Nanoscale self-templating for oxide epitaxy with large symmetry mismatch

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Direct observations using scanning transmission electron microscopy unveil an intriguing interfacial bi-layer that enables epitaxial growth of a strain-free, monoclinic, bronze-phase VO$_2$(B) thin film on a perovskite SrTiO$_3$ (STO) substrate. We observe an ultrathin (2–3 unit cells) interlayer best described as highly strained VO$_2$(B) nanodomains combined with an extra (Ti,V)O$_2$ layer on the TiO$_2$ terminated STO (001) surface. By forming a fully coherent interface with the STO substrate and a semi-coherent interface with the strain-free epitaxial VO$_2$(B) film above, the interfacial bi-layer enables the epitaxial connection of the two materials despite their large symmetry and lattice mismatch.

Epitaxial synthesis of complex oxides has stimulated considerable interest in creating novel functionalities and physical properties, where various means are used to control the close interactions among the order parameters, including lattice, spin, charge, and orbital. Heterostructures of oxide materials have also played an important role in discovering novel phenomena as they can produce well-defined interfaces to couple electronic and magnetic ground states, structure, lattice, crystallographic symmetry, etc. Most studies on the epitaxial growth of complex oxides have focused on isostructural materials, e.g. perovskites on perovskites. While many binary oxides, such as TiO$_2$ and VO$_2$, also offer intriguing physical properties, only a few substrates are available with similar structures (lattice parameters and crystal symmetry) for epitaxy thereon. Thus, gaining fundamental insight into the epitaxial growth of binary oxide thin films on lattice and symmetry mismatched substrates is of vital importance for exploring their unprecedented potential.

Recently, high quality VO$_2$ polymorphs were successfully stabilized as epitaxial thin films using pulsed laser epitaxy (PLE) on perovskite substrates, such as SrTiO$_3$. Among VO$_2$ polymorphs, bronze-phase VO$_2$(B) has a monoclinic structure (with C2/m symmetry) whose lattice constants are $a = 12.03$, $b = 3.69$, $c = 6.42$ Å, and $\beta = 106.6^\circ$, whereas SrTiO$_3$ (with Pm3m symmetry) has a cubic structure with the lattice constant of 3.905 Å. Note that while many previous studies focused on rhombohedral (R) and monoclinic (M1) phase VO$_2$, recent studies in developing advanced energy storage found VO$_2$(B) to be a promising cathode material for Li ion batteries.

In oxide epitaxy, the important role of octahedral connectivity has been well established in perovskite-based oxide heterostructures. Previous studies for heterostructures with a large symmetry mismatch observed the formation of a thin interlayer between the film and substrate induced by either phase transition or phase separation. Moreover, incorporation of such an interfacial buffer layer seems to be critical, enabling the epitaxial growth between large-symmetry-mismatch materials. Interestingly, a previous study based on a STEM observation reported the formation of an imperfect structure at the VO$_2$(B)/SrTiO$_3$ interface. However, details about the interface structure have not been explored.

In this work, we report how two very dissimilar materials can form an epitaxial heterostructure by aberration-corrected scanning transmission electron microscopy (STEM) imaging and electron energy-loss spectroscopy (EELS). We have found an interfacial bi-layer at the VO$_2$(B)/STO interface that enables epitaxial growth of a structurally complex, low symmetry film on a high symmetry substrate. It is rather surprising that VO$_2$(B) films with corner- and edge-sharing oxygen octahedra (see Fig. 1a and b) can be epitaxially grown on STO with corner-sharing octahedra, despite the different oxygen networks and the large biaxial lattice mismatch.

Results and Discussion

High quality VO$_2$(B) epitaxial films were grown on (001)-oriented STO by PLE under well-optimized growth conditions. The details on the epitaxial growth and crystal quality as well as associated physical properties can
be found elsewhere. Figure 1 shows atomic structure projections and corresponding cross-sectional high-angle annular dark-field (HAADF) images taken along the [100] and [010] directions of VO₂(B). In the Z-contrast HAADF images, the cation columns containing Ti (Z = 22), V (Z = 23), and Sr (Z = 38) are seen with intensities strongly dependent on their atomic number, while columns containing only light O (Z = 8) atoms are hardly visible. The image shown in Figure 1d provides the reason why VO₂(B) is of particular interest for energy storage as the atomic structure seen from the [010] direction features an open framework that offers a good ionic diffusion pathway. The structural projection along [010] also reveals the clear symmetry mismatch between the film and substrate. Thus, we chose this orientation for the majority of the STEM investigations.

