



# Article Coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) Polymorphous Thin Films with Multiphase-Driven Insulator–Metal Transition

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**Abstract:** Reversible insulator–metal transition (IMT) and structure phase change in vanadium dioxide (VO<sub>2</sub>) remain vital and challenging with complex polymorphs. It is always essential to understand the polymorphs that coexist in desired VO<sub>2</sub> materials and their IMT behaviors. Different electrical properties and lattice alignments in VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases have enabled the creation of versatile functional devices. Here, we present polymorphous VO<sub>2</sub> thin films with coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases and phase-dependent IMT behaviors. The presence of VO<sub>2</sub> (B) phases may induce lattice distortions in VO<sub>2</sub> (M). The plane spacing of (011)<sub>M</sub> in the VO<sub>2</sub> (M) phase becomes widened, and the V-V and V-O vibrations shift when more VO<sub>2</sub> (B) phase exists in the VO<sub>2</sub> (M) matrix. Significantly, the coexisting VO<sub>2</sub> (B) phases promote the IMT temperature of the polymorphous VO<sub>2</sub> thin films. We expect that such coexistent polymorphs and IMT variations would help us to understand the microstructures and IMT in the desired VO<sub>2</sub> materials and contribute to advanced electronic transistors and optoelectronic devices.

Keywords: vanadium dioxide; polymorphs; monoclinic phase; insulator-metal transition

## 1. Introduction

Polarizable metal-oxygen bonds [1] and strong correlations among localized valance electrons in transition metal oxides [2,3] have sparked intensive interest, and they have shown promise in optoelectronics [4–7], sensors [8–11] and catalysis [12–15]. As one of the correlated electronic oxides,  $VO_2$  has several polymorphs, including  $VO_2$  (R) [16],  $VO_2$  (B) [17] and  $VO_2$  (M) [18]. Various crystalline symmetries and electronic structures in these polymorphs have shown versatile potential applications [19–21]. Wherein, the stable monoclinic VO<sub>2</sub> (M) ( $P2_1/c$ ) phase has attracted widespread attention due to a reversible IMT near 340 K. Lattice variations are often connected with the transformation between delocalized and localized states during IMT in VO<sub>2</sub>. Meanwhile, pure electronic behaviors have been observed due to strain-engineering and lattice-freezing during IMT processes [22,23]. Companied with IMT, structural distortion generally occurs within a first-order phase change from a low-temperature monoclinic  $VO_2$  (M) phase to a hightemperature rutile  $VO_2$  (R) phase [24]. In the insulating  $VO_2$  (M) phase, adjacent vanadium atoms form zigzag chains with two types of vanadium-vanadium bond lengths along the  $c_R$  axis, and the shorter one may form a vanadium–vanadium dimer, which makes the electrons localized [25].

The polymorphous lattices and crystalline phases often affect electrical and optical behaviors in VO<sub>2</sub>, which are closely related to the vanadium–vanadium bonds. Different from the VO<sub>2</sub> (M) phase, the VO<sub>2</sub> (B) (C2/m) phase is a Wadsley phase with a quasi-layered monoclinic structure [26] and undergoes IMT over a wide temperature range from 180 K to



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 300 K [27], while the vanadium–vanadium pairs induce layered alignments. It is noted that the edge-sharing VO<sub>6</sub> octahedra in the VO<sub>2</sub>(B) phase aid ion diffusion and gas reduction in ion batteries and energy storage devices [28]. When VO<sub>2</sub> (B)-like vanadium–vanadium bonds exist in VO<sub>2</sub> (M) lattices, the microstructures, the electronic states and IMT behaviors in VO<sub>2</sub> (M) may be modified due to the variations in crystal field energy and orbital occupancies near the Fermi level [29]. Actually, it is still of significance and challenging to understand microstructural changes and IMT in the coexistent polymorphs in VO<sub>2</sub> towards versatile applications [30].

