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REPORT



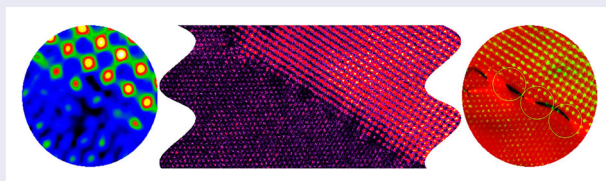
Mechanism of strain relaxation: key to control of structural and electronic transitions in VO₂ thin-films

Adele Moatti^a, Ritesh Sachan^b and Jagdish Narayan^a

^aDepartment of Materials Science and Engineering, North Carolina State University, Raleigh, NC, United States; ^bDepartment of Mechanical and Aerospace Engineering, Oklahoma State University, Stillwater, OK, United States

ABSTRACT

VO₂ is a smart transition-metal oxide, which exhibits a tetragonal-to-monoclinic phase transition at ~ 68°C. We report a case where both tetragonal and monoclinic phases exist in relaxed and strained domains, respectively, above the transition temperature. The epitaxial nucleation of these relaxed domains of VO₂ over the strained one occurs when the critical thickness criterion is met through the emergence of interfacial dislocations under domain-matching epitaxy paradigm. Below this critical thickness, the film isostructurally (across the transition temperature range) adopts a strained-monoclinic phase. Above the critical thickness, domains are structurally free to transform from tetragonal to monoclinic.



IMPACT STATEMENT

We studied formation and atomic-scale characterization of a novel heterostructure of relaxed (tetragonal/monoclinic) and unrelaxed (monoclinic) VO₂ phases. The monoclinic-to-tetragonal structural transition occurs at the critical thickness of ~ 15 nm.

ARTICLE HISTORY

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KEYWORDS

Relaxation mechanism; critical thickness; VO₂; dislocation core; strain analysis

Introduction

Vanadium dioxide is considered a multi-stimuli responsive smart material which undergoes a reversible, fast, and close to room temperature transition [1–5]. This ability allows VO₂ to be used as memory, field-effect transistor (FET) devices, infrared sensors, and smart windows [6–12]. The VO₂-based device's performance depends on size, and some other factors like defect content, dopant, and crystallinity of this structure which are affected by thickness [2,13–17]. As the electronics industry is aiming to miniaturize the length-scales of films and electronic devices, it becomes inevitable to understand the behavior of materials in that scale. One of the main characteristics that are defined for thin-film growth is the critical thickness above which misfit dislocations nucleate and glide to the interface for thin-film relaxation [18,19]. However, in the case of transition-metal

oxides, the important question arises about the determination of the structure and strain-state of thin-films across the critical thickness. It is reported previously with *in-situ* studies that below the critical thickness, the structural transition is pinned [20,21]. The question remains to answer whether it is possible to derive structural phase transition across the critical thickness.

To shed light on these questions, we deposited VO₂ thin-films at the critical thickness to capture the initiation of the strain relaxation as there are subnanometer thickness fluctuations which assist in the coexistence of phases below and above the critical thickness. We use the high-angle annular dark-field (HAADF) images to investigate the nucleation and propagation of misfit dislocations to the interface between different structural phases below and above the critical thickness. The interface (grain boundary) characteristics are described at

CONTACT Adele Moatti ✉ amoatti@ncsu.edu Biomedical Partnership Center - CVM, 1001 William Moore Dr. Raleigh, NC 27606

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high and low temperatures. The favorable glide planes are also defined based on slip systems and surface energies. In the vicinity of critical thickness, the presence of hybrid VO₂ structures provides two different metal-to-insulator transitions behavior with different transition temperatures that can be utilized for hybrid applications and thermal regulation [21,22]. The insulator to metal transition temperature in the strained and relaxed VO₂ films was reported to have about 10 degrees difference [21]. Furthermore, we can study both Mott and Peierls physics simultaneously in the same system [21].