Figures 2a and b show cross-sectional HAADF images of an epitaxial VO₂(B) film grown on a STO substrate. The images were taken along the [100] direction. As shown in Figures 2a and b, the film is found to contain at least two domains aligned parallel to the [100] and [010] directions, i.e. orthogonally positioned with respect to the [100] direction of the STO substrate. In fact, the film contains two additional domains that are rotated 180 degrees about the surface normal from those imaged in Fig. 2. A thin (typically ~2 nm thick) interfacial layer (IL) can be seen between the VO₂(B) film and the STO substrate. Based on fast-Fourier transformation (FFT) analysis, an array of misfit dislocations has formed between the IL and the structurally relaxed VO₂(B) film (as indicated in Fig. 2a and b, and in the corresponding FFT images in Figure S1 in Supporting Information). The interface between the STO substrate and the IL appears to be fully coherent. As shown in Figure 2a and b, the average spacing between dislocations observed along the [100] direction is 3.6 ± 0.9 nm, while it is 7.9 ± 1.1 nm when seen along the [010] direction. These spacings are in good agreement with calculated values of ~3.5 nm and ~7.2 nm obtained using the lattice mismatch of +5.5% for the [100] VO₂(B) || [100]STO
projection and −2.7% for the orthogonal [010]VO₂(B)||[100]STO projection. This result reveals unambiguously
that the large bi-axial lattice mismatch between the film and substrate is accommodated by the creation of dislo-
cations at the VO₂(B)/TL interface, i.e. strain-free VO₂(B) epitaxial films are obtained.

Figure 2c shows a low-angle annular dark-field (LAADF) image taken from the sample seen along the
[010]VO₂(B)/[100]STO direction. The LAADF image highlights the interlayer, which is substantially brighter than
the film or the substrate. This brighter contrast in a LAADF image indicates that the IL has a higher level of struc-
tural disorder, which leads to the electron dechannelling of the incident beam. Based on a geometric phase
analysis (GPA), it is also seen that the VO₂ in the IL undergoes a significant lattice expansion along the film sur-
face normal as compared to the VO₂(B) film (see Figure S2 in Supporting Information). This result is consistent
with the rather large in-plane compression (−5.5%) of the VO₂(B) film in the [100]VO₂(B)/[100]STO projection that
will cause the observed out-of-plane expansion.

Figure 3a shows a HAADF image of the IL taken along the [010]VO₂(B) direction. While there is a region
of the IL (Fig. 3b) that clearly duplicates the projected structure of the relaxed VO₂(B) film above it (except
that it is rotated 180 degrees about the surface normal), most of this layer (and its FFT, Fig. 3d,e) looks to be a superposition of [100], [−100], [010], and [0−10] projections of epitaxially strained VO₂(B). The other
important feature of the IL is the extra atomic layer between the STO and VO₂(B) indicated with a black
arrow in Fig. 3b and c. The atomic layer shows a periodic, but different arrangement of B-site atoms than
that of the TiO₂-terminated STO surface. The HAADF images show the out-of-plane lattice spacing between
the topmost TiO₂ layer of STO and the extra (Ti,V)-O layer to be 2.4 ± 0.1 Å, which is significantly larger
than the 1.9 Å (001) plane spacing in STO. The intensity variations indicate, in this [100]STO projection, the extra layer contains additional (Ti,V) columns with roughly 1/2 the B-site density of its neighboring
atom columns.

Spatially resolved STEM-EELS data from the interfacial region is presented in Fig. 4. Figure 4a and b respec-
tively show element maps using the Ti L₂,₃ and V L₂,₃ signals taken from the same interfacial region shown in
Fig. 4c. The V L₂,₃ signal in Fig. 4a shows a chemically abrupt interface between the film and STO substrate.
On the other hand, the Ti-L\textsubscript{2,3} signal is seen to extend into the IL. Figure 4d shows background-subtracted Ti-L\textsubscript{2,3}, V-L\textsubscript{2,3}, and O-K EELS profiles obtained layer-by-layer across the IL. Standard spectra obtained from single-crystalline VO\textsubscript{2}(B) (V\textsuperscript{4+}) and V\textsubscript{2}O\textsubscript{3} (V\textsuperscript{3+}) thin films are also included for comparison. The peak position of V-L\textsubscript{2,3} edges are seen to remain fixed indicating little to no change in the valence state of V in the IL and the VO\textsubscript{2}(B) film.

