Title
Strain-Mediated Interfacial Dynamics during Au–PbS Core–Shell Nanostructure Formation

Permalink
https://escholarship.org/uc/item/1f50n69v

Journal
ACS Nano, 10(6)

ISSN
1936-0851

Authors
Niu, Kai-Yang
Liu, Miao
Persson, Kristin A
et al.

Publication Date
2016-06-28

DOI
10.1021/acsnano.6b02331

Peer reviewed

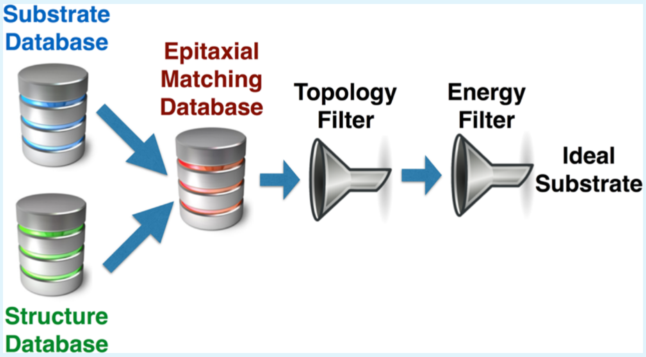
ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

Computational Approach for Epitaxial Polymorph Stabilization through Substrate Selection

Hong Ding,[†] Shyam S. Dwaraknath,[†] Lauren Garten,[‡] Paul Ndione,[‡] David Ginley,[‡] and Kristin A. Persson*,[†,§]

[†]Energy Technologies, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
[‡]Materials Chemistry Science and Technology, National Renewable Energy Laboratory, Golden, Colorado 80401, United States
[§]Department of Materials Science and Engineering, University of California Berkeley, Berkeley, California 94704, United States

ABSTRACT: With the ultimate goal of finding new polymorphs through targeted synthesis conditions and techniques, we outline a computational framework to select optimal substrates for epitaxial growth using first principle calculations of formation energies, elastic strain energy, and topological information. To demonstrate the approach, we study the stabilization of metastable VO_2 compounds which provides a rich chemical and structural polymorph space. We find that common polymorph statistics, lattice matching, and energy above hull considerations recommends homostructural growth on TiO_2 substrates, where the VO_2 brookite phase would be preferentially grown on the $a-c$ TiO_2 brookite plane while the columbite and anatase structures favor the $a-b$ plane on the respective TiO_2 phases. Overall, we find that a model which incorporates a geometric unit cell area matching between the substrate and the target film as well as the resulting strain energy density of the film provide qualitative agreement with experimental observations for the heterostructural growth of known VO_2 polymorphs: rutile, A and B phases. The minimal interfacial geometry matching and estimated strain energy criteria provide several suggestions for substrates and substrate−film orientations for the heterostructural growth of the hitherto hypothetical anatase, brookite, and columbite polymorphs. These criteria serve as a preliminary guidance for the experimental efforts stabilizing new materials and/or polymorphs through epitaxy. The current screening algorithm is being integrated within the Materials Project online framework and data and hence publicly available.



KEYWORDS: *epitaxy, substrate selection, topology, elastic energy, homoepitaxy, heteroepitaxy*

1. INTRODUCTION

Discovery and synthesis of new functional materials is essential in materials research to enable breakthrough technologies in energy storage, delivery, and utilization. Although computational approaches to predicting novel materials are becoming increasingly popular,[1] the ability to theoretically predict the preferred synthesis conditions of a target new material is less routine. In this context, synthesis of highly textured or epitaxial films—the natural or artificial growth of crystals on a crystalline substrate—provides an ideal platform as it allows for many control variables such as substrate selection, temperature, interfacial chemistry, and deposition rates, etc., to favor a specific local minimum in the free-energy landscape[2] corresponding to the target material. Among the variable conditions for epitaxy, the substrate selection is particularly important as it can decrease the nucleation energy of a given target, specifically metastable, phase which can exhibit dramatically different physical or chemical properties compared to the ground state.[3] This is beautifully illustrated by the recent 2014 Nobel Prize in Physics, which was awarded for the invention of efficient blue-light-emitting diodes based on epitaxially stabilized cubic GaN on a (001)-GaAs substrate.[4] An extensive overview of the applications, physics, and challenges in epitaxial growth, partially concerning transition-metal oxide heterointerfaces, can be found in references 5 and 6.

Usually, an epitaxial substrate is manually selected from a pool of common candidates using visualization software to select an appropriate surface, a rough lattice parameter matching, and intuition.[7] To broadly explore new functional polymorphs using epitaxy, a more systematic, efficient, and rational screening methodology of substrates is desirable. Several recent experimental combinatorial efforts[8,9] highlight the need to correctly identify a suitable substrate and the experimental conditions for high-throughput epitaxial film growth. Computationally, Mehta et al.[10] used ionic substitution