Results and discussion

The vanadium dioxide thin-films are grown at different thicknesses by pulsed laser deposition method on the *c*-sapphire substrate using NiO as a buffer layer. The NiO is used as the buffer layer because the VO₂ film on top can be fully relaxed above the critical thickness through domain matching epitaxy (DME) paradigm with near bulk behavior. As the VO₂ reaches the critical thickness, the misfit dislocations nucleate at the surface and glide all the way down to the interface. The critical thickness (h_c) at which it becomes energetically favorable for a thin-film to contain dislocations is h_c [23]:

$$h_c = \frac{b(1 - \nu \cos^2 \theta) \sin \theta \cos \theta}{4\pi(1 + \nu)\epsilon_0} \ln(\alpha h_c / b) \quad (1)$$

where b is the magnitude of Burgers vector of the dislocation, ν is the Poisson's ratio, θ is the angle between Burgers vector and dislocation line, ϕ is the angle between the normal of the dislocation plane and film plane, and α is the dislocation core radius factor which varies with strain ϵ_0 . The slip systems in the VO₂ monoclinic structure are $\frac{1}{2} [0\bar{1}1](011)$ and $\frac{1}{2} [10\bar{1}](101)$. Thus, we will have h_c as:

$$h_c = \frac{0.048b}{\epsilon_0} \ln \left(\alpha \frac{h_c}{b} \right) \quad (2)$$

Accordingly, the magnitude of Burgers vector is calculated to be 1.749 Å and 1.553 Å, respectively for above-mentioned slip systems. Based on this information, the h_c calculated to be ~ 15 nm. It is important to note that, tensile strain at the interface moderately increases the kinetic barrier for dislocation nucleation. Even though thermodynamically the h_c is calculated at 15 nm, kinetically dislocations do not form up to a bit higher value due to enhanced dislocation nucleation barrier enforced by the tensile strain [18,24].

To capture the event of strain relaxation, we create three cases: (i) above the h_c where the VO₂ film is fully relaxed, (ii) below the h_c where film is uniformly strained due to the misfit strain, and (iii) in the vicinity of the

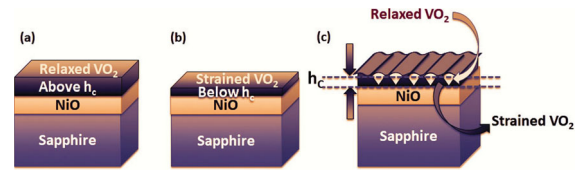


Figure 1. (a) The schematic illustration of VO₂/NiO/*c*-sapphire heterostructures where VO₂ is grown above the critical thickness (h_c) of ~ 15 nm. (b) The schematic illustration of VO₂/NiO/*c*-sapphire heterostructures where VO₂ is grown below the critical thickness. (c) The schematic illustration of VO₂/NiO/*c*-sapphire heterostructures where VO₂ is grown in the vicinity of the critical thickness. The red area represents a relaxed area where the film is reached h_c value and dislocations glide using the slip plane.

h_c where any thickness variation causes local relaxation (within a sphere with the critical thickness radius) using slip systems. The schematic in Figure 1 illustrates these three cases which are subsequently analyzed using atomic resolution HAADF imaging. Figure 2 shows the HAADF micrographs corresponding to the real case of above-mentioned schematic VO₂/NiO/*c*-sapphire heterostructures. Thin-film heterostructures with completely relaxed NiO buffer layers have been synthesized to allow a complete control over strains in the VO₂ films. Thus, the NiO layer thickness can vary anywhere in the regime of above the critical thickness. Figure 2(a) and (b) illustrate the heterostructures where VO₂ is grown above and below the h_c , respectively. Above the h_c , the VO₂ film is relaxed through DME paradigm [25]. The periodic dislocations are marked in the fast Fourier transform (FFT) image at the interface of VO₂/Ni₂VO₄ (~ 5 nm Ni₂VO₄ layer forms at the interface of VO₂/NiO) in Figure 2(a). However, below the h_c , there is no dislocation formation (see the FFT image at the interface of VO₂/Ni₂VO₄ in Figure 2(b)). Figure 2(c) and (d) illustrate the atomic resolution HAADF images of VO₂ above and below the h_c , respectively. It is found that the structure below the h_c belongs to the strain-stabilized monoclinic phase [21]. This structure was shown to have a smaller difference between the V-V dimmers bond length [21]. See Supplementary Results for more information on epitaxial relationships. Figure 2(e) represents the sample that is grown in the vicinity of the h_c and captures an image of a grain that is reached above the h_c limit (due to the thickness variation) and laid within the matrix below the h_c . This behavior was observed in multiple grains above the critical thickness and it represents the mechanism of relaxation for the VO₂ thin-film as it reaches the h_c limit. The h_c is the radius of a sphere as marked in Figure 2(f) where energetically it is favorable for dislocations to nucleate at the free surface and glide toward the interface. These dislocations are frozen at the interface between unrelaxed