The Ti-L\textsubscript{2,3} EELS fine structure obtained from the extra (Ti,V)-O layer on the STO substrate surface shows broadened L\textsubscript{3} and L\textsubscript{2} edges, as well as a shift of the e\textsubscript{g} peaks toward lower energy-loss (see Fig. 4d). The observed electronic state and atomic structure of this extra layer are in good agreement with previous theoretical simulations\textsuperscript{42} and STEM observations\textsuperscript{43} of a c (4 × 2) reconstructed STO (001) surface composed of a double-layer TiO\textsubscript{2}. The topmost layer of this reconstructed surface was predicted to contain clustered quartets of edge-sharing square-pyramidal TiO\textsubscript{5}\textsuperscript{42,43}. The extra (Ti,V)-O layer on TiO\textsubscript{2}-terminated STO can introduce edge-sharing oxygen containing units, which are more consistent with the VO\textsubscript{2}(B) structure. To our knowledge, the formation of such an interface bi-layer can not be explained by any existing growth model that involves either phase transition\textsuperscript{25-30} or phase separation\textsuperscript{31-33} at film/substrate interfaces to accommodate inter-phase structural discontinuities.

The observed results reveal unambiguously, at the initial growth stage, the formation of an interfacial layer composed of VO\textsubscript{2}(B) nanodomains that enable the epitaxy of VO\textsubscript{2}(B) on STO. This epitaxy with a large symmetry mismatch involves a structural reconstruction process at the substrate surface to facilitate the symmetry transition between the two distinct component structures. The VO\textsubscript{2}(B) nanodomains form a fully coherent interface with the STO substrate and are subject to considerable lattice strain. Once the strain energy in the VO\textsubscript{2}(B) nanodomains exceeds a critical level, misfit dislocations are introduced, followed by the growth of fully relaxed VO\textsubscript{2}(B). The much larger domain size in the relatively strain-free film is an expected result of...
increased adatom mobility on the relaxed surface. Formation of the interfacial VO$_2$(B) nanodomains indicates a nanoscale self-templating process that enables the epitaxy of strain-free VO$_2$(B) films on STO substrates. Therefore, the results not only enable novel insights into atomic mechanism of complex heterostructure interface at an atomic scale, but also shed light on the epitaxial design of two materials with large symmetry and lattice mismatch.

**Methods**

**Epitaxial synthesis.** VO$_2$(B) epitaxial films were deposited on (001) SrTiO$_3$ substrates by pulsed laser epitaxy. A sintered ceramic VO$_2$ target was ablated with a KrF excimer laser ($\lambda = 248$ nm) at a repetition rate of 5 Hz and laser fluence of 1 J cm$^{-2}$. The optimized substrate temperature and oxygen pressure to grow high quality thin films were 500°C and 20 mTorr, respectively, and the samples were in-situ post-annealed in 1 atm of O$_2$ for 1 hour at the growth temperature to ensure the oxygen stoichiometry. Detailed information on the synthesis of single-crystalline VO$_2$(B) (V$^{4+}$) and VO$_x$ (V$^{3+}$) thin films utilized for EELS analysis can be found elsewhere.

**Scanning Transmission Electron Microscopy (STEM).** Cross-sectional specimens oriented along the [100] STO direction for STEM analysis were prepared using ion milling after mechanical thinning and precision polishing (using water-free abrasive). High-angle annular dark-field (HAADF) and low-angle annular dark-field (LAADF) imaging and electron-energy loss spectroscopy (EELS) analysis were carried out in Nion UltraSTEM200 operated at 200 keV. The microscope is equipped with a cold field-emission gun and a corrector of third- and fifth-order aberrations for sub-angstrom resolution. Inner/outer detector angles of 78/240 mrad were used for HAADF and LAADF imaging, respectively. The convergence semi-angle for the inner and outer detector was 30 mrad at 200 keV. UltraSTEM200 operated at 200 keV. The microscope is equipped with a cold field-emission gun and a corrector of third- and fifth-order aberrations for sub-angstrom resolution. Inner/outer detector angles of 78/240 mrad were used for HAADF and LAADF imaging, respectively. The convergence semi-angle for the electron probe was set to 30 mrad.