Herein, we described the lattice variations and IMT behaviors in VO<sub>2</sub> thin films with coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases. The widened plane spacing of  $(011)_M$  and varied V-V and V-O phonon vibrations were induced by the coexisting VO<sub>2</sub> (B) phase in the VO<sub>2</sub> (M) thin films, as confirmed via Raman spectra and X-ray diffraction (XRD). The IMT temperature for the VO<sub>2</sub> (M) thin films increased when more VO<sub>2</sub> (B) phases were presented in the polymorphous thin films. We expected such phase-dependent IMT behaviors to aid our understanding of polymorphous lattice variations and electronic phase changes in correlated vanadium oxides and enable the fabrication of advanced optical, electronic and even energy devices.

#### 2. Results and Discussion

According to previous work [31], we exploited atomic layer deposition and postannealing processes to obtain coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases in the VO<sub>2</sub> thin films. Figure 1a displays a cross-sectional TEM image for a ~32 nm thick VO<sub>2</sub> thin film. When the XRD measurement was performed on the VO<sub>2</sub> thin film, diffraction peaks were obvious in the XRD patterns, as shown in Figure 1b. The diffraction peaks near  $2\theta = 28.00^{\circ}$  were ascribed to monoclinic VO<sub>2</sub>(PDF #09-0142) [29], indicating the presence of a VO<sub>2</sub> (M) phase in the resulting thin film. In the TEM image (Figure 1c), obvious lattice fringes were also found with a *d-spacing* of  $10d \approx 3.17$  nm, which further confirmed the existence of a VO<sub>2</sub> (M) phase [32]. As expected for the VO<sub>2</sub> (M) phase, the VO<sub>2</sub> (B) phase was also found in the resulting VO<sub>2</sub> thin film, as shown in Figure 1. XRD peaks near  $2\theta = 14.40^{\circ}$  and  $2\theta = 29.00^{\circ}$ in Figure 1b corresponded to VO<sub>2</sub> (B) (PDF #81-2392) [33], which was also verified by a *d-spacing* of  $10d \approx 6.14$  nm for the lattice fringes in VO<sub>2</sub> (B) [34] in Figure 1d. All these results suggested the presence of coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases in the as-prepared VO<sub>2</sub> thin film.



**Figure 1.** (a) TEM cross-section image and (b) XRD pattern for the VO<sub>2</sub> thin films with coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases, and magnified TEM images for (c) VO<sub>2</sub> (M) and (d) VO<sub>2</sub> (B) phases.