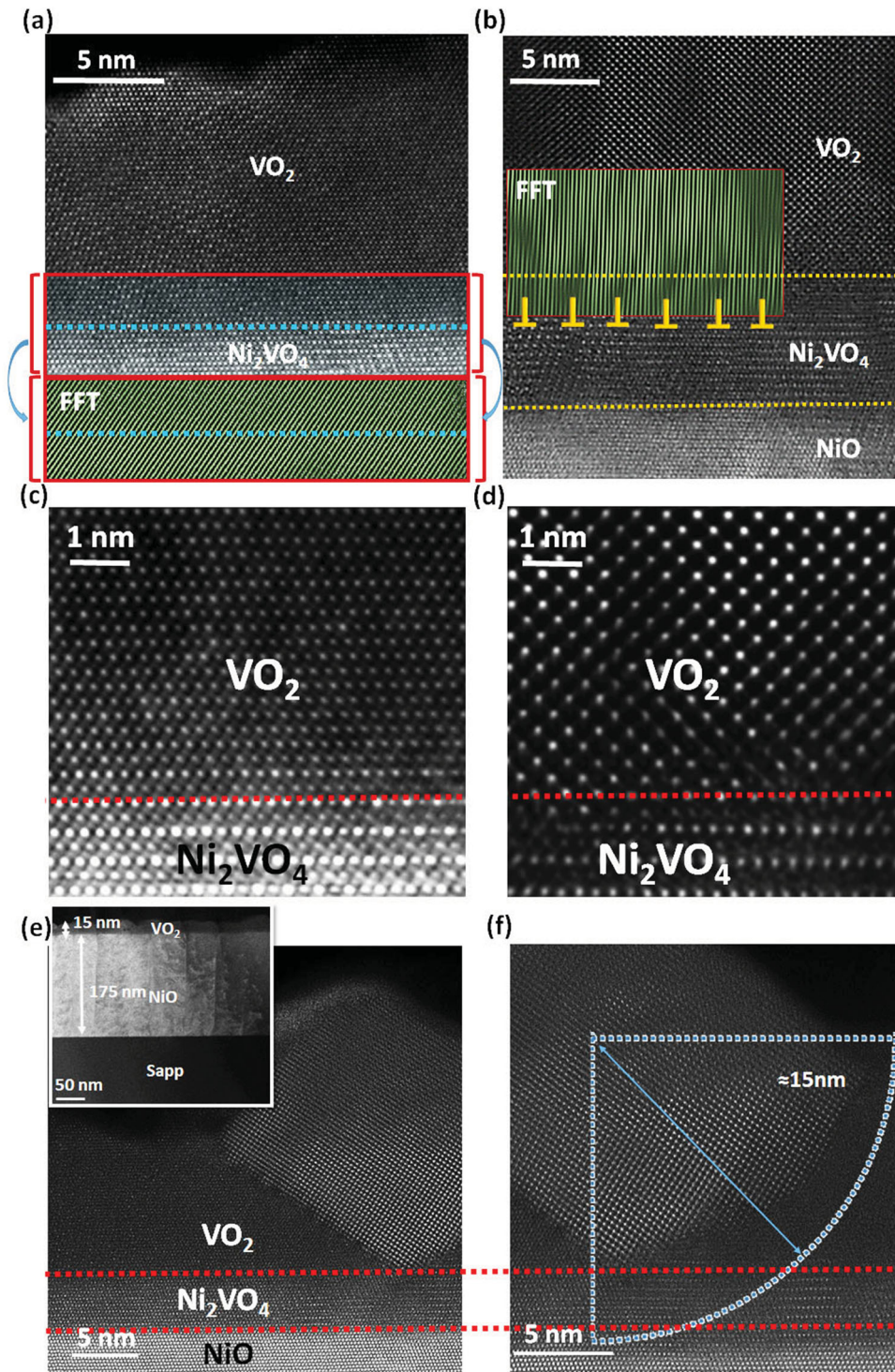


Figure 2. (a) The HAADF image of VO₂/NiO/c-sapphire heterostructures where VO₂ has grown above the critical thickness of ~ 15 nm. (b) The HAADF image of VO₂/NiO/c-sapphire heterostructures where VO₂ is grown below the critical thickness. (c, d) The atomic resolution HAADF image of VO₂ structure belongs to (a) and (b), respectively. (e) The HAADF image taken by STEM showing both strained and relaxed state of VO₂ below and above the critical thickness along $[1\bar{2}1]$ NiO zone axis. The inset figure represents the low-mag image of the VO₂/NiO/c-sapphire heterostructures and their thicknesses. (f) The HAADF image of the relaxed monoclinic VO₂ grain which is reached above the critical thickness.

(below the critical thickness) matrix and the relaxed grain since the film does not uniformly reach the h_c limit.

Figure 3(a) shows the interface between the relaxed-monoclinic and the strained-monoclinic phase below it. In the inset of Figure 3(a), the indexed FFT patterns for

