undergo a transition from the anatase to the rutile phase via brookite<sup>25</sup>. As the crossover instability in  $\text{TiO}_2$  polymorphs was understood by closely balanced enthalpy among these phases<sup>26</sup>, further thermodynamic studies will be useful to understand the phase instability in  $\text{VO}_2$ . The thermal instability of  $\text{VO}_2(\text{A})$  and  $\text{VO}_2(\text{B})$  explains the formation of mixed phase  $\text{VO}_2$  polymorphs with  $\text{VO}_2(\text{R})$  as an impurity phase often observed from films grown above 430 °C. The observation of MIT at 68 °C in  $\text{VO}_2(\text{A})$  and  $\text{VO}_2(\text{B})$  films grown above 430 °C clearly indicates inclusion of  $\text{VO}_2(\text{R})$  as an impurity phase<sup>14</sup>. We note that, on the other hand, the  $\text{VO}_2(\text{M1})$  phase was converted into  $\text{VO}_2(\text{R})$  at ~68 °C upon heating and was stable up to 600 °C (data not shown). Upon cooling,  $\text{VO}_2(\text{R})$  was converted back to  $\text{VO}_2(\text{M1})$ , indicating a reversible phase evolution with good thermal stability.

Since the  $\text{VO}_2$  polymorphs have distinct structures, one can expect highly contrasting vibrational characteristics of lattice. Thus, identifying the phonon mode is a good measure of phase purity. In order to comparatively understand the phonon modes, Raman spectroscopy was carried out for the  $\text{VO}_2$  polymorphs by growing films on LAO substrates. The latter were used because dominant Raman spectral features of LAO are isolated at very low wavelength (32 and 123  $\text{cm}^{-1}$ )<sup>27</sup>. As shown in Fig. 4, the  $\text{VO}_2$  polymorphs revealed contrasting Raman spectra compared to each other. As compared to Raman data available from nanostructured materials<sup>28–30</sup>, we were able to confirm the phase purity of our epitaxial films.

In addition to the phase confirmation, the Raman spectra from  $\text{VO}_2$  provide more detailed information about the local structure. There are three sets of V–O modes<sup>31</sup> within wavenumber of 100–1100  $\text{cm}^{-1}$ . At low wavenumber (< 400  $\text{cm}^{-1}$ ), the bands are assigned to V–O–V bending modes; at intermediate wavenumber (400–800  $\text{cm}^{-1}$ ), the bands are attributed to V–O–V stretching modes; and at high wavenumber (> 800  $\text{cm}^{-1}$ ), the bands are assigned to V=O stretching modes of distorted octahedra and distorted square-pyramids. As shown in Fig. 4a, the phonon modes in epitaxial films of  $\text{VO}_2(\text{B})$  were mainly observed at low and intermediate wavenumbers (152, 263 and 480  $\text{cm}^{-1}$ ), indicating that bending and stretching modes of V–O–V are dominant in  $\text{VO}_2(\text{B})$ . On the other hand, as shown in Fig. 4b, the phonon modes in  $\text{VO}_2(\text{A})$  were mainly observed at high and intermediate wavenumbers (152, 485 and 887  $\text{cm}^{-1}$ ), which imply that the stretching modes of V–O–V and V=O are dominant lattice motions in  $\text{VO}_2(\text{A})$ . The phonon modes in  $\text{VO}_2(\text{M1})$  are very complex and composed of stretching and bending of V–O–V and zigzag chains of V–V. The phonon modes in  $\text{VO}_2(\text{R})$  dominantly include stretching modes of V–O–V, which indicate that the crystal structure of  $\text{VO}_2(\text{R})$  is more symmetric than  $\text{VO}_2(\text{M1})$ <sup>30,32,33</sup>.