As mentioned above, the microstructures of VO<sub>2</sub> (M) thin films may be changed due to the existence of the  $VO_2$  (B) phase. Figure 2 displays the microstructure variations in  $VO_2$  (M) thin films when the content of  $VO_2$  (B) phases increased in the as-prepared polymorphous  $VO_2$  thin films. Figure 2a,b displays the XRD patterns of the polymorphous  $VO_2$  thin films with various  $VO_2$  (B) contents, referred to as  $D_M$  ( $VO_2$  thin film with few  $VO_2$  (B) phases),  $D_{M-B}$  (VO<sub>2</sub> thin film with some VO<sub>2</sub> (B) phases) and  $D_{B-M}$  (VO<sub>2</sub> thin film with more VO<sub>2</sub> (B) phases). The XRD peaks around  $2\theta = 28.00^{\circ}$  appeared in all D<sub>M</sub>,  $D_{M-B}$  and  $D_{B-M}$  thin films and were assigned to the (011) plane of VO<sub>2</sub> (M). Notably, XRD peaks near  $2\theta = 14.40^{\circ}$  and  $2\theta = 29.00^{\circ}$  were obvious and found in the D<sub>M-B</sub> and D<sub>B-M</sub> thin films, and they were assigned to the (001) and (002) planes in VO<sub>2</sub> (B) (PDF #81-2392), respectively. For the D<sub>M</sub> thin film, XRD peaks near  $2\theta$  = 14.40 ° were hardly observed, which indicated the main lattice was the  $VO_2$  (M) phase in the  $D_M$  thin film, and few  $VO_2$ (B) phases might have existed. We also found the intensity ratios at the XRD peaks near  $2\theta = 28.00^{\circ}$  and  $2\theta = 29.00^{\circ}$  were different in the case of the D<sub>M-B</sub> and D<sub>B-M</sub> thin films. For the  $D_{B-M}$  thin film, a larger ratio implied that there was more  $VO_2$  (B) phases in the  $VO_2$ thin films with coexistent  $VO_2$  (M) and  $VO_2$  (B) phases. Figure 2a suggests that the XRD patterns were different and related to the content of  $VO_2$  (B) phases. More  $VO_2$  (B) phases would have enhanced the intensity at about  $2\theta = 29.00^{\circ}$ , while the intensity declined at about  $2\theta = 28.00^{\circ}$  for VO<sub>2</sub> (M). The color changed in the temperature-dependent optical images for the  $D_{M-B}$  thin film upon heating (Figure S1 in SI), which indicated that the  $VO_2$ (M) phase was dominant in the  $D_{M-B}$  thin film. In contrast, the invariant color in the optical images (Figure S1 in SI) above room temperature for the D<sub>B-M</sub> thin film implied that the  $VO_2$  (B) phase dominated in the  $D_{B-M}$  thin film, because the IMT process associated with the  $VO_2$  (B) phase occurred between 180 K and 300 K. All measurements and analyses above suggested that the contents of the  $VO_2$  (B) phase in the  $D_M$ ,  $D_{M-B}$  and  $D_{B-M}$  thin films increased gradually.



**Figure 2.** (a) XRD patterns, (b) fitted XRD patterns, and (c) XPS spectra for the  $D_M$ ,  $D_{M-B}$  and  $D_{B-M}$  thin films with coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases.

Subsequently, we fitted the XRD curves and checked the peak variations for the  $(011)_M$  plane in the VO<sub>2</sub> (M) phase, as shown in Figure 2b. For the D<sub>M</sub>, D<sub>M-B</sub> and D<sub>B-M</sub> thin films, the corresponding  $2\theta$  were about  $28.05^{\circ}$ ,  $28.00^{\circ}$  and  $27.98^{\circ}$ , respectively. According to Bragg's law [35], the *d*-spacings for the  $(011)_M$  plane in VO<sub>2</sub> (M) were calculated to be about 3.179 Å, 3.184 Å and 3.186 Å by using the above  $2\theta$  values for the D<sub>M</sub>, D<sub>M-B</sub> and D<sub>B-M</sub> thin films, respectively. The *d*-spacing of  $(011)_M$  plane directly impacted the distance of the V-V lattice along the c<sub>R</sub> axis, which was related to electron–electron and electron–phonon