Received: February 6, 2016
Accepted: May 4, 2016
Published: May 4, 2016

DOI: 10.1021/acsami.6b01630
ACS Appl. Mater. Interfaces 2016, 8, 13086−13093

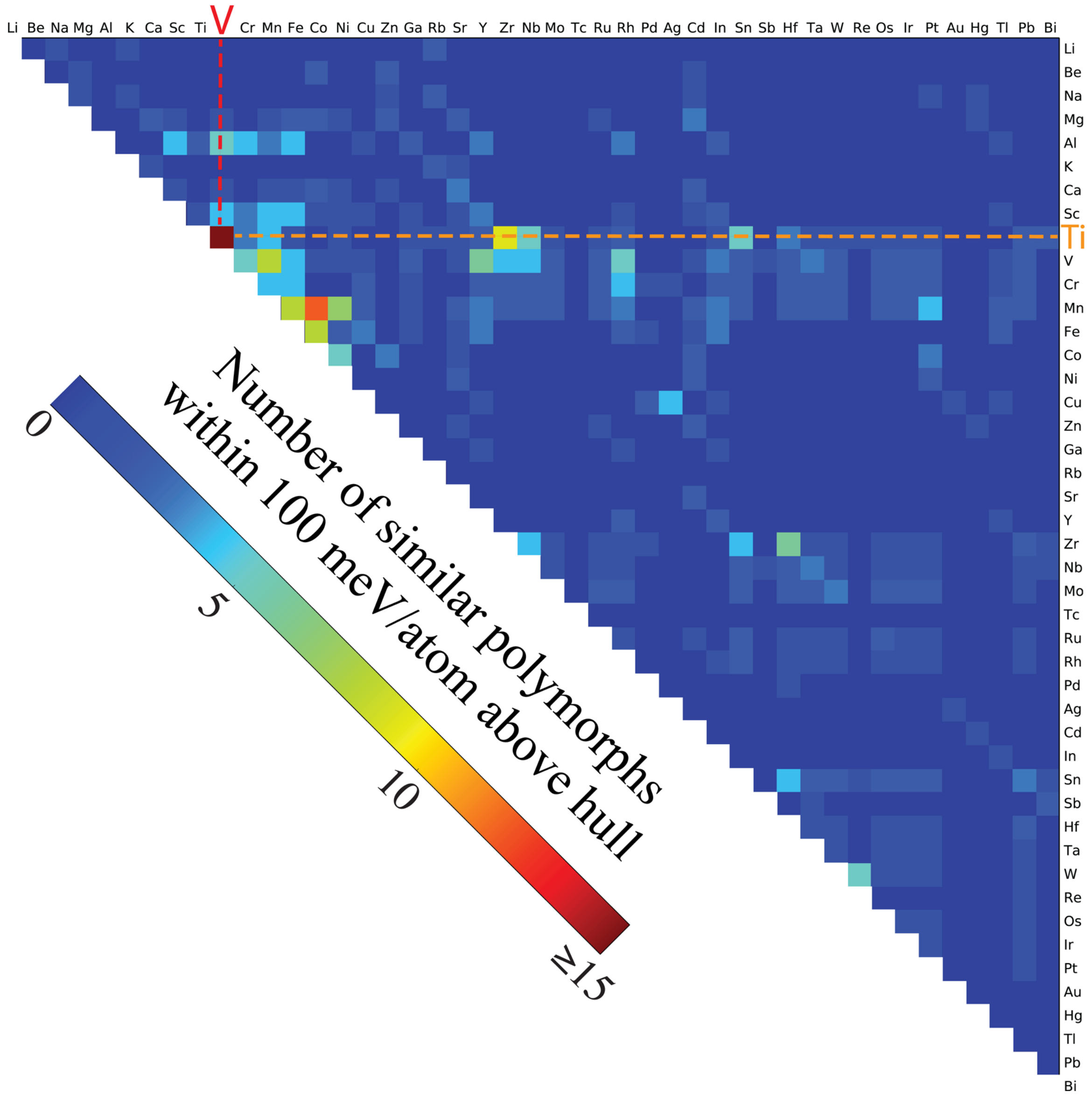


Figure 1. Illustration of the number of conformal oxide polymorphs within 100 meV/atom of the hull between two elements. Reddish color indicates a high number of shared polymorphs, indicating that the two elements would be ideal for oxide homoepitaxy. The data are taken from the Materials Project Database, which contains mainly experimentally verified compounds from the ICSD[33] but also an increasing number of "hypothetical" structures created by ionic substitution, removal of ions, and structure prediction methods, etc. To obtain a measure of chemical similarity, the structures considered here were filtered on the "energy above Hull" less than 100 meV/atom, which provides a reasonable upper bound of accessible metastability.[34]

to evaluate polymorph metastability within several metal dioxide systems where, not surprisingly, the calculated formation energy of the target compound was found to be a guiding but inconclusive criteria to predict the resulting epitaxial phase. To include an approximate effect of the substrate, the bulk modulus of each polymorph was computed to construct a free energy substrate−film model to evaluate the accessibility of the target phase. It is worth noticing that the work by Mehta et al.[10] focused on which polymorph is accessible through epitaxial growth, but did not address the reverse question: given a particular target material/polymorph, what is the optimal substrate selection and resulting epitaxial orientation?

To facilitate the synthesis of novel functional metastable materials, the goal of this work is to propose and implement an efficient and general computational screening approach for substrate selection. Given a target chemical compound and/or polymorph, we envision a process where the method and criteria are specified, the pool of candidate substrates is selected (could be up to a hundred or more), and the list of best possible substrate matches, as well as the corresponding orientation relationship with the target film, is generated in real time.

The presented methodology is benchmarked for the specific case of VO_2 polymorph growth using available references in the literature. Polymorphism in vanadium dioxide VO_2 has long attracted significant interest particularly due to its metal−insulator transition which can manifest as a function of temperature, strain, applied electric field, and defect chemistry.[11−13] At high temperatures, VO_2 presents a metallic rutile (R) structure, which—upon cooling past a critical temperature—undergoes a dimerization of the vanadium into a

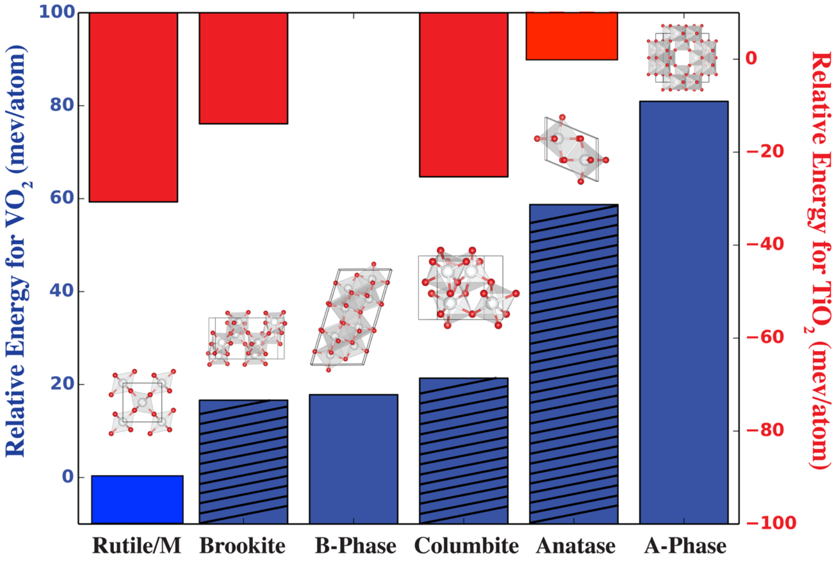


Figure 2. To estimate the accessible window of metastability we compare the calculated relative formation energies of various polymorphs in TiO_2 (red) and VO_2 (blue). The lowest-energy structure (anatase for TiO_2 and rutile for VO_2) is used as the reference state. Dashed bars indicate the polymorphs that have not been synthesized.

distorted semiconducting monoclinic structure (M1). Additionally, two other structures, the A and B phases, have been synthesized under hydrothermal and/or physical vapor deposition conditions,[14,15] while other structures such as anatase, brookite, and columbite seen in TiO_2 have not yet been observed for VO_2. Hence, we are especially interested in finding recommendations for growing these hitherto unseen VO_2 polymorphs.

