

## Oxide Epitaxy with Large Symmetry Mismatch: Bronze-phase VO<sub>2</sub> on SrTiO<sub>3</sub>

Hunter Sims<sup>1,2</sup>, Xiang Gao<sup>2</sup>, Shinbuhm Lee<sup>2</sup>, John A. Nichols<sup>2</sup>, Tricia L. Meyer<sup>2</sup>, T. Zac Ward<sup>2</sup>, Sokrates T. Pantelides<sup>1,2</sup>, Matthew F. Chisholm<sup>2</sup>, and Ho Nyung Lee<sup>2</sup>

<sup>1</sup>. Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA.

<sup>2</sup>. Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

Epitaxial synthesis of complex oxides has stimulated considerable interest in creating novel functionalities and physical properties by controlling the interplay among the order parameters, i.e. lattice, spin, charge, and orbital order [1]. Heterostructures of oxide materials allow for well defined interfaces at which electronic and/or magnetic order can be coupled or tuned, as well as giving rise to emergent behavior distinct from the bulk properties of either material. 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<sub>2</sub> and VO<sub>2</sub>, also offer intriguing physical properties [2-7], there are no substrates available with similar structures (lattice parameters and crystal symmetry). Thus, the ability to grow epitaxial thin films of binary oxides on lattice- and symmetry-mismatched substrates is of vital importance for exploring their unprecedented potential [8,9].

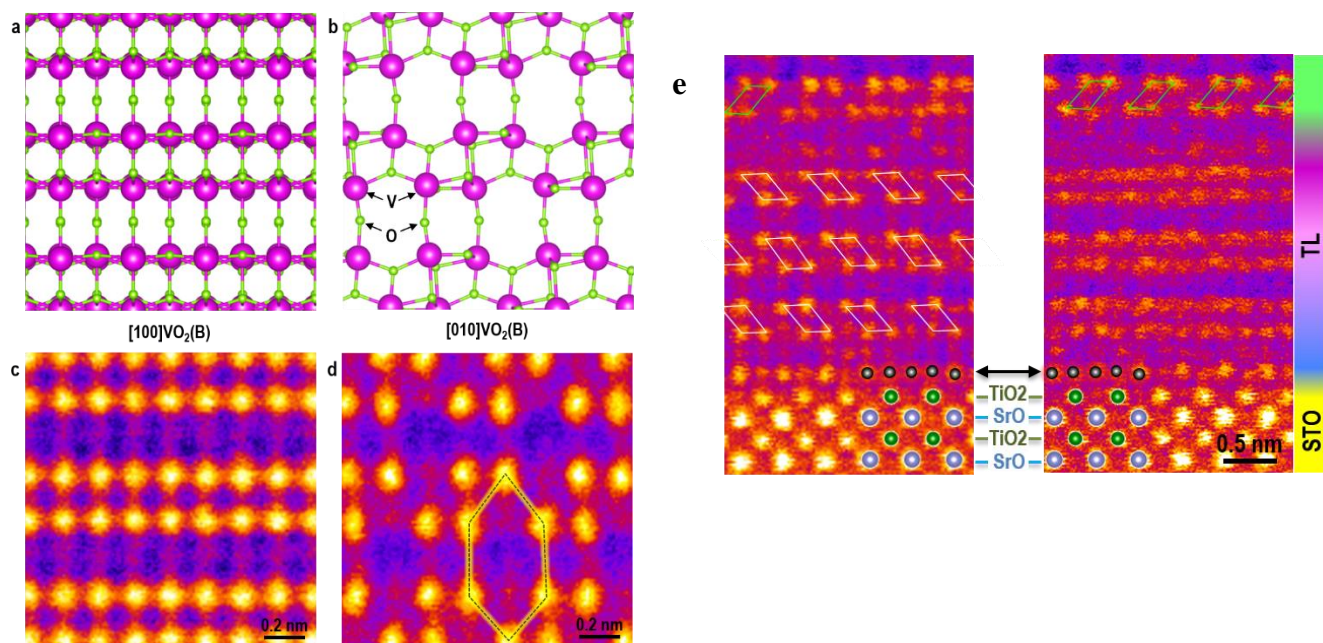
Recently, high quality VO<sub>2</sub> polymorphs were successfully stabilized as epitaxial thin films using pulsed laser epitaxy (PLE) on perovskite substrates, such as SrTiO<sub>3</sub> [10-12]. Bronze-phase VO<sub>2</sub>(B) has a monoclinic structure (with *C2/m* symmetry) whose lattice constants are  $a = 12.03$ ,  $b = 3.69$ ,  $c = 6.42$  Å, and  $\beta = 106.6^\circ$ , whereas SrTiO<sub>3</sub> (with *Pm3m* symmetry) has a cubic structure with a lattice constant of 3.905 Å [12,13]. Note that while many previous studies focused on R and M1 phase VO<sub>2</sub>, recent studies in developing advanced energy storage found VO<sub>2</sub>(B) to be a promising cathode material for Li-ion batteries [14,15]. It is rather surprising that VO<sub>2</sub>(B) films with corner- and edge-sharing oxygen octahedra (see Figures 1a and b) can be epitaxially grown on STO with corner-sharing octahedra, despite the different oxygen sublattices and the large biaxial lattice mismatch.

In this work, we report aberration-corrected scanning transmission electron microscopy (STEM) imaging and electron energy-loss spectroscopy (EELS) data [16], as well as density functional theory calculations, and use these results to understand how two dissimilar materials can form an epitaxial heterostructure. Based on the atomic-scale investigation by STEM, we found an interfacial bi-layer at the VO<sub>2</sub>(B)/STO interface that results in epitaxial growth of a structurally complex, low-symmetry film on a high-symmetry substrate. The upper interfacial layer is characterized by B-site (Ti) columns of alternating full and partial intensity and an interlayer distance within the bi-layer much larger than that in bulk SrTiO<sub>3</sub> ( $2.4 \pm 0.1$  Å compared to 1.95 Å). This intensity pattern suggests a different second layer than the stoichiometric (2x1) reconstruction previously proposed for bare STO surfaces [17].

Supported by first-principles calculations, we propose a new double-layer structure that agrees with the observed intensities and interlayer distances. Using total energy calculations, we compare the relative stability of the reconstructions. Differences in bonding behavior between the old and new models for the reconstructed interfacial layer lead us to propose an explanation for the epitaxial growth of the VO<sub>2</sub>(B) films that suggests a path for the creation of new symmetry-mismatched heterostructures [18].

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**Figure 1.** Atomic structure of  $\text{VO}_2(\text{B})$ . (a, b) Schematics (V: large purple balls, O: small green balls) and (c, d) corresponding cross-sectional HAADF images of  $\text{VO}_2(\text{B})$  seen along (a, c) the  $[100]$  and (b, d)  $[010]$  directions. The hexagon in (d), indicates the large open channels in  $\text{VO}_2(\text{B})$ . (e) Magnified HAADF images showing the V cation structure (diamonds), substrate Sr and Ti ions (larger silver and green balls), and extra atomic plane (smaller silver balls). Reproduced with permission from [16].