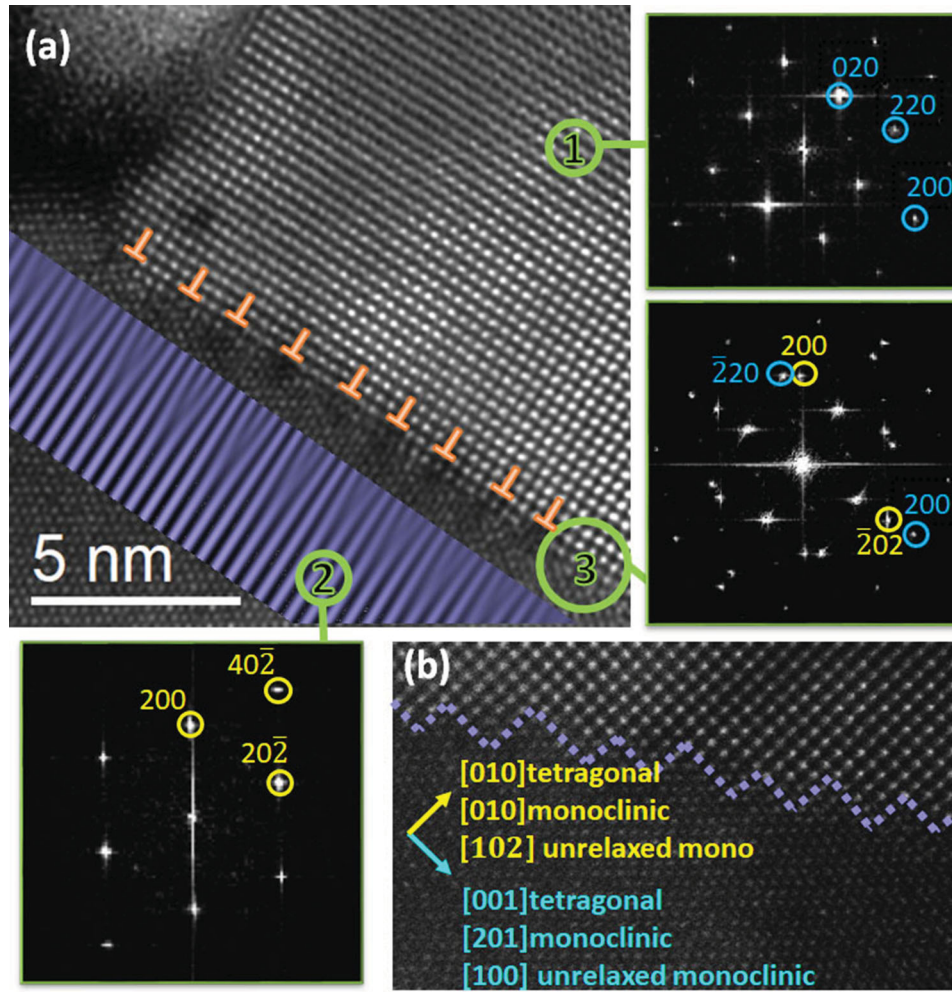


Figure 3. (a) The HAADF image taken by STEM showing the interface between the strained and relaxed state of VO_2 . The periodic appearance of misfit dislocation at the interface is captured during the transition of strained to a relaxed state. The FFT pattern belongs to the relaxed monoclinic, strained monoclinic, and at the interface of both states is indicated by 1, 2, and 3, respectively. (b) The formation of steps along low energy directions at the interface of a strained and relaxed state of VO_2 to minimize the total energy of the system.

spots marked as 1, 2, and 3 are shown. According to these patterns, the epitaxial relationship at room-temperature established to be VO_2 -strained monoclinic($\bar{1}01$)|| VO_2 -relaxed monoclinic- $M_1(100)$ || VO_2 -tetragonal(001). Using domain matching epitaxy [23,26], at the growth temperature, the misfit strain between the tetragonal(001) and unrelaxed monoclinic($\bar{1}01$) is calculated to be $\approx 18.58\%$ ($d_{(002)\text{tetragonal}} = 5.703\text{\AA}$, $d_{(1\bar{0}1)\text{monoclinic}} = 4.809\text{\AA}$). This results in close to 4/5 integral multiple of lattice planes at the interface. The 4/5 plane matching and formation of dislocations are shown in HAADF image across the interface in Figure 3(a). During the cooling down from the growth to room temperature, tetragonal to monoclinic transition occurs in