2. METHODOLOGY

2.1. Computational. We aim to provide a fast and efficient model to preselect substrates from a given pool for epitaxial growth of a target polymorph/material. Here we investigate two different approaches and a variety of criteria associated with each. In the following we present analyses, benchmarking, and recommendations for the following:

- Homostructural epitaxy. where a chemically and structurally similar substrate material is selected based on common polymorph statistics, lattice matching, and energy above the hull. In this model the optimal orientation relationship between the film and the substrate is chosen as the smallest lattice mismatch between the common structures.
- Heterostructural epitaxy. where the pool of candidate substrates can generally comprise any chemical system and the orientation relationship between the film and the substrate is obtained through a set of criteria based on the minimal interfacial geometry matching and estimated strain energy as a function of the substrate−film pair.

Both models are explored and implemented within the infrastructure of the Materials Project and benchmarked using available literature references for the case of VO_2 polymorph stabilization. We emphasize that a detailed investigation of interfacial chemical interactions—while beyond this work—may be critical in some cases and can be performed using slab calculations as an added, albeit more time-consuming, computational approach. For a comprehensive collection of candidate substrates, we used the Materials Project database[16] as an "a priori" calculated data set to search representative structures and evaluate the corresponding polymorph thermodynamic stability. Density-functional-theory (DFT) calculations were performed as necessary using the projector augmented wave (PAW) method[17,18] as implemented in the Vienna Ab Initio Simulation Package (VASP)[19,20] within the Perdew−Burke−Enzerhof (PBE) Generalized Gradient Approximation (GGA) formulation of the exchange-correlation functional.[21] A cutoff for the plane waves of 520 eV is used and a uniform k-point density of approximately 1000 per reciprocal atom is employed. We note that the computational and convergence parameters were chosen consistently with the settings used in the Materials Project[16,22] to enable direct comparisons with the large set of available MP data.

3. RESULTS AND DISCUSSION

To demonstrate the various ways computational guidance can be leveraged for selecting a suitable substrate for epitaxial growth, we first choose a target film system. Because of the extensive polymorphism, diverse chemistry, and oxidation states of the vanadium oxides, as well as their potential interest for electronic applications, such as transparent conducting films and catalysts, etc.,[23−25] we find the family of VO_2 polymorphs well suited to focus and illustrate our analysis and substrate screening process. Previously epitaxially grown VO_2 polymorphs, available in the literature, are used as benchmarks for our models. For metastable VO_2 polymorphs that have yet to be observed or successfully synthesized—and which could have interesting properties—substrate recommendations for future epitaxial growth are made.

3.1. Homostructural Epitaxy. The easiest way to use available computational resources to select a potential substrate is to use chemical and structural similarity as a guide to homostructural growth. Essentially, if one wants to grow a new metastable polymorph, a naive guess for a substrate would be a material with the same structure, low lattice mismatch, and similar chemistry. To generally explore this concept and exemplify it for our chosen VO_2 system, we perform simple data statistics of common polymorphism within the binary oxides. For all MO_x oxide structures available in the Materials Project, Figure 1 illustrates the number of similar oxide structures found within 100 meV/atom of the ground state hull[26] for each pair of metal elements. We hypothesize that a large number of identical (within a given structural similarity tolerance) metastable structures close to the ground state hull correlate with chemical similarity between the systems. This speculation is corroborated by high numbers for intuitively similar elements such as Ti−V, Mn−V, Mn−Fe, Mn−Co, Mn−

Ni, Co−Fe, and Zr−Ti, which all exhibit more than five similar polymorph structures within the given energy range. The binary titanium oxides show an exceptionally high degree of common polymorphism with VO_2, although we caution that this result may be somewhat skewed by the high degree of interest in these systems (e.g., more structures reported and explored) due to their electronic and magnetic versatility as a function of small structural changes. Given the large number of similar structures common to the titanium and vanadium oxides, we select the TiO_2 system as a basis for homostructural growth, as well as a good benchmark. In natural minerals, TiO_2 has three well-known polymorphs, i.e., anatase, rutile, and brookite. The columbite structure of TiO_2 is also found in suevite from the Nördlinger Ries crater which was likely formed under impact-induced high-pressure conditions.