interactions and the IMT behaviors of VO2 (M) [25]. The above results suggested that the  $VO_2$  (B) phases may affect the lattice, especially the *d*-spacing of the (011)<sub>M</sub> plane in  $VO_2$ (M) in the  $VO_2$  thin films with coexistent  $VO_2$  (M) and  $VO_2$  (B) phases.  $VO_2$  (B) usually formed in an oxygen-excess environment, while  $VO_2$  (M) formed in an oxygen-deficient environment. An appropriate amount of V could support an environment where  $VO_2$  (B) was formed [36]. The thin films with more  $VO_2$  (B) phases annealed at a slower heating rate, resulting in the formation of VO<sub>2</sub> (B) at a lower temperature and insufficient activation energy to fully convert to stable  $VO_2$  (R), which would transform to  $VO_2$  (M) below about 340 K [37]. X-ray photoelectron spectroscopy (XPS) measurements were used to analyze the binding energy and oxidation state related to vanadium [38] (Figures 2c and S2). Figure S2 indicates the fitted peaks for varied oxidation states involving  $V^{+4}$  (with binding energies at about 516.2 eV and 523.4 eV) and  $V^{+5}$  (with binding energies at about 517.4 eV and 525.2 eV) for the V 2p core-level peaks [38]. We made calculations according to the XPS peaks and found that the valence of V<sup>+4</sup> was dominant in the D<sub>B-M</sub> (~57.5%), D<sub>M-B</sub> (~59.2%) and  $D_M$  (~67.6%) thin films, while the V<sup>+5</sup> contents in the  $D_{B-M}$  and  $D_{M-B}$  thin films were higher than that in the  $D_M$  thin film. The presence of  $V^{+5}$  might have been induced by surface oxidation and adsorption or the precursor of vanadium pentoxide [38]. Noticeably, the binding energy between vanadium atoms had a tendency to decrease from the  $D_M$  to  $D_{M-B}$ , and then to  $D_{B-M}$  thin films (Figure 2c). As verified in the XRD patterns, the XPS spectra suggested that the increased binding energy possibly corresponded to more VO<sub>2</sub> (B) existing in the polymorphous thin films. The layered lattice alignments and surfaceinduced V<sup>+5</sup> components might have increased the binding energy and stabilized the VO<sub>2</sub> (B) phases in the  $D_{M-B}$  and  $D_{B-M}$  thin films [36,39].

Raman spectra were adopted to identify the phases and lattice distortion in the D<sub>M</sub>,  $D_{M-B}$  and  $D_{B-M}$  thin films, as shown in Figures 3 and S3. The distinguishable Raman shifts at about 137, 195, 224 and 615 cm<sup>-1</sup> corresponded to the VO<sub>2</sub> (M) in the D<sub>M</sub> and D<sub>M-B</sub> thin films [40], while the one at about 520 cm<sup>-1</sup> was from silicon substrate. For the D<sub>B-M</sub> thin film, the Raman vibration modes at around 96, 191, 403 and 668  $cm^{-1}$  were obvious and assigned to  $VO_2$  (B). The strong Raman peaks (520 cm<sup>-1</sup>) from silicon substrate indicated a deeper detective depth, which implied that the vibration modes of the whole thin film could be obtained along the vertical direction. The vibration mode at about 96  $cm^{-1}$ corresponded to the translations of adjacent layers, and the vibration modes at around 191 and 403 cm<sup>-1</sup> were related to the bending and stretching of the V-O-V structure in VO<sub>2</sub> (B) [40]. Generally, the Raman shift at about 195 cm<sup>-1</sup> (referred as  $\omega_{V1}$ ) corresponded to the tilting motion of the V-V dimer, while the one at around 615 cm<sup>-1</sup> (referred as  $\omega_{V-O}$ ) was used to identify the V-O bond vibrations in  $VO_2$  [41]. Line-scanned Raman mapping in Figure 3 further displays the variations in the phonon vibration modes in the  $D_M$ ,  $D_{M-B}$ and D<sub>B-M</sub> thin films. Here, about 100 statistical points were obtained with a scan length of 100  $\mu$ m and a step of 1  $\mu$ m during micro-Raman mapping. The thermal effect of the laser could be ignored because no obvious shift was found at 520 cm<sup>-1</sup> for the silicon substrates [42]. Figure 3a,c show the Raman details at each scan position around 194 cm<sup>-1</sup> (dashed blue box in Figure 3b) and 640  $\text{cm}^{-1}$  (dashed yellow box in Figure 3b) for the D<sub>M</sub>, D<sub>M-B</sub> and D<sub>B-M</sub> thin films. In Figure 3a, Raman peaks shift towards low frequencies from around 198.5 cm<sup>-1</sup> in the D<sub>M</sub>, to around 195 cm<sup>-1</sup> in the D<sub>M-B</sub>, and then to around 191 cm<sup>-1</sup> in the  $D_{B-M}$  thin film. The Raman peak around 224 cm<sup>-1</sup> for the VO<sub>2</sub> (M) phase was observed in both the  $D_M$  and  $D_{M-B}$  thin films, while this peak was hardly observed in the case of the D<sub>B-M</sub> thin film. As shown in Figure 3c, the  $\omega_{V-O}$  peak around 668 cm<sup>-1</sup> was obvious in the  $D_{B-M}$  thin film, while the ones around 629 cm<sup>-1</sup> and 619 cm<sup>-1</sup> were for the D<sub>M</sub> and D<sub>M-B</sub> thin films, respectively. The above peaks indicated the variations in the  $\omega_{V1}$  and  $\omega_{V-O}$  modes in the D<sub>M</sub>, D<sub>M-B</sub> and D<sub>B-M</sub> thin films. When comparing the varied  $\omega_{V1}$  and  $\omega_{V-O}$  modes in the D<sub>M</sub> to D<sub>M-B</sub> thin films, we found an obvious shift because of the presence of VO<sub>2</sub> (B), as shown in Figures 3 and S3. In the D<sub>M</sub> thin film, the  $\omega_{V-O}$  peaks were dispersed and changed with the scanning position, while the  $\omega_{V-O}$  peaks in the D<sub>M-B</sub> thin film shifted and were concentrated. Meanwhile, the VO<sub>2</sub> (B) domains were distributed