While the transport properties of  $\text{VO}_2(\text{M1})$  and  $\text{VO}_2(\text{R})$  have been extensively studied<sup>1–3,8,9,24,32–34</sup>, the physical properties of  $\text{VO}_2(\text{B})$  and  $\text{VO}_2(\text{A})$  phases have not been much explored due to difficulty in preparing phase pure thin films. Figure 5 shows the transport characteristics of  $\text{VO}_2(\text{B})$ ,  $\text{VO}_2(\text{A})$  and  $\text{VO}_2(\text{M1})$  films grown on STO substrates.  $\text{VO}_2(\text{A})$  showed a monotonic decrease of resistivity as increasing the temperature, typical for insulators. While still insulating over the temperature range we measured,  $\text{VO}_2(\text{B})$  revealed more or less semiconducting behaviours with much smaller resistivity compared to that of  $\text{VO}_2(\text{A})$ , i.e.,  $\rho_{\text{VO}_2(\text{B})}^{300\text{K}} \approx 0.02 \Omega \cdot \text{cm}$  and  $\rho_{\text{VO}_2(\text{A})}^{300\text{K}} \approx 60 \Omega \cdot \text{cm}$ . The resistivity in our  $\text{VO}_2(\text{A})/\text{STO}(011)$  is higher than that reported in  $\text{VO}_2(\text{A})/\text{STO}(001)$ <sup>15</sup> by one order of magnitude. The reason is unclear, but one can consider that the film on (001)STO is under a different strain state or that the growth on a (001)STO substrate may include a small amount of  $\text{VO}_2(\text{B})$  since their thermal phase boundary is relatively low<sup>10,12,16</sup>, as shown in Fig. 3. In the case of  $\text{VO}_2(\text{M1})$  phase, we also observed the MIT at 340 K from  $\text{VO}_2(\text{M1})$  to  $\text{VO}_2(\text{R})$  phase change upon heating, similarly observed from many previous studies<sup>1–3,8,9,24,32–34</sup>. The MIT accompanied a sudden decrease of the resistivity by 3–4 orders of magnitude, which is comparable to high quality epitaxial films grown on  $\text{Al}_2\text{O}_3(0001)$ <sup>24</sup>. This excellent performance could be attributed to the high crystallinity of our epitaxial films ( $\Delta\omega < 0.1^\circ$ ). The transition temperature is consistent with structural phase transition from  $\text{VO}_2(\text{M1})$  to  $\text{VO}_2(\text{R})$ , as shown in XRD  $\theta-2\theta$  scan in the inset of Fig. 2c. We note