Using DFT, we computationally relaxed the aforementioned high-symmetry polymorphs of interest for VO_2 and TiO_2: rutile, A and B phases (experimentally observed for VO_2), as well as anatase, brookite, and columbite (experimentally observed for TiO_2 but not VO_2). First, to obtain a sense of the accessible energy scale through various synthesis techniques we compare the calculated thermodynamic stability with available evidence of successful synthesis, for both VO_2 and TiO_2. Figure 2 shows the relative bulk formation energies (at $T = 0$) for the various VO_2 structures and TiO_2. For TiO_2, PBE-DFT erroneously predicts anatase (−3.51 eV/atom) as the ground state at zero pressure. This is well within the standard DFT error on formation energies for oxides which is normally distributed with a mean of zero and a standard deviation of 25 meV/atom.[27] The other three naturally occurring TiO_2 polymorphs, i.e., rutile, brookite, and columbite, are close in energy, about 15−30 meV/atom higher than anatase. These results are consistent with previous examinations of the TiO_2 system.[28] We now turn to the VO_2 family of polymorphs. Because the strong lattice correspondence between the rutile and M1 phase and the small lattice expansion observed (1%),[29] we will in this work consider them as one system, referred to as the "R/M" phase. Among the polymorphs considered for the VO_2 system, the R/M phase exhibits the lowest formation energy (−2.48 eV/atom). Brookite and columbite VO_2 have comparable formation energies, which are about 20 meV/atom higher than that of the R/M phase, whereas anatase has a higher relative energy (about 60 meV/atom). These results are also consistent with previous studies, which assessed the VO_2 formation energies in different prototype structures[10] for a range of different functionals.[30,31] To further evaluate the correlation between accessibility (e.g., successful synthesis) and the calculated zero Kelvin energy difference, we also present the results of the A and B phases. Our calculations show that the B phase is similar in energy to the brookite and columbite structures, while the energy of the A phase is higher than all other structures considered here (about 80 meV/atom higher than the rutile structure). Comparing the energy range of the polymorph space with evidence of successful synthesis (at some conditions) provides us with a estimated "accessible energy" scale. For example, we note that the metastable A phase has been successfully synthesized using hydrothermal[14] and physical vapor deposition techniques.[32] Hence, the present results indicate, rather encouragingly, that a large exploration energy window of metastability (up to 80 meV/atom including potential inaccuracies in DFT) may be overcome using customized synthesis techniques and conditions. Specifically, we note that any failure of DFT to obtain the correct ground state for either substrate or target system is of less importance in this work, as long as consideration is taken to include that error into the estimated accessible energy window and that the other criteria (lattice matching and chemical similarity) are applicable.

Second, the relaxed VO_2 crystal structures and lattice parameters are listed in Table 1, in comparison with TiO_2.

Table 1. Calculated Structures of TiO_2 and VO_2 Polymorphs

			lattice parameter (Å)		
structure	space group	oxide	a	b	c
		TiO_2 polymorphs			
rutile	$P4_2/mnm$	TiO_2	4.65	4.65	2.97
		VO_2	4.51	4.51	3.03
brookite	$Pbca$	TiO_2	5.18	5.51	9.27
		VO_2	5.21	5.41	9.19
columbite	$Pbcn$	TiO_2	4.59	4.94	5.58
		VO_2	4.53	5.00	5.44
anatase	$I4_1/amd$	TiO_2	3.81	3.81	9.72
		VO_2	3.90	3.90	9.17
		VO_2 polymorphs			
A phase	$P4/ncc$ (130)	VO_2	8.57	8.57	3.85
B phase	$C2/m$ (12)	VO_2[a]	12.39	3.75	6.49

[a] $\beta = 106.8°$.

Not surprisingly, the lattice constants of the same TiO_2 and VO_2 prototype structures are very similar, where the largest relative difference ($\Delta = 5.6\%$) is shown along the c-axis for the anatase structure. The small differences in lattice parameter between TiO_2 and VO_2 for the same prototype structure suggest new VO_2 polymorphs may be achieved through homostructural VO_2 epitaxial growth on TiO_2. Indeed, pseudomorphic growth work by Gao et al.[35,36] achieved a few atomic layers of anatase VO_2 on TiO_2 which is consistent with an approximate critical layer thickness of 4 nm. Epitaxial growth typically requires a lattice mismatch between the substrate and film below 5% in lattice parameter.[37] From Table 1, we note that the a and c axes provide an interfacial preference between the VO_2 and TiO_2 brookite structures, while the $a-b$ plane would be more favored for homostructural VO_2 growth on TiO_2 columbite and the anatase. We also compared the structural parameters of the A and B phases for VO_2 with experimental measurements and found agreement within 2%.[15]

Hence, for the stabilization of metastable VO_2 polymorphs, we find that common polymorph statistics, lattice matching, and energy above hull considerations recommend homostructural growth on TiO_2 substrates. The VO_2 brookite phase would be preferentially grown on the TiO_2 brookite $a-c$ plane and the VO_2 columbite and anatase phases favor growth on the TiO_2 $a-b$ columbite and anatase planes, respectively.

3.2. Heterostructural Epitaxy. To build a more versatile substrate selection algorithm we have to go beyond the simple lattice parameter and chemical similarity matching between homomorphic (e.g., growing VO_2 anatase on TiO_2 anatase) structures. A general model would ideally allow us to look beyond common substrates for any orientation relationship between the substrate and the target film. A coherent interface between the substrate and target film implies a translational symmetry that is compatible with both surfaces. Zur and McGill[38] proposed a topological interface matching approach based on the minimization of the coincident area of matching 2D superlattices from the various faces of the substrate and film

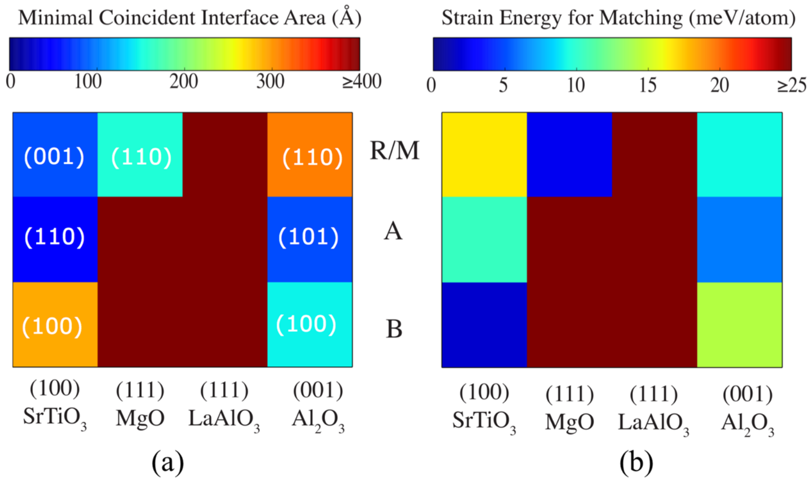


Figure 3. (a) Calculated minimal coincident interface area for substrate and VO_2 polymorph pairs and (b) corresponding film strain energy. The orientation of the target film is labeled with the corresponding Miller index in (a).

