The tetragonal-like to rutile structural phase transition in epitaxial VO₂/TiO₂ (001) thick films

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Abstract

A controllable metal–insulator transition (MIT) of VO₂ has been highly desired due to its huge potential applications in memory storage, smart windows or optical switching devices. Recently, interfacial strain engineering has been recognized as an effective approach to tuning the MIT of epitaxial VO₂ films. However, the strain-involved structural evolution during the MIT process is still not clear, which prevents comprehensively understanding and utilizing interfacial strain engineering in VO₂ films. In this work, we have systematically studied the epitaxial VO₂ thick films grown on TiO₂ (001) single crystal substrate and the structural transition at the boundary of MIT region. By using in situ temperature-dependent high-resolution x-ray diffractions, a tetragonal-like ("T-like") to 'rutile' structural phase transition is identified during the MIT process. The room-temperature crystal phase of epitaxial VO₂/TiO₂(001) thick film is clarified to be tetragonal-like, neither strained-rutile phase nor monoclinic phase. The calculated atomic structure of this T-like phase VO₂ resembles that of the M1 phase VO₂, which has been verified by their similar Raman spectra. More, the crystal lattices of the coexisted phases in the MIT region were revealed in detail. The current findings will not only show some clues on the MIT mechanism study from the structural point of view, but also favor the interface engineering assisted VO₂-based devices and applications in the future.

Introduction

Vanadium dioxide (VO₂) with its unique property of metal–insulator transition (MIT) has been widely investigated and discussed since Morin’s discovery in 1959 [1]. Because of its large changes in resistivity (10⁴ ~ 10⁵ orders in magnitudes) [2] and infrared transmittance [3] at the critical temperature (~68 °C) [4], VO₂ becomes a promising material for wide potential applications, such as smart windows [5], memory materials [6], optical filter or switching [7] and so on. Accompanying the MIT, a structural phase transition (SPT) from the monoclinic phase (M1; space group P2₁/c) to the tetragonal rutile phase (R; space group P4₂/ mnm) has often been found therein (see supplemental figure S1) [8, 9]. Besides, M2-phase [10–12], B-phase [13, 14], A-phase [15] are recognized to be the intermediate phase during the phase transition. However, the relationship between MIT and SPT is still under debate. Both experimental evidences on closed relationship and separation of MIT and SPT have been reported [16–18]. Although some mechanisms have been put forward for
the MIT transition, such as Mott transition, Peierls transition and their combination, the final conclusion has
still not been confirmed [19–24].

VO₂ epitaxial films are more attractive for investigating the relationship between MIT and SPT, due to the
single-crystal-like quality and interfacial strain controllable transition [12, 25]. Although the structural
transition in VO₂/Al₂O₃ films is similar as that in the bulk [26], recent works on VO₂ epitaxial films on a more
matching substrate TiO₂ suggest a total different structural transition. As far as we know, the first study on VO₂/
TiO₂ film was reported by Z Zhang et al in 1992, which focused on the interfacial electronic interactions [27].
Later, Sambi et al successfully grew ultrathin epitaxial VO₂ on (110) TiO₂ surface and the room temperature
phase of the VO₂/TiO₂ films were regarded as ‘pseudomorphic to substrate’ with semiconductor character
based on the data of XPD, LEED and angle resolved photoemission extended fine structure [28, 29]. In 2001,
Muraoka et al grew VO₂ thin films on the TiO₂ (001) and (110) substrates, and revealed that compressive strain
along c-axis will induce reduction in the MIT transition temperature. In their work, they utilized specular x-ray
theta-2theta scan and pole figure to verify the epitaxial relationship between the film and substrate as well as to
measure the out-of-plane lattice constants. Without carefully structural analysis, their VO₂ films were suggested
to be in a strained rutile phase [30]. Later, Jiwei Lu et al also studied the anisotropic conductivity of epitaxial VO₂
films grown on TiO₂ (011), and their work did not focus on the crystal structure of the VO₂ thin films [31]. 2012,
Elsa et al used a combination of temperature-dependent THz time-domain spectroscopy and XRD to study the
relationship between the electrical and structural transitions in the VO₂ thin films grown on the TiO₂ (100)
substrates, in which the low-temperature phase of their films was supposed to be rutile or M4 [32]. Very recently,
our colleagues Zou et al explored the strain dynamics of ultrathin VO₂ films epitaxially grown on TiO₂ (001)
substrates and revealed the continuous interfacial strain tunable TLMIT by using high-resolution XRD-RSM and
first-principles calculations [33]. In Zou’s work, the tetragonal phase was identified by TEM in the VO₂ layers
adjacent to the TiO₂ substrate, and XRD-RSM performed by Luo also suggested no monoclinic phase exists in
the films with thicknesses up to 74 nm at room temperature. Almost at the same time, Jiwei Lu group reported
their work on ultrathin VO₂ films and claimed that the highly strained epitaxial VO₂ thin films were rutile in the
insulating state as well as in the metallic state, i.e., the films underwent an electronic phase transition without the
concomitant Peierls transition [34]. The above results from Zou and Lu groups raise a hypothesis that the low-
temperature phase of ultrathin VO₂/TiO₂ (001) films shares the same rutile structure as the high-temperature
phase, and VO₂ films experience a MIT without SPT when heating. In other words, the epitaxial stress
originating from the VO₂/TiO₂ interface may suppress the SPT and separate the electronic-lattice correlation.
According to the above hypothesis and considering it’s hard to accurately determine the lattice constants and
symmetry of ultrathin films, detailed temperature-dependent structural analysis is imperative to clarify whether
a structural transition accompanies the MIT transition in VO₂/TiO₂ thick films and to ascertain the structural
nature of the room temperature phase.