in the  $D_{M-B}$  film, which may have induced an abrupt shift [43]. For the  $D_M$  and  $D_{M-B}$  thin films, the variations in the  $\omega_{V-O}$  modes were different, which may have been attributed to the content or grain size of the VO<sub>2</sub> (B) phase [43,44] in the corresponding thin films. In addition, the characteristic peaks around 668 cm<sup>-1</sup> for VO<sub>2</sub> (B) kept in the  $D_{B-M}$  thin film. In general, the phonon behavior in the  $D_{B-M}$  thin film was mainly attributed to the VO<sub>2</sub> (B) phase. All these results further verified the role of VO<sub>2</sub> (B) in the  $D_M$ ,  $D_{M-B}$  and  $D_{B-M}$  thin films, which were consistent with those indicated during the above XRD measurements.



**Figure 3.** (a) Raman spectra at around 194 cm<sup>-1</sup> (the blue dashed box in (b)), (b) line-scanned Raman mapping and (c) Raman spectra at around 640 cm<sup>-1</sup> (the yellow dashed box in (b)) in the  $D_{B-M}$ ,  $D_{M-B}$  and  $D_M$  thin films. The blue and yellow dashed lines were used to show the position variations of Raman peaks at around 195 and 620 cm<sup>-1</sup> among the  $D_{B-M}$ ,  $D_{M-B}$  and  $D_M$  thin films, respectively.