lattices within a given strain constraint. This approach is an improvement from traditional lattice parameter matching, which is is not applicable for systems where the epitaxial layer has a different orientation, or a completely different crystal structure, than the substrate. Additionally, while devoid of any chemical interaction between the target film and substrate, the model provides a rapid and robust geometrical screening and we select it for implementation in pymatgen[39] (the open python-based analysis software adopted for MP) and dissemination within the Materials Project Design environment. In this process, we take advantage of existing surface modules and symmetry operations within pymatgen to generate all possible surface orientations of Miller index (*hkl*) below a certain cutoff and terminations.[34,39] The candidate substrates can be automatically selected from the Materials Project or generated from an external list. To accommodate a lattice match within the Zur and McGill model, the film is considered to be strained within the epitaxial plane. Hereafter, we will refer to this epitaxial plane as the $x-y$ plane. If we assume the substrate surface is rigid with no structural relaxation perpendicular to the $x-y$ plane, the strain energy (ΔE_s) imposed on the film can be expressed as $\Delta E_s = V \cdot e^{x-y}$, where V is the volume of the film per atom and e^{x-y} is the film strain energy density induced in the $x-y$ plane. Here, we adopt the recently developed elastic constant (C_{ijkl}) high-throughput computation framework[22] within the Materials Project which allows for an easy estimate of e^{x-y} as

$$e^{x-y} = V\cdot\frac{1}{2}C^{*}_{ijkl}\epsilon^{x-y}_{ij}\epsilon^{x-y}_{kl} \tag{1}$$

where C^{*}_{ijkl} is obtained by the transformation of the fourth-order tensor C_{ijkl} into the new lattice orientation correspondence between the substrate and the film. Through this procedure, we can preliminarily identify appropriate substrates and the lattice orientations that geometrically fit the target polymorph film as a function of the film strain energy. We note that there is a DFT error affecting the energy ordering of systems as previously witnessed in the formation energies for VO_2 and TiO_2. The DFT evaluations of the elastic tensor are relatively accurate, within 15% of the experimental value,[22] and will at worst contain a systematic error that should have a small effect in the overall ranking of different substrates for epitaxy.

Generally considering heteroepitaxy of metastable structures we note that the epitaxial constraint aims to overcome the difference in total energy (e.g., formation energy at $p,T = 0$ + strain energy) for the target structure vs all other polymorphs including the ground state. In the case of the VO_2 system, the differences in free energy between different polymorphs are quite small, and for clarity and transparency of inherent DFT errors, we present and evaluate the strain energy and the geometric matching area as separate selection tools in choosing epitaxial substrates with optimal selectivity. However, we emphasize that the total energy change under epitaxial strain is straightforward to include in the current approach and an example is provided further down in this section. Following the Zur and McGill convention, for each pair of substrate and film, one value of minimal common unit cell area can be derived. Whereas the substrate and its orientation can be selectively chosen under experimental conditions, films with different orientations that fall within the epitaxial geometrical limit are all feasible and will compete with one another. To imitate this competition, we consider the growth orientation that yields the lowest minimal common unit cell area and hence the least incoherent interface, for any particular film. Hereafter, we refer to the corresponding common unit cell area as the minimal coincident interface area (MCIA) and we estimate a "small" MCIA criteria by taking 40 integers of a typical unit surface cell, e.g. ≤ 400 Å^2. Using the two concepts of the geometric surface area matching and the film strain energy separately as selection criteria we evaluate the model on a set of substrate−VO_2 pairs for which experimental results are available in the literature. Figure 3 shows epitaxial lattice matching results with a maximal 3% strain for three known VO_2 polymorphs (R/M, A, and B phase) on the following substrates: $SrTiO_3$, MgO, $LaAlO_3$, and Al_2O_3, which have all been previously used for epitaxial growth of VO_2. Our calculations show that both R/M and A phases have small MCIAs (≤ 150 Å^2), with the corresponding ΔE_s of 17 and 10 meV/atom, respectively. The B phase has a relatively large MCIA (290 Å^2) while the corresponding ΔE_s (2 meV/atom) is the lowest among the three polymorphs. Hence, considering both the geometric area and the strain energy, we find no strong preference among the three polymorphs and would suggest that they could all be grown on a (100)-$SrTiO_3$ substrate. Indeed, Srivastava et al.[32] found that either R/M, A, or B phase films can be grown epitaxially on a (100)-$SrTiO_3$

substrate through pulsed laser deposition and that the obtained phase selectivity depended on the oxygen pressure and laser frequency. Considering the next substrate, (111)-MgO, we find only large MCIA (495 and 449 Å^2) for the A or B phases, respectively, while the R/M phase yields relatively low values of MCIA (155 Å^2) and strain energyΔE_s (3 meV/atom). This is again corroborated by available experiments: radio frequency sputtering techniques were utilized to deposit VO_2 on (111)-MgO and (111)-$LaAlO_3$ followed by annealing, which both present R/M structured epitaxial films.[40] For (111)-$LaAlO_3$, our results suggest that none of the three polymorphs can be easily grown epitaxially due to relatively large values of MICA and strain energy. Experimentally,[40] the R/M phase was observed which could either be a result of a small interfacial buffer phase, or an indication of limiting factors (surface defects, interfacial chemistry) in the current model. Lastly, our model predicts that a (0001)-Al_2O_3 (sapphire) substrate should favor epitaxial growth of a VO_2 A phase film, however R/M is frequently[41] found. Interestingly, it is worth noticing that Zhou et al.[41] did observe a transition or buffer layer at the VO_2/(0001)-Al_2O_3 interface, indicating that a direct epitaxial relationship may not exist between the substrate and the epitaxially grown film. A buffer layer is likely to favor the ground state, in this case the R/M phase, which explains the apparent mismatch between the theoretical prediction and experimental results. Overall, we find that the current model which incorporates a geometric unit cell area matching between the substrate and the target film as well as the resulting strain energy density of the film provide qualitative agreement with experimental observations, though a detailed nature of the lattice−substrate interface, e.g., the atomic orientation, termination preference, and chemical character etc., requires further research efforts.