**References**

1. Hwang, H. Y. et al. Emergent phenomena atoxide interfaces. *Nature materials* 11, 103–113 (2012).
2. Zubko, P., Gariglio, S., Gabay, M., Ghosez, P. & Trisccone, J.-M. Interface physics in complex oxide heterostructures. *Annu. Rev. Condens. Matter Phys.* 2, 141–163 (2011).
3. Jeon, H. et al. Reversible redox reactions in an epitaxially stabilized SrCoO$_x$ oxygen sponge. *Nature materials* 12, 1057–1063 (2013).
4. Gora, P., Wysolmerski, J., Samoliewski, S., Graboy, L. & Kaul, A. Epitaxial stabilization of oxides in thin films. *Chemistry of materials* 14, 4026–4043 (2002).
5. Moor, F. Oxides which show a metal-to-insulator transition at the Neel temperature. *Physical Review Letters* 3, 34 (1959).
6. Oregan, B. & Grifiths, M. A. Low-cost, high-efficiency solar cell based on dye-sensitized. *nature* 353, 737–740 (1991).
7. Arico, A. S., Bruce, P., Scrosati, B., Tarascon, J.-M. & Van Schalkwijk, W. Nanostructured materials for advanced energy conversion and storage devices. *Nature materials* 4, 366–377 (2005).
8. Khan, S. U., Al-Shahry, M. & Ingler, W. B. Efficient photochemical water splitting by a chemically modified n-TiO$_2$. *science* 297, 2243–2245 (2002).
9. Yuan, Z., Ko, L. & Ramanathan, S. Oxide electronics utilizing ultrafast metal-insulator transitions. *Annual Review of Materials Research* 41, 337–367 (2011).
10. Park, J. H. et al. Measurement of a solid-state triple point at the metal-insulator transition in VO$_2$. *nature* 500, 431–434 (2013).
11. Morrison, V. R. et al. A photoduced metal-like phase of monoclinic VO$_2$ revealed by ultrafast electron diffraction. *science* 346, 445–448 (2014).
12. Jeong, J. et al. Suppression of metal-insulator transition in VO$_2$ by electric field–induced oxygen vacancy formation. *science* 339, 1402–1405 (2013).
13. Luttrell, T. et al. Why is anatase a better photocatalyst than rutile?-Model studies on epitaxial TiO$_2$ films. *Scientific reports* 4 (2014).
14. Lee, S., Meyer, T. L., Park, S., Egami, T. & Lee, H. N. Growth control of the oxidation state in vanadium oxide thin films. *Appl. Physics Letters* 105, 223515 (2014).
15. Chen, A. et al. Textured metastable VO$_2$(B) thin films on SrTiO$_3$ substrates with significantly enhanced conductivity. *Applied Physics Letters* 104, 071909 (2014).
16. Srivastava, A. et al. Selective growth of single phase VO$_2$(A, B, and M) polymorph thin films. *APL materials* 3, 026101 (2015).
17. Lee, S., Ivanov, I. N., Keum, J. K. & Lee, H. N. Epitaxial stabilization and phase instability of VO$_2$ polymorphs. *Scientific reports* 6 (2016).
18. Pokrovskii, B. & Khachaturyan, A. The concentration wave approach to the pairwise interaction model for predicting the crystal structures of ceramics. *I. Journal of Solid State Chemistry* 61, 137–153 (1986).
19. Li, W., Dahn, J. R. & Wainwright, D. S. Rechargeable lithium batteries with aqueous electrolytes. *Science-AAAS-Weekly Paper Edition—including Guide to Scientific Information* 264, 1115–1117 (1994).
20. Mai, L. et al. Nanoscrolled Biferroic Nanostructural VO$_2$(B) Cathodes for High-Rate and Long-Life Lithium Storage. *Advanced Materials* 25, 2969–2973 (2013).
21. Niu, C. et al. VO$_2$ nanowires assembled into hollow microspheres for high-rate and long-life lithium batteries. *Nano letters* 14, 2873–2878 (2014).
22. Rundinelli, J. M., May, S. J. & Freeland, J. W. Control of octahedral connectivity in perovskite oxide heterostructures: An emerging route to multifunctional materials discovery. *MRS bulletin* 37, 261–270 (2012).
23. Meyer, T. L. et al. Symmetry-Driven Atomic Rearrangement at a Brownmillerite–Perovskite Interface. *Advanced Electronic Materials* 2 (2016).
24. Kim, T. et al. Polar metals by geometric design. *Nature* 533, 68–72 (2016).