As shown in Figures 4 and S4, variable-temperature Raman measurements were taken to detect the thermal-induced structural evolutions in the  $D_{B-M}$ ,  $D_{M-B}$  and  $D_M$  thin films. Figure 4a displays the peak variations in the temperature-dependent Raman spectra for the  $D_{B-M}$ . The two modes at around ~191 and 400 cm<sup>-1</sup> were related to the bending and stretching vibration of the V-O-V structure in the VO2 (B) phase. When the temperature rose from 220 K to 280 K, the mode at ~394 cm<sup>-1</sup> shifted to ~403 cm<sup>-1</sup> (Figure 4a'). The vibration mode around ~195 cm<sup>-1</sup> at 200 K shifted to ~193 cm<sup>-1</sup> at 280 K, and then to ~191 cm<sup>-1</sup> at 320 K. Meanwhile, the intensity of the Raman peak around ~195 cm<sup>-1</sup> increased obviously from 200 K to 320 K (Figure 4a). There was no significant change in Raman spectra for the  $D_{B-M}$  above 320 K. Due to the semimetal nature of the VO<sub>2</sub> (B) phase at room temperature [44], we could still observe a relatively resolvable Raman shift. In the  $D_{M-B}$  thin film, the  $\omega_{V1}$  vibration mode of ~195 cm<sup>-1</sup> at 343 K shifted to ~201 cm<sup>-1</sup> at 358 K, while the  $\omega_{V-O}$  vibration mode changed from ~620 cm<sup>-1</sup> to ~647 cm<sup>-1</sup> due to the thermal-induced lattice distortion. Above 358 K, the  $\omega_{V1}$  and  $\omega_{V-O}$  modes vanished due to the formation of metallic rutile VO<sub>2</sub> during IMT (Figures 4b,b' and S4b). The metallic rutile phase did not contribute to a discriminable Raman signal, and thus, a flat Raman spectrum indicated its presence. Meanwhile, in the  $D_M$  thin film, the  $\omega_{V1}$  vibrations suddenly changed from ~195 cm<sup>-1</sup> at 343 K to ~201 cm<sup>-1</sup> at 353 K, and the  $\omega_{V-O}$  mode at 620 cm<sup>-1</sup> shifted to 638 cm<sup>-1</sup>. In Figures 4c,c' and S4c, both two modes disappeared above 353 K, which also resulted from the formation of rutile VO<sub>2</sub> during IMT. Although the  $\omega_{V1}$  and  $\omega_{V-O}$  modes in the  $D_{M-B}$  and  $D_M$  thin films were similar at room temperature, the structural evolution in the  $D_{M-B}$  thin film finished at a higher temperature (at 358 K) than that in the  $D_M$  thin film (at 353 K). We believed that the higher evolution temperature



was attributed to the increased content of  $VO_2$  (B) in the coexistent  $VO_2$  (M) and  $VO_2$  (B) thin films.

**Figure 4.** Temperature-dependent Raman modes at around (**a**) 191 and (**a**') 403 cm<sup>-1</sup> for the D<sub>B-M</sub> thin film. Temperature-dependent (**b**)  $\omega_{V1}$  and (**b**')  $\omega_{V-O}$  modes for the D<sub>M-B</sub> thin film, and temperature-dependent (**c**)  $\omega_{V1}$  and (**c**')  $\omega_{V-O}$  modes for the D<sub>M</sub> thin film.

As indicated by the XRD and Raman measurements, the coexistent VO2 (M) and  $VO_2$  (B) phases were likely to modify the microstructure and the temperature-dependent structure evolutions. Subsequently, the temperature dependent resistance of the D<sub>M</sub>, D<sub>M-B</sub> and  $D_{B-M}$  thin films is shown in Figures 5 and S5. The resistance of the  $D_{B-M}$  and  $D_{M-B}$ thin films changed and underwent a change of over 2 orders of magnitude when the temperature went from 200 K to 300 K, which was related to the IMT process of the  $VO_2$ (B) phase [27]. However, no such decrease occurred in the  $D_M$  thin film, as displayed in Figure 5b. The following drop in the resistance of the  $D_M$ ,  $D_{B-M}$  and  $D_{M-B}$  thin films at around 350 K was related to  $VO_2$  (M) (Figure 5c) [45]. For the  $D_{M-B}$  thin film, the small change in resistance from 200 K to 300 K shown in Figure 5b may have resulted from the lower  $VO_2$  (B) content and the poorer crystallinity [32]. Figure 5c further suggests the variations in resistance changed from 300 K to 400 K in the  $D_M$ ,  $D_{M-B}$  and  $D_{B-M}$  thin films [46]. Notably, the increased content of  $VO_2$  (B) would have greatly reduced the resistance variations in the as-prepared coexistent  $VO_2$  (M) and  $VO_2$  (B) thin films from 300 K to 400 K [29]. By taking the derivation curves and using a Gaussian fit, we obtained the transition temperature ( $T_{IMT}$ ) above room temperature of about 345, 357 and 360 K for the  $D_{M}$ ,  $D_{M-B}$  and  $D_{B-M}$  thin films, respectively (Figure 5d). As we obtained in the temperature-dependent Raman spectra, the increased contents of  $VO_2$  (B) led to an increase in  $T_{IMT}$  [44]. In addition, the  $T_{IMT}$  increased with the widened plane spacing from the  $D_M$ to  $D_{M-B}$  and then to  $D_{B-M}$  thin films. These results implied that coexistent polymorphs and lattice distortion accompanied and caused such changes in the VO<sub>2</sub> thin films with the coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases [45].