In this work, we presented the structural evolution of a typical 300 nm-thick VO₂ film grown on TiO₂ (001)
examined by temperature-dependent high-resolution x-ray diffraction θ–2θ scans and reciprocal space
mapping. The results reveal the anomalous T-like to Rutile SPT in the epitaxial VO₂/TiO₂(001) thick films.

Experimental methods

Rutile TiO₂ is an attractive substrate for fabricating high-quality VO₂ films because of its thermal stability and
matching lattice parameters with tetragonal VO₂ [32]. In this work, the VO₂ epitaxial films were deposited on
(001) oriented TiO₂ single crystal substrates in size of 5 × 5 × 0.5 mm by RF-magnetron sputtering [34–36]. A
99.99%-purity vanadium metal was used as the target and the sputtering power was 60 W. The flux of Ar and O₂
were 60 sccm and 0.5 sccm, respectively. During the sputtering, the pressure was maintained at 0.43 Pa while the
substrate temperature was hold at 350 °C. Here, films with different thickness were prepared by controlling the
deposition time.

The temperature-dependent electrical transport property of the films was measured on a home-made
hotplate with the typical two-probe method. The temperature of the plate was accurately tuned by a digital
controller with a precision of ~0.01 °C.

The temperature-dependent x-ray diffraction θ–2θ scans were performed at the 4B9A beamline of Beijing
Synchrotron Radiation Facility (BSRF) (λ = 1.4253 Å) while the high-resolution XRD-RSM were performed at
14B beamline of Shanghai Synchrotron Radiation Facilities (SSRF) (λ = 1.2398 Å). During the measurements,
the temperature increase from room temperature to 100 °C, across the MIT of VO₂. The resulting RSMs are
presented in the reciprocal lattice units of TiO₂, and the diffractions of VO₂ are indexed in the rutile notation.
Here, a typical 300 nm thick VO₂ film is chosen for the detailed structural study, which will produce diffraction
spots smaller enough to distinguish monoclinic phase from tetragonal phase.
Based on the room-temperature lattice constants obtained from the XRD RSMs, the atomic structure of the T-like phase was calculated using \textit{ab initio} plane-wave pseudopotential density functional theory as implemented in the CASTEP code. During the calculation, the generalized gradient approximation was used to account for exchange and correlation in the PW91 form. Norm-conserving pseudopotentials were used for geometry optimization with a cutoff energy of 600 eV.

Temperature-dependent Raman spectra of the 300 nm thick VO$_2$ film were measured by the XploRA™ Raman spectrometer (HORIBA Scientific, Ltd). A 532 nm laser with power of 0.25 mW was used as the excitation source with a 100× microscope objective. A home-made heat stage was equipped on the sample with an accuracy of 0.3 °C.