25. Lazarides, N., Paltoglou, V., Maniadis, P., Tzirosin, G. & Panagopoulos, C. Strain-induced interface reconstruction in epitaxial heterostructures. *Physical Review B* 84, 245428 (2011).
26. Zhou, H., Chisholm, M. F., Yang, T.-H., Pennycook, S. J. & Narayan, J. Role of interfacial transition layers in VO$_2$/Al$_2$O$_3$ heterostructures. *Journal of Applied Physics* 110, 073515 (2011).
27. Bayati, M. et al. Domain epitaxy in TiO$_{2x}$, Al$_2$O$_3$ thin film heterostructures with TiO$_2$ transient layer. *Applied Physics Letters* 100, 251606 (2012).
28. Chen, A. et al. A New Class of Room-Temperature Multiferroic Thin Films with Bismuth‐Based Supercell Structure. *Advanced Materials* 25, 1028–1032 (2013).
29. Zhu, Y. et al. Research Updates: Epitaxial strain relaxation and associated interfacial reconfigurations: The driving force for creating new structures with integrated functionality. *APL materials* 1, 050702 (2013).
30. Pennycook, S. et al. Misfit accommodation in oxide thin film heterostructures. *Acta Materialia* 61, 2725–2733 (2013).
31. Lazarov, V. K., Chambers, S. A. & Gajardziska-Josifovska, M. Polar oxide interface stabilization by formation of metallic nanocrystals. *Physical Review Letters* 90, 216108 (2003).
32. Turner, S. et al. Structural phase transition and spontaneous interface reconstruction in La$_{2/3}$Ca$_{1/3}$MnO$_3$/BaTiO$_3$ superlattices. *Physical Review B* **87**, 035418 (2013).
33. Gao, X. et al. Structural Distortion and Compositional Gradients Adjacent to Epitaxial LiMn$_2$O$_4$ Thin Film Interfaces. *Advanced Materials Interfaces* **1** (2014).
34. Li, L. et al. Strain and Interface Effects in a Novel Bismuth-Based Self-Assembled Supercell Structure. *ACS applied materials & interfaces* **7**, 11631–11636 (2015).
35. Zhang, K. et al. Water-Free Titania-Bronze Thin Films with Superfast Lithium-Ion Transport. *Advanced Materials* **26**, 7365–7370 (2014).
36. Lee, D. et al. Oxygen surface exchange kinetics and stability of (La, Sr)$_2$CoO$_{4+x}$/La$_{1-x}$Sr$_x$MnO$_3$ (M= Co and Fe) hetero-interfaces at intermediate temperatures. *Journal of Materials Chemistry A* **3**, 2144–2157 (2015).
37. Lee, D. et al. Strontium influence on the oxygen electrocatalysis of La$_{2-x}$Sr$_x$NiO$_{4+z}$ (0.0 ≤ $x$ ≤ 1.0) thin films. *Journal of Materials Chemistry A* **2**, 6480–6487 (2014).
38. Lee, D. et al. Enhanced Oxygen Surface Exchange Kinetics and Stability on Epitaxial La$_{0.8}$Sr$_{0.2}$CoO$_{3-δ}$ Thin Films by La$_{0.8}$Sr$_{0.2}$MnO$_3$ Decoration. *The Journal of Physical Chemistry C* **118**, 14326–14334 (2014).
39. Cowley, J. & Huang, Y. De-channelling contrast in annular dark-field STEM. *Ultramicroscopy* **40**, 171–180 (1992).
40. Hillyard, S. & Silcox, J. Detector geometry, thermal diffuse scattering and strain effects in ADF STEM imaging. *Ultramicroscopy* **58**, 6–17 (1995).
41. Pennycook, S. J. & Nellist, P. D. *Scanning transmission electron microscopy: imaging and analysis*. (Springer Science & Business Media, 2011).
42. Erdman, N. et al. Surface structures of SrTiO$_3$ (001): A TiO$_2$-rich reconstruction with ac (4 × 2) unit cell. *Journal of the American Chemical Society* **125**, 10050–10056 (2003).
43. Zhu, G.-z., Radtke, G. & Botton, G. A. Bonding and structure of a reconstructed (001) surface of SrTiO$_3$ from TEM. *nature* **490**, 384–387 (2012).

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**Author Contributions**
X.G. carried out STEM measurements under guidance of M.F. C. S.L., J.N., T.L.M. and T.Z.W. assisted for sample synthesis and basic characterization. X.G. conceived the experiments under supervision of H.N.L. All authors participated in discussions and manuscript writing.

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