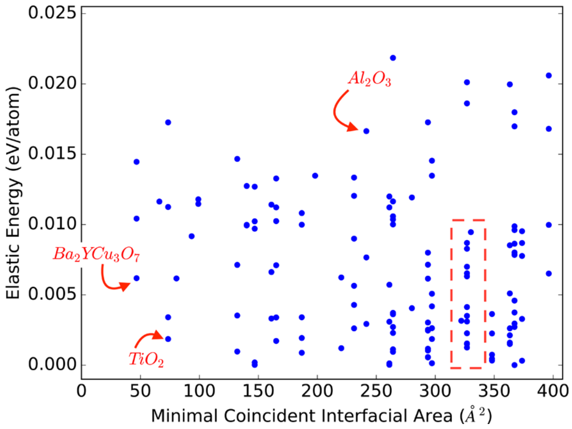


Figure 4. Minimal coincident interface area (MCIA) and the corresponding strain energy density (ΔE_s between A Phase VO_2 and 66 selected substrates. Red arrows highlight three different substrates for A phase growth: Al_2O_3 (MCIA:73 Å^2:3 meV/atom), $Ba_2YCu_3O_7$ (MCIA:46 Å^2:6 meV/atom), and TiO_2 (MCIA:73 Å^2:1 meV/atom). One example of superlattice grouping is highlighted with a dashed red box.

Table 2. All Heteroepitaxy Substrates Considered and Analyzed for the Growth of VO_2 Polymorphs

$La_2Be_2O_5$	$BaAl_2O_4$	ZnO	$KTiAsO_5$	$Y_3Al_5O_{12}$
Fe_2O_3	CdTe	$SrTiO_3$	$LaAlO_3$	TiO_2
YVO_4	$Li_2B_4O_7$	$Ba(NO_3)_2$	Au	AlN
Bi_2Te_3	CaF_2	CdS	$BaTiO_3$	$Ge(Bi_3O_5)_4$
$MoSe_2$	MgF_2	$KTaO_3$	GaN	$Ge_3(BiO_3)_4$
$LiNbO_3$	PbS	$Gd_3Ga_5O_{12}$	Ge	$MgAl_2O_4$
$PbWO_4$	CaAs	$YAlO_3$	$LiTaO_3$	Fe_3O_4
GaSb	GaP	ZnTe	KI	$LiAlO_2$
Mg_2SiO_4	$CaTiO_3$	$Ba_2YCu_3O_7$	$GdScO_3$	KBr
AlNi	$TbScO_3$	$DyScO_3$	LiF	LaF_3
BaF_2	KCl	$ZnGeP_2$	InP	Cu
NaCl	ZnSe	Ni	$CdWO_4$	$LiGaO_2$
Bi_2Se_3	Ag	MoS_2	Al_2O_3	InSb

Finally, with the ultimate goal of finding new polymorphs through targeted synthesis conditions and techniques, the aforementioned approach can also act as a preliminary substrate selector for any target phase and any given pool of substrate materials. In the case of VO_2, we are interested in finding appropriate substrates for growing the hitherto hypothetical anatase, brookite, and columbite polymorphs. Hence, we collected and screened 66 commonly used single-crystalline substrates (as listed in Table 2), where the lattice information is taken from the calculated compounds in the Materials Project. Figure 4 maps the MCIA and the corresponding elastic strain energy for all possible orientation relationships between the A phase VO_2 and the 66 considered substrates. First of all, we note that the MCIA and elastic energy are highly uncorrelated indicating that a geometric approach based on matching lattice vectors alone is unlikely to find a minimum energy relationship. For example, in Figure 4 (see highlighted dashed red box) superlattices present as vertically aligned points where the differences in elastic energies are due to the slightly different shear and normal deformations needed for the VO_2 A phase to conform to the substrates. Second, we observe that—even compared to a larger substrate set—the homostructural growth relation (VO_2 growth on TiO_2) is well optimized in terms of the topological and strain matching metrics. Third, Figure 4 shows that while substrates such as Al_2O_3 would be a conventional choice for heteroepitaxy, this approach can identify superior and unconventional substrates such as $Ba_2YCu_3O_7$ that would be neglected by a conventional search. To stabilize the anatase, brookite, and columbite polymorphs, we select the substrate surface orientations that yield the smallest values for both MCIA and ΔE_s for a particular VO_2 polymorph. Our lattice match results suggest that (101)-$CdWO_4$ and 110-AlN would be suitable for growing VO_2 columbite, and (100)-$Ba_2YCu_3O_7$, (101)-$LaAlO_3$, (111)-$SrTiO_3$, (001)-$BaTiO_3$, and (001)-GaN would be suitable for growing anatase. For VO_2 brookite, the following substrates are recommended: (001)-Fe_3O_4, (111)-$La_2Be_2O_5$, (101)-$LiAlO_2$, (100)-$LiTaO_3$, (011)-$YAlO_3$, and (001)-$BaAl_2O_4$. In general, we emphasize that care should be taken to evaluate factors not considered here such as substrate stability, availability, and epitaxial interface chemistry. A good example of this decision making process would be the epitaxial growth of A phase, where (0001)-Al_2O_3 could serve as a conventional substrate, but closer examination of the MCIA/ΔE_s space suggests that either (010)-$Ba_2YCu_3O_7$ or (001)-TiO_2 would be more appropriate. We the note that a limiting case of heterostructural growth is the homostructural condition, which is found in this search methodology as the growth of A phase VO_2 on TiO_2 and suggests that these two criteria nicely encompass the homostructural growth case in the substrate selection process. As previously mentioned, we can also consider the total energy change under epitaxial strain. As an example, we consider the problem of stabilizing the VO_2 columbite phase. An initial search would identify the substrate, and ideally the plane, that induces the largest strain energy difference between the desired phase and ground state. Considering the 66 substrates in Table 2, the most suitable substrate can be narrowed down to (011)-$YAlO_3$. Figure 5 shows the total energy as a function of the epitaxial strain for the six polymorphs of VO_2 considered in this study on (011)-$YAlO_3$. The rutile phase is the lowest energy phase up to 3.6% strain, above which columbite exhibits the lowest energy. Hence, we predict that the (011)-$YAlO_3$ substrate enables a phase-stability cross over at a modest strain of 3.6%, where columbite is promoted over the rutile VO_2 ground state. While the epitaxial constrain preferentially stabilizes the columbite phase among the considered phases, we also note that the energy difference between columbite and brookite is very small even up to 9% total strain, which may limit the phase selectivity.