**Results and discussions**

The temperature-dependent x-ray diffraction $\theta$–$2\theta$ scans around VO$_2$ (002) diffraction are shown in figure 1(a) and the corresponding $R$ (resistance)–$T$ (temperature) curve with a two-order magnitude jump in resistance is shown in figure 1(b), where the two figures share the same Y-axis trick labels for contrast. In figure 1(a), two obvious peaks appear and are marked as Peak 1 (low temperature) and Peak 2 (high temperature), respectively. With the increasing temperature, Peak 1 tends to shift towards lower angle and eventually vanishes around 70 °C, whereas Peak 2 emerges from 50 °C and becomes stable above 70 °C. It is interesting that both these two peaks shift away from each other in the coexistence temperature range, indicating that they belongs to two distinct phases without continuous lattice evolution between them. On the other hand, the MIT shown in figure 1(b) spreads ~20 °C in width around 60 °C and covers almost the same temperature range as the two phase coexistence, which is highlighted with yellow color. The above results clearly demonstrate that a SPT exists in the 300 nm thick VO$_2$/TiO$_2$ epitaxial film and accompanies with the electrical MIT transition, namely, the room-temperature phase is not strained rutile VO$_2$. The obvious phase separation found in the MIT range was previously reported by Basov and Yong Zhao \textit{et al} where the two crystalline phases identified in their temperature-dependent and injected-current-dependent Raman results were claimed to be monoclinic and rutile phases [37, 38].

To identify the crystallographic type of the room-temperature phase in the VO$_2$/TiO$_2$ epitaxial films, all high-resolution RSMs around [112] and [202] Bragg spots were measured and the corresponding theoretical analysis were performed. Figures 2(a) and (b) schematically show the cubic–on–cubic growth of tetragonal and monoclinic VO$_2$ on TiO$_2$ (001) surface, as well as the corresponding RSM patterns around $hhl$ or $h0l$ Bragg spots in the reciprocal space. In the case of monoclinic VO$_2$ on TiO$_2$, the $a$-axis of VO$_2$ will incline along in-plane $a$-
axis or $b$-axis of TiO$_2$ because $\beta$ is not 90°. Considering the four-fold-symmetry of TiO$_2$ (001) surface, the tilting direction of different VO$_2$ crystal domains may be along with one of the $a^+$, $a^-$, $b^+$ or $b^-$ -axis of TiO$_2$, and thus it produce four sets of reciprocal lattice presentations in the reciprocal space. As shown in figure 2(a), the resulting diffractions of monoclinic VO$_2$ around all none-specular Bragg spots will splits and the splitting interval depends on the angle $\beta$. By contrast, there’s no split in the case of tetragonal VO$_2$ on TiO$_2$ (001) surface with a similar analysis. Whether splitting occurs in RSM is critical to recognize the monoclinic phase from tetragonal phase. Theoretically, M1 phase VO$_2$ epitaxially grown on TiO$_2$ (001) will produce $\{11l\}$ diffraction patterns with a splitting bigger than 0.01 r.l.u. between the spots along the 00$L$ axis. Figure 2(c) plots the experimental measured high-resolution RSMs around $\{112\}$ and (d) $\{202\}$ Bragg spots at room temperature.

Table 1. The crystallographic data of VO$_2$ phases: M1, M2, B, A and R.

| Phase of VO$_2$ | Space group | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (°) | $Z$ | Unit volume per VO$_2$ (Å$^3$) | Reference |
|-----------------|-------------|--------|--------|--------|---------|---|-----------------------------|-----------|
| M1              | P21/c       | 5.753  | 4.526  | 5.383  | 122.61  | 4 | 29.398                     | [8]       |
| M2              | C2/m        | 9.066  | 5.797  | 4.255  | 91.88   | 8 | 27.938                     | [10]      |
| B               | C2/m        | 12.03  | 3.693  | 6.42   | 106.6   | 8 | 34.139                     | [11]      |
| A$_{h}$         | P42/nmc     | 8.440  | 8.440  | 7.680  | 16      | 16 | 34.192                    | [13]      |
| A$_{h}$         | I4/m        | 8.476  | 8.476  | 3.824  | 8       | 34.341            | [13]      |
| R               | P42/mnm     | 4.554  | 4.554  | 2.856  | 2       | 29.501                | [9]       |

Figure 2. Schematics for the lattice unit cell of (a) monoclinic, (b) tetragonal VO$_2$ epitaxial films grown on tetragonal TiO$_2$, and the corresponding schematic of RSMs. Green lines represent TiO$_2$ substrate, while the red and blue lines show the monoclinic lattice and tetragonal lattice of VO$_2$, respectively. The measured RSMs around (c) $\{112\}$ and (d) $\{202\}$ Bragg spots at room temperature.
room-temperature phase of epitaxial VO₂/TiO₂ thick films is an interface-induced T-like phase, which has not been carefully identified previously.