**Figure 5.** (a) Temperature-dependent resistance curves for the  $D_M$ ,  $D_{M-B}$  and  $D_{B-M}$  thin films during a heating process. The resistance–temperature curves in the temperature range of (b) 200–300 K and (c) 300–400 K, and (d) the derivation curves for calculating  $T_{IMT}$  for the  $D_M$ ,  $D_{M-B}$  and  $D_{B-M}$  thin films.

## 3. Conclusions

We have demonstrated the lattice variations and phase-dependent IMT behaviors in the polymorphous thin films with coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B). XRD and Raman measurements revealed that the increased (011)<sub>M</sub> plane spacing and the red-shifted V-V and V-O vibrations in VO<sub>2</sub> (M) were triggered by the presence of more VO<sub>2</sub> (B) phases. Temperature-dependent electrical and Raman analyses indicated that increased VO<sub>2</sub> (B) phases would promote the transition temperature and reduce the strength of IMT in the polymorphous VO<sub>2</sub> thin films. We believe that such a study will contribute to uncovering the coexistent polymorphous phases and the underlying physics behind IMT in VO<sub>2</sub> towards advanced electronic and optical devices.

#### 4. Experimental Section

The polymorphous VO<sub>2</sub> thin films were obtained with a combination of ALD and postannealing procedures according to the processes previously reported [31]. The temperaturedependent optical images were obtained via a optical microscope with a home-made heating stage. Raman spectra (Nanofinder 30, Tokyo Instruments, Inc., Tokyo, Japan, the spot size of laser was about 500 nm, power was 1 mW and the grating was 1800 g/mm), micro-XRD (Bruker D8 Discover, Bruker, Karlsruhe, Germany), XRD (Bruker D8, Bruker, Karlsruhe, Germany), X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+, Thermo Fischer Scientific Inc., Waltham, MA, USA) and transmission electron microscopy (TEM, JOEL JEM-2100F, JOEL Ltd., Tokyo, Japan) were used to characterize the VO<sub>2</sub> thin films. Electrical curves were recorded at variable temperatures from 77 K to 450 K on a cryogenic probe station (Lakeshore TTPX, Lake Shore Cryotronics, Inc., Woburn, MA, USA) with a semiconductor characterization system (Keithley 2636B, Tektronix, Inc., Beaverton, OR, USA).

**Supplementary Materials:** The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/nano13091514/s1, Figure S1: Optical microscopy images for the  $D_{M-B}$  (a) and  $D_{B-M}$  (b) thin films at varied temperatures, Figure S2: (a) The V 2p and O 1s XPS spectra and (b) the fitted V 2p XPS spectra for the  $D_M$ ,  $D_{M-B}$  and  $D_{B-M}$  thin films with coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases, Figure S3: (a) Raman spectra for the polymorphous VO<sub>2</sub> thin films with coexistent VO<sub>2</sub> (M) and VO<sub>2</sub> (B) phases, and details at around 640 cm<sup>-1</sup> for the  $D_{B-M}$  (b),  $D_{M-B}$  (c) and  $D_M$  (d) thin films, Figure S4: Temperature-dependent Raman spectra for the  $D_{B-M}$  (a),  $D_{M-B}$  (b) and  $D_M$  (c) thin films, Figure S5: Temperature-dependent resistance curves and their derivative curves for the  $D_{B-M}$  (a),  $D_{M-B}$  (b) and  $D_M$  (c) thin films.

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