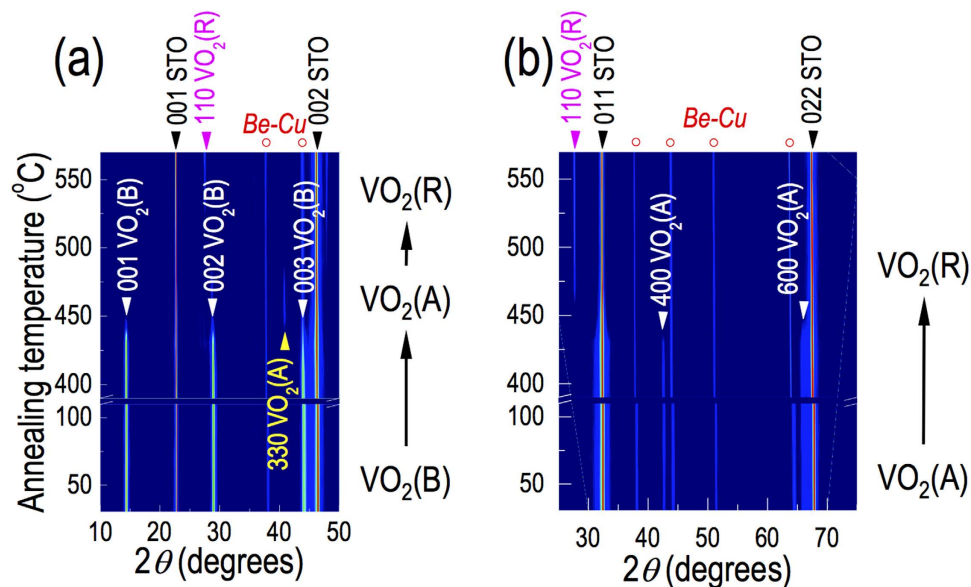


**Figure 2.** XRD  $\theta-2\theta$  scans of (a) VO<sub>2</sub>(B), (b) VO<sub>2</sub>(A) and (c) VO<sub>2</sub>(M1) thin films on STO (001), (011) and (111) substrates, respectively. The inset in (c) shows XRD scans of the VO<sub>2</sub>(R) phase (red line) obtained at 100 °C by heating the VO<sub>2</sub>(M1) film (blue line), which is above the  $T_c = 68^\circ\text{C}$ . From  $\phi$  scans shown in (d) VO<sub>2</sub>(B), (e) VO<sub>2</sub>(A) and (f) VO<sub>2</sub>(M1) and VO<sub>2</sub>(R) thin films, in-plane lattice matching is schematically illustrated as shown in (g-i).

that the transport properties of the films grown on LAO substrates were almost identical except for slightly decreased resistivity for films on LAO (data not shown).

Overall, as explained above, the VO<sub>2</sub> polymorphs revealed a wide range of electronic ground states, i.e., metal [VO<sub>2</sub>(R)], semiconductor [VO<sub>2</sub>(B)] and insulator [VO<sub>2</sub>(A) and VO<sub>2</sub>(M1)], depending on their crystal structure. This wide range of electronic ground states makes VO<sub>2</sub> highly attractive over other transition metal dioxides, since most other binary oxides are either metal (CrO<sub>2</sub>:  $\alpha$ -phase and  $\beta$ -phase) or insulator (TiO<sub>2</sub>: rutile, brookite and anatase). While it is not the main focus of this paper, it is worth mentioning that Goodenough<sup>32,34</sup> obtained a





**Figure 3.** Real time XRD  $\theta$ – $2\theta$  scans of (a)  $\text{VO}_2(\text{B})/\text{STO}(001)$  and (b)  $\text{VO}_2(\text{A})/\text{STO}(011)$  samples as a function of temperature in 0.37 Torr of air. A clear phase change was observed from both samples, indicating that the phases are in close proximity with each other. The phase changes were, however, irreversible upon cooling. It is also worth noting that there are temperature gaps where the XRD peaks are hardly seen before showing up the polycrystalline phases. They are 470–520 °C in (a) and 430–470 °C in (b). We attribute this to the films in metastable state undergoing polycrystallization during the phase transition, even though it is hard to clearly identify due to the suppressed XRD peaks.

semiempirical expression for the room temperature critical V–V separation  $R_c \approx 2.92$ – $2.94$  Å for localized and itinerant  $3d$  electrons in vanadium oxides.

$$R < R_c \rightarrow \text{Itinerant } 3d \text{ electron} \rightarrow \text{Metal};$$

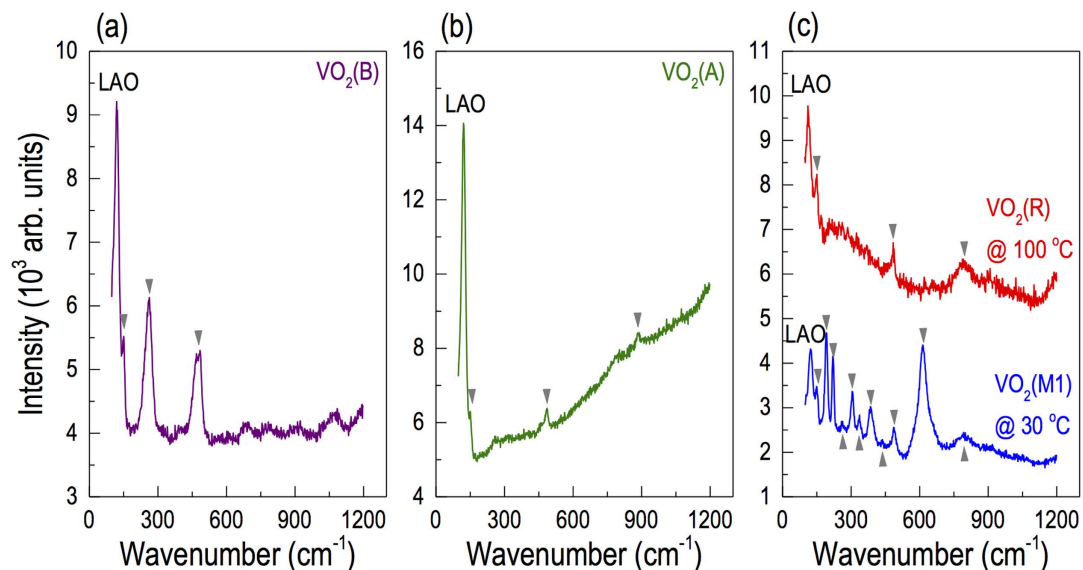
$$R > R_c \rightarrow \text{Localized } 3d \text{ electron} \rightarrow \text{Insulator}.$$