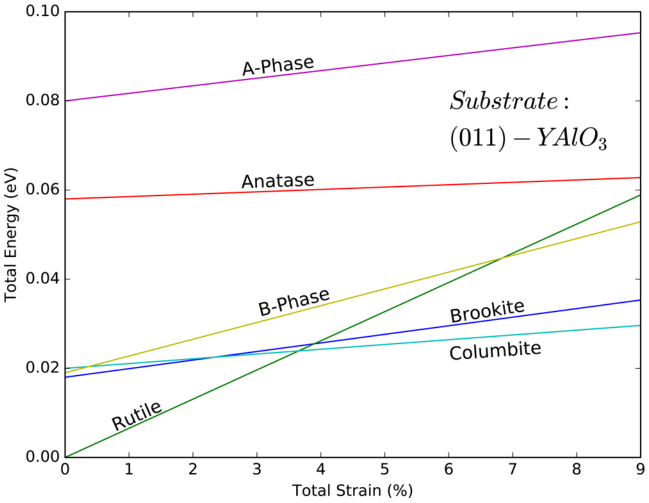


Figure 5. Total energy of VO_2 polymorphs as strained on (110)-$YAlO_3$ referenced to the unstrained rutile formation energy. The total energy is the sum of the formation energy and the elastic strain energy. Dashed red lines highlight one example of superlattice grouping.

4. CONCLUSION

In summary, driven by the need for rational polymorph selection during synthesis, we present a computational framework involving a combination of first-principles calculations of formation energy, elastic strain energy, and topological lattice matching. Using the outlined framework, we prescreen a set of optimal substrates for epitaxial growth, given a target material and/or polymorph. In a simple scenario we examine using homostructural growth selecting a chemically similar system based on common polymorph statistics, lattice matching, and energy above hull. Specifically, for VO_2 polymorphs, we find—not surprisingly—that TiO_2 substrates, where the VO_2 brookite phase would be preferentially grown on the *a*−*c* plane while the columbite and anatase structures favor growth on the *a*−*b* plane. To support a more general selection scenario, we consider heterostructural growth, where the pool of candidate substrates can generally comprise any chemical system and the orientation relationship between the film and the substrate is obtained through a set of criteria based on the minimal interfacial geometry matching and estimated strain energy as a function of the substrate−film pair. Specifically, for the test case of VO_2 polymorphs we find that (101)-$CdWO_4$ and 110-AlN are recommended for growing VO_2 columbite, and (100)-$Ba_2YCu_3O_7$, (101)-$LaAlO_3$, (111)-$SrTiO_3$, (001)-$BaTiO_3$, and (001)-GaN are recommended for growing anatase. For VO_2 brookite, the following substrates are selected by the model: (001)-Fe_3O_4, (111)-$La_2Be_2O_5$, (101)-$LiAlO_2$, (100)-$LiTaO_3$, (011)-$YAlO_3$, and (001)-$BaAl_2O_4$. In this work, while the energy contributions are presented and analyzed separately, it is straightforward to utilize a total energy vs strain criterion. This selection scheme is exemplified for the case of VO_2 columbite, which shows (011)-$YAlO_3$ to be a suitable substrate. In general, we recommend that the evaluation scheme is flexible and can change depending on the system, such that the total energy and its separate components be considered valid screening parameters. These methodologies will be implemented within the Materials Project. We found that the outlined framework and chosen criteria can be used as a preliminary guide for substrate selection and aid experimental efforts in stabilizing new materials and/or polymorphs, as well as to inspire further investigations into the governing principles of polymorph selection through epitaxy.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kapersson@lbl.gov.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported as part of the Center for Next Generation Materials by Design, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Awards DE-AC02-05CH11231 and DE-AC36-089028308. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy. The Materials Project (BES DOE Grant EDCBEE) is acknowledged for infrastructure and algorithmic support. We gratefully acknowledge Dr. John Perkins for his helpful discussion in compiling this manuscript.

■ REFERENCES

(1) Jain, A.; Shin, Y.; Persson, K. A. Computational predictions of energy materials using density functional theory. *Nature Reviews Materials* **2016**, *1*, 15004.

(2) Abarca, A.; Gómez-Sal, P.; Martín, A.; Mena, M.; Poblet, J. M.; Yélamos, C. Ammonolysis of mono(pentamethylcyclopentadienyl) titanium(IV) derivatives. *Inorg. Chem.* **2000**, *39*, 642−651.

(3) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press, 2012.

(4) Amano, H. Nobel Lecture: Growth of GaN on sapphire via low-temperature deposited buffer layer and realization of *p*-type GaN by Mg doping followed by low-energy electron beam irradiation*. *Rev. Mod. Phys.* **2015**, *87*, 1133−1138.

(5) Chakhalian, J.; Millis, A.; Rondinelli, J. Whither the oxide interface. *Nat. Mater.* **2012**, *11*, 92−94.

(6) Poeppelmeier, K. R.; Rondinelli, J. M. Oxide interfaces: Mismatched lattices patched up. *Nat. Chem.* **2016**, *8*, 292−294.

(7) Lee, K.-S.; Baik, S. Domain structure of epitaxial PbTio3 thin films: Effects of substrate selection and film thickness. *Integr. Ferroelectr.* **1999**, *25*, 61−69.

(8) Zhang, Y.; Schultz, A. M.; Li, L.; Chien, H.; Salvador, P. A.; Rohrer, G. S. Combinatorial substrate epitaxy: A high-throughput

method for determining phase and orientation relationships and its application to BiFeO3/TiO2 heterostructures. *Acta Mater.* **2012**, *60*, 6486−6493.

(9) Havelia, S.; Wang, S.; Balasubramaniam, K.; Schultz, A. M.; Rohrer, G. S.; Salvador, P. A. Combinatorial substrate epitaxy: a new approach to growth of complex metastable compounds. *CrystEngComm* **2013**, *15*, 5434−5441.