the relaxed grain. However, no more dislocation is added to the interface since the temperature is low and kinetically it is impossible for new dislocations to nucleate based on the misfit strain at room-temperature. As it was explained earlier, the slip systems in the VO_2 monoclinic structure are $\frac{1}{2}$

$[0\bar{1}1](011)$ and $\frac{1}{2} [10\bar{1}](101)$. The slip systems in tetragonal are $\frac{1}{2}\{100\} < 001\}$ and $\frac{1}{2}\{101\} < 10\bar{1}\}$ for primary and secondary slip systems, respectively. Interestingly, the interface glides are in the slip plane and follow the slip directions, along $[10\bar{1}]$ of monoclinic or $[001]$ of the tetragonal phase.

In addition, we also observed formation of steps at the bottom side of the relaxed grain, along low energy directions which lie in low energy planes to minimize the energy of the systems [18]. In the monoclinic structure, these steps are formed along $[010]$ and $[201]$ directions as it is shown in the HAADF image in Figure 3(b). These steps are usually formed at the interface of two crystals due to dislocation formation along the grain boundary in the perpendicular direction and termed as disconnections. This suggests that in the tetragonal structure, the steps were formed along $[010]$ and $[001]$ directions at high temperature. These directions belong to the low energy surfaces of $\{100\}$ and $\{110\}$ with surface energies