This semiempirical criterion indicates that  $\text{VO}_2$  polymorphs can be either metal or insulator depending on the V–V separation in the distinguishable crystal structures. The  $\text{VO}_2(\text{R})$  phase has a uniform V–V separation of  $R = 2.88$  Å (ref. 32), resulting in a metallic ground state. As shown in Fig. 1c, the  $\text{VO}_2(\text{M1})$  phase has zigzag V–V chains of  $R = 2.65$  Å and 3.12 Å (ref. 32). The  $\text{VO}_2(\text{A})$  phase also has zigzag V–V chains of  $R = 3.25$  Å, 3.11 Å and 2.77 Å (ref. 17) as shown in Fig. 1b. The insulating behaviours that we have observed for those M1 and A-phases are attributed to the localized electrons in shorter V–V chains with  $R = 2.65$  Å [ $\text{VO}_2(\text{M1})$ ] and 2.77 Å [ $\text{VO}_2(\text{A})$ ]. Thus, overall transport behaviours of our epitaxial thin films can be well explained by Goodenough's criterion<sup>32,34</sup>. Since  $\text{VO}_2$  polymorphs have a wide range of physical properties and, in particular,  $\text{VO}_2(\text{B})$  phase is on the verge of becoming a metal, our report on epitaxial synthesis of high quality thin films can open the door to the discovery of novel phenomena and physical properties by deliberate control of the order parameters by various means, including strain, dimensionality, confinement, etc., which can be accessible via epitaxial heterostructuring.

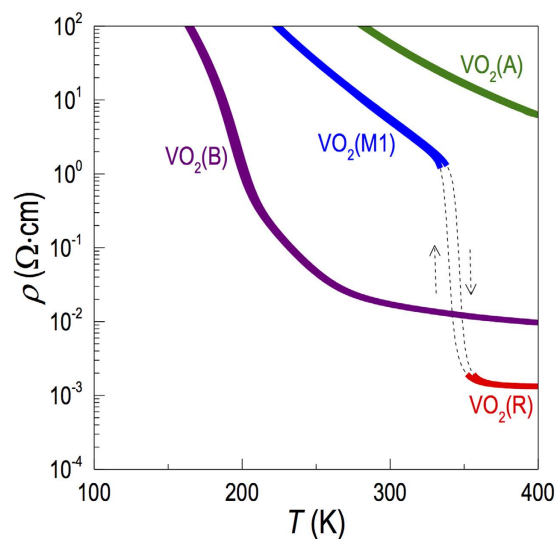
In conclusion, we grew epitaxial films of  $\text{VO}_2$  polymorphs. For the growth of phase pure  $\text{VO}_2$  polymorphs, a careful selection of the growth conditions was necessary especially for the temperature and oxygen pressure. Depending on the crystal orientation of substrates, we found that different phases of  $\text{VO}_2$  could be selectively grown, i.e.,  $\text{VO}_2(\text{B})/\text{ABO}_3(001)$ ,  $\text{VO}_2(\text{A})/\text{ABO}_3(011)$ ,  $\text{VO}_2(\text{M1})/\text{ABO}_3(111)$ , and  $\text{VO}_2(\text{R})/\text{ABO}_3(111)$ . Such phases revealed unique phonon modes due to the distinctly different crystal structures and physical properties in spite of the same chemical composition. Since the  $\text{VO}_2$  polymorphs have a wide range of electronic ground states from metal [ $\text{VO}_2(\text{R})$ ] and semiconductor [ $\text{VO}_2(\text{B})$ ] to insulator [ $\text{VO}_2(\text{A})$  and  $\text{VO}_2(\text{M1})$ ], our epitaxial thin films, which are known to be challenging to grow, will expedite our understanding of underlying physics and developing  $\text{VO}_2$  polymorphs-based electronic devices utilizing the wide selection of the electronic properties from a single composition.