Based on the room-temperature lattice constants obtained from the XRD RSMs, the atomic structure of the T-like phase was calculated and the result is plotted in figure 3 as well as those of M1 and rutile crystal structures for comparison. It could be noticed that the T-like phase and the M1 phase have almost the same atomic structures although their crystal symmetries are tetragonal and monoclinic, respectively. Consequently, the T-like phase could be regarded as a distorted M1 phase. From this point of view, the nature of the rutile → T-like structural transition should resemble that of the conventional rutile → M1 phase transition, i.e. V⁴⁺−V⁴⁺ dimerized along the rutile c-axis during cooling while the V⁴⁺−V⁴⁺ linear chains transform to zigzag chains. It could be understood that the monoclinic phase can be strained to be tetragonal phase due to the interfacial stress in epitaxial growth. But, it is interesting that this sputtered VO₂/TiO₂ film does not relax even when the film...
thickness reaches 300 nm. The exact reason has not been clear yet. The T-like VO₂ phase revealed in this work seems considerable stable and is of insulating state at room temperature.

The similarity in lattice constants and atomic structures of the two phases: the T-like phase and M1 phase were further demonstrated by Raman spectra. As in figure 4, the temperature-dependent Raman spectra of the sputtered VO₂/TiO₂ (001) film present similar peak profiles and evolution as that in the M1 to rutile SPT. This phenomenon verified the similar vibration modes in these two low-temperature phases due to the similar atomic structures. In other words, it’s hard to distinguish these two phases by merely using Raman spectra.

To investigate the structural evolution during this intriguing ‘T-like’ to ‘tetragonal’ phase transition, temperature-dependent high-resolution XRD-RSMs were performed around (002) and (112), and the results are presented in figure 5 as animations. In these animations, the variation of position and intensity of the VO₂ diffractions unanimously show that this phase transition takes place from 50 °C to 70 °C. And a phase coexistence state appears therein, which is consistent with the θ–2θ scans. The temperature-dependent lattice constants of these two crystalline phases were calculated from the RSMs and plotted in figure 6.

According to the tendency of the curves, the phase transition experience three stages: (1) from room temperature to 50 °C, the VO₂ film is T-like phase with \( a_t = 4.527 \, \text{Å} \) and \( c_t = 2.876 \, \text{Å} \); (2) above 70 °C, rutile VO₂ is the only phase and the lattice is stabilized as \( a_r = 4.541 \, \text{Å} \) and \( c_r = 2.860 \, \text{Å} \), which indicates a residual strain of ~0.285% (horizontal) and ~0.14% (vertical), respectively; (3) 50 °C to 70 °C is the phase transition range, as highlighted by the yellow color, where the lattice parameters of both T-like phase and rutile phase

Figure 5. Temperature-dependent evolution of RSMs around (a) (002) and (b) (112) diffractions, see stacks.iop.org/NJP/17/113016/mmedia.
changing dramatically due to the in-plane squeezing and competing. Please note the anomalous lattice evolution at the stage of phases-coexistence, where the relative big in-plane lattice $a$, become much bigger while the relative small lattice $c$, become much smaller. The reason for this interesting phenomenon is that there is an in-plane residual compressive strain in the rutile VO$_2$ after deposition at high temperature. When part of rutile transform to the T-like phase, although there is enough in-plane space for rutile to relieve its in-plane compressive stress, rutile phase will still compress the T-like phase until all of its in-plane compression is released. The evolution of $c$ and $c_\ell$ reflects the lattice extrusion effect of rutile and T-like, which is the so-called lattice unit volume conservation. The Poisson ratios of the low-temperature T-like phase and high-temperature rutile phase were calculated to be $\sim$0.3 and $\sim$0.2, respectively, indicating the different elastic properties of these lattices.

**Conclusions**

By using temperature-dependent high-resolution x-ray diffractions, the ‘T-like’ to ‘rutile’ SPT is revealed in epitaxial VO$_2$ thick films grown on TiO$_2$ (001) single substrate, accompanying the electrical MIT. The low-temperature insulating phase of the epitaxial VO$_2$ thick films is identified to be a tetragonal-like phase, neither strained-rutile phase nor monoclinic phase, implying monoclinic-tetragonal phase transition is not a necessity for the MIT transition of VO$_2$. The atomic structure and Raman spectra of this insulating tetragonal-like VO$_2$ phase resemble those of the M1 VO$_2$ phase, suggesting this T-like phase is a distorted M1 phase. The revealed hetero-interface induced unusual structural transition demonstrates that interface engineering could play an important role in both mechanism study and performance optimization of applied materials.

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