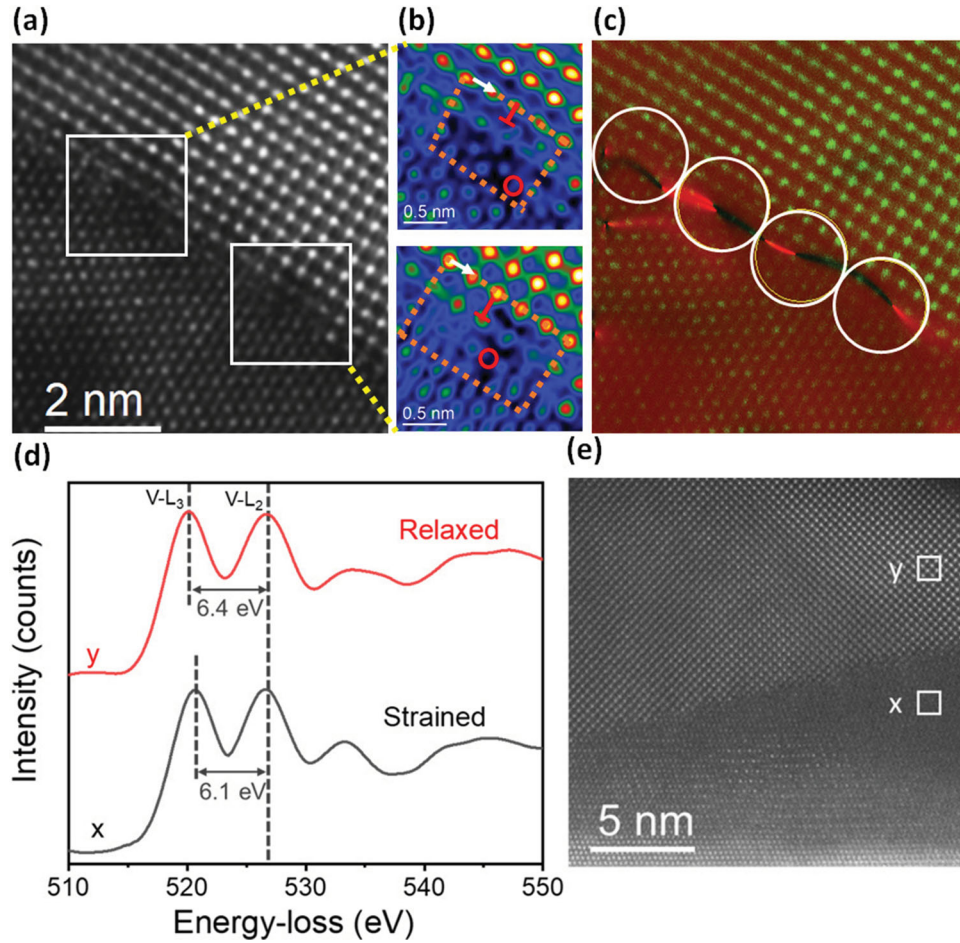


Figure 4. (a) The indication of two dislocation cores in the HAADF image of the interface. (b) the atomic rearrangements around the dislocations' core (the image processing technique is used). The dislocation loop and Burgers vector is illustrated for each dislocation. There is one atomic column missing, marked by a circle, in the vicinity of each dislocation core, marked by T, to compensate for the generated strain. (c) Strain analysis along the relaxed and strained interface represents the strain centers. The red color is a positive strain going to black color for negative strains. The presence of periodic compressive and tensile strains around the dislocation cores also is an indication of atomic rearrangement to minimize the local strain. (d) Selected electron energy loss spectrum collected from two different states marked as x and y belong to strained and relaxed VO₂, respectively, (e) HAADF image showing two different orientations of VO₂ belong to strained and relaxed states marked by squares x and y, respectively, on the NiO buffer layer along [1 $\bar{2}$ 1].

of 0.29 and 0.42 J/m², respectively, in the tetragonal phase of VO₂.