(10) Mehta, P.; Salvador, P. A.; Kitchin, J. R. Identifying Potential BO2 Oxide Polymorphs for Epitaxial Growth Candidates. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3630−3639.

(11) Qazilbash, M. M.; Brehm, M.; Chae, B.-G.; Ho, P.-C.; Andreev, G. O.; Kim, B.-J.; Yun, S. J.; Balatsky, A.; Maple, M.; Keilmann, F.; et al. Mott transition in VO2 revealed by infrared spectroscopy and nano-imaging. *Science* **2007**, *318*, 1750−1753.

(12) Appavoo, K.; Lei, D. Y.; Sonnefraud, Y.; Wang, B.; Pantelides, S. T.; Maier, S. A.; Haglund, R. F., Jr. Role of defects in the phase transition of VO2 nanoparticles probed by plasmon resonance spectroscopy. *Nano Lett.* **2012**, *12*, 780−786.

(13) Kim, M.-W.; Jung, W.-G.; Cho, H.; Bae, T.-S.; Chang, S.-J.; Jang, J.-S.; Hong, W.-K.; Kim, B.-J. Substrate-mediated strain effect on the role of thermal heating and electric field on metal-insulator transition in vanadium dioxide nanobeams. *Sci. Rep.* **2015**, *5*, 10861.

(14) Theobald, F. Etude hydrothermale du systme VO2-VO2,5-H2O. *J. Less-Common Met.* **1977**, *53*, 55−71. cited by 46.

(15) Oka, Y.; Ohtani, T.; Yamamoto, N.; Takada, T. Phase Transition and Electrical Properties of VO_2 (A). *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi* **1989**, *97*, 1134−1137.

(16) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. a. The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater.* **2013**, *1*, 011002.

(17) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953−17979.

(18) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758−1775.

(19) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *47*, 558.

(20) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169.

(21) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(22) de Jong, M.; Chen, W.; Angsten, T.; Jain, A.; Notestine, R.; Gamst, A.; Sluiter, M.; Krishna Ande, C.; van der Zwaag, S.; Plata, J. J.; et al. Charting the complete elastic properties of inorganic crystalline compounds. *Sci. Data* **2015**, *2*, 150009.

(23) Bavykin, D. V.; Friedrich, J. M.; Walsh, F. C. Protonated titanates and TiO2 nanostructured materials: synthesis, properties, and applications. *Adv. Mater.* **2006**, *18*, 2807−2824.

(24) Lin, H.; Li, L.; Zhao, M.; Huang, X.; Chen, X.; Li, G.; Yu, R. Synthesis of high-quality brookite TiO2 single-crystalline nanosheets with specific facets exposed: Tuning catalysts from inert to highly reactive. *J. Am. Chem. Soc.* **2012**, *134*, 8328−8331.

(25) Di Paola, A.; Bellardita, M.; Palmisano, L. Brookite, the least known TiO2 photocatalyst. *Catalysts* **2013**, *3*, 36−73.

(26) Ping Ong, S.; Wang, L.; Kang, B.; Ceder, G. Li- Fe- P- O2 phase diagram from first principles calculations. *Chem. Mater.* **2008**, *20*, 1798−1807.

(27) Hautier, G.; Ong, S. P.; Jain, A.; Moore, C. J.; Ceder, G. Accuracy of density functional theory in predicting formation energies of ternary oxides from binary oxides and its implication on phase stability. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 155208.

(28) Shirley, R.; Kraft, M.; Inderwildi, O. R. Electronic and optical properties of aluminium-doped anatase and rutile TiO_2 from *ab initio* calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 075111.

(29) Eyert, V. The metal-insulator transitions of VO2: A band theoretical approach. *Ann. Phys.* **2002**, *11*, 650−704.

(30) Mellan, T. A.; Grau-Crespo, R. Density functional theory study of rutile VO_2 surfaces. *J. Chem. Phys.* **2012**, *137*, 154706.

(31) Finazzi, E.; Di Valentin, C.; Pacchioni, G.; Selloni, A. Excess electron states in reduced bulk anatase TiO2: Comparison of standard GGA, GGA+U, and hybrid DFT calculations. *J. Chem. Phys.* **2008**, *129*, 154113.

(32) Srivastava, A.; Rotella, H.; Saha, S.; Pal, B.; Kalon, G.; Mathew, S.; Motapothula, M.; Dykas, M.; Yang, P.; Okunishi, E.; et al. Selective growth of single phase VO2 (A, B, and M) polymorph thin films. *APL Mater.* **2015**, *3*, 026101.

(33) Hellenbrandt, M. The Inorganic Crystal Structure Database (ICSD)Present and Future. *Crystallogr. Rev.* **2004**, *10*, 17−22.

(34) Sun, W.; Ceder, G. Efficient creation and convergence of surface slabs. *Surf. Sci.* **2013**, *617*, 53−59.

(35) Gao, W.; Wang, C. M.; Wang, H.; Henrich, V. E.; Altman, E. I. Growth and surface structure of vanadium oxide on anatase (001). *Surf. Sci.* **2004**, *559*, 201−213.

(36) Gao, W.; Altman, E. Growth and structure of vanadium oxide on anatase (101) terraces. *Surf. Sci.* **2006**, *600*, 2572−2580.

(37) Chen, Y.; Washburn, J. Structural Transition in Large-Lattice-Mismatch Heteroepitaxy. *Phys. Rev. Lett.* **1996**, *77*, 4046−4049.

(38) Zur, A.; McGill, T. Lattice match: An application to heteroepitaxy. *J. Appl. Phys.* **1984**, *55*, 378−386.

(39) Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G. Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis. *Comput. Mater. Sci.* **2013**, *68*, 314−319.

(40) Wong, F. J.; Zhou, Y.; Ramanathan, S. Epitaxial variants of VO 2 thin films on complex oxide single crystal substrates with 3m surface symmetry. *J. Cryst. Growth* **2013**, *364*, 74−80.

(41) Zhou, H.; Chisholm, M. F.; Yang, T.-H.; Pennycook, S. J.; Narayan, J. Role of interfacial transition layers in VO2/Al2O3 heterostructures. *J. Appl. Phys.* **2011**, *110*, 073515.