## Methods

**Epitaxial film growth.** We deposited epitaxial films (100 nm in thickness) of  $\text{VO}_2$  polymorphs on perovskite oxide substrates by pulsed laser epitaxy. We ablated a sintered  $\text{VO}_2$  target, which contains mainly the M1 phase, by a KrF excimer laser (248 nm in wavelength) at a laser fluence of  $1 \text{ J cm}^{-2}$  and at a laser repetition rate of 10 Hz. By growing thin films under a wide range of  $P(\text{O}_2)$  and  $T_s$  ( $2 \text{ mTorr} < P(\text{O}_2) < 25 \text{ mTorr}$  and  $350^\circ\text{C} < T_s < 600^\circ\text{C}$ ), we found the optimal condition for  $\text{VO}_2(\text{A})$ ,  $\text{VO}_2(\text{B})$  and  $\text{VO}_2(\text{M1})$ , as described in Table 1. It should be noted that  $\text{V}_2\text{O}_3$  was formed at  $P(\text{O}_2) < 5 \text{ mTorr}$  and  $\text{V}_2\text{O}_5$  was formed for  $P(\text{O}_2) > 25 \text{ mTorr}$ , due to the multivalent nature of vanadium<sup>24</sup>.



**Figure 4.** Raman spectra of (a) VO<sub>2</sub>(B), (b) VO<sub>2</sub>(A), (c) VO<sub>2</sub>(M1) and VO<sub>2</sub>(R) grown on LAO substrates. The spectra were recorded at room temperature except the VO<sub>2</sub>(R) phase shown in (c), which was obtained by heating the M1 phase sample to 100 °C in air.



**Figure 5.** Temperature dependent resistivity for VO<sub>2</sub>(B), VO<sub>2</sub>(A), VO<sub>2</sub>(M1) and VO<sub>2</sub>(R) phases grown on (001), (011), and (111) STO substrates, respectively, exhibiting distinctly contrasting transport behaviours.

**Characterization of physical properties.** To investigate the *dc* transport properties, a physical property measurement system (Quantum Design Inc.) was used with Pt contacts in four-probe geometry. X-ray diffraction (XRD) measurements were carried out with a four-circle high-resolution X-ray diffractometer (X'Pert Pro, Panalytical) using the Cu-K $\alpha_1$  radiation equipped with a hot stage (DHS 900, Anton Paar). High-temperature environmental XRD measurements were conducted under vacuum with base pressure of 0.37 Torr air. Raman spectra were recorded at various temperatures using a temperature control stage (Lincam Scientific Instruments). A Renishaw 1000 confocal Raman microscope was used to measure Raman spectra in back scattering configuration. Each spectrum is a sum average of seven individual spectra taken at different place on the sample through 20 $\times$  objective. The wavelength of the Raman laser used in these measurements was 532 nm.

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## Author Contributions

S.L. conceived and designed the experiments under supervision of H.N.L. S.L. fabricated the samples and measured electrical transport. S.L. also conducted high temperature XRD measurements with help of J.K.K. I.N.I performed Raman spectroscopic measurements. S.L. and H.N.L. wrote the manuscript and other authors reviewed it.

## Additional Information

**Competing financial interests:** The authors declare no competing financial interests.

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