We further investigated the interface (Figure 4(a)) between relaxed and unrelaxed monoclinic phase to study the interfacial atomic rearrangement. Figure 4(b) shows the magnified images of two such dislocation cores (from Figure 4(a)) along the interface. Around the dislocation core, there is an atomic rearrangement to accommodate the strain. Interestingly, with each dislocation in relaxed-monoclinic phase, there is an atomic column missing in the unrelaxed-monoclinic phase. This can locally decrease the energy of the system. These pair of dislocations and missing atomic column are shown in Figure 4(b). Figure 4(c) represents the strain distribution along the interface, which has both the compressive and tensile strain components. This analysis explains the wave-like behavior of strain where the negative and

positive source of strain cancel out each other and lower the energy of the system.

Figure 4(d) shows the electron energy-loss spectra (EELS) from the strained (site x) and relaxed (site y) regions of the VO₂ thin-film, indicated in the HAADF image in Figure 4(e). The EEL spectra of the two regions consist of the V-L₃₂ and O-K core-loss edges corresponding to transitions between 2p^{3/2} (V-L₃) and 2p^{1/2} (V-L₂) to 3d and 1s^{1/2} (O-K) to 2p, respectively. While analyzing the EEL spectra, it is observed that the energy-gap between L₃ and L₂ peaks of V core-loss edge reduces to 6.1 eV in the strained region from 6.4 eV in the relaxed region of the film. This suggests the narrowing of the crystal field splitting in the strained phase attributed to the presence of tensile strain along the a-axis of the monoclinic VO₂ structure which causes different metal-to-insulator transition temperatures [21,25]. In addition,

the L_{32} ratios in the two spectra are estimated to be the same which signifies no reduction in vanadium oxidation state in the two regions.

At room temperature, as it is shown in Supplementary Figure S1, the grain boundary between unrelaxed and relaxed grains in the monoclinic phase can be described as $30^\circ [\bar{1}0\bar{1}], (\bar{1}01)/(010)$ according to Coincidence Site Lattice: CSL method (see Supplementary) [27,28]. The grain boundary is created due to a twist of 90° between the relaxed and strained crystal of VO_2 while maintaining the same out-of-plane direction. At the deposition temperature, the relaxed grain is in the tetragonal phase which is a typical state for the relaxed high-temperature VO_2 . It is shown previously in our work that the strained monoclinic VO_2 can maintain its structure at high temperature while insulator to metal transition occurs [21]. Using DFT + U calculations and experimental corroboration, it is shown that the electronic structure in the strained monoclinic VO_2 film (10 nm thick) is modified as compared to the relaxed VO_2 film, leading to a considerable bandgap narrowing. This occurs by decreasing the difference between long and short V-V bond length (Δ_{V-V}) in the strained monoclinic VO_2 thin-films. This modified structure with smaller bandgap allows the transition to follow Mott physics without the structural transition, while the relaxed VO_2 film follows Peierls assisted Mott physics. Further analysis of grain boundary is presented in Supplementary Results.

Conclusions

We show an atomically sharp structural transition from a strained monoclinic to a relaxed tetragonal state of VO_2 thin-films at a certain h_c (~ 15 nm) during the epitaxial growth on $\text{NiO}/c\text{-Al}_2\text{O}_3$ heterostructures. Below this h_c , the film pseudomorphically adopts a strained monoclinic phase even at the growth temperature. As it reaches to the h_c limit, the strained monoclinic phase transitions into a completely relaxed tetragonal phase with the formation of interfacial dislocations which subsequently glide into the film/substrate (VO_2/NiO) interface following DME paradigm through active slip systems. Using atomic-resolution electron microscopy analysis and strain analysis, we find a periodic formation of misfit dislocations, the strain centers, and the atomic rearrangement near the dislocations core. Interestingly at the vicinity of dislocation cores, for each dislocation, there is one atomic column missing to locally minimize the energy, which produces periodically positive and negative strain centers. This study provides us with the tool to manipulate the structure of VO_2 and exploit the strain center at the dislocation core through external and internal stimuli leading to novel predictable properties.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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ORCID

Adele Moatti  <http://orcid.org/0000-0002-6946-5370>

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