Determining interface structures in vertically aligned nanocomposite films

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Vertically aligned nanocomposites (VANs) films have self-assembled pillar-matrix nanostructures. Owing to their large area-to-volume ratios, interfaces in VAN films are expected to play key roles in inducing functional properties, but our understanding is hindered by limited knowledge about their structures. Motivated by the lack of definitive explanation for the experimentally-found enhanced ionic conductivity in Sm-doped-CeO$_2$/SrTiO$_3$ VAN films, we determine the structure at vertical interfaces using random structure searching and explore how it can affect ionic conduction. Interatomic potentials are used to perform the initial searching, followed by first-principles calculations for refinement. Previously unknown structures are found, with lower energy than that of an optimized hand-built model. We find a strongly distorted oxygen sub-lattice which gives a complex landscape of vacancy energies. The cation lattice remains similar to the bulk phase, but has a localized strain field. The excess energy of the interface is similar to that of high angle grain boundaries in SrTiO$_3$.

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I. INTRODUCTION

Oxide thin films have a wide range of applications in electronic, magnetic and energy devices. Vertically aligned nanocomposite (VAN) films are a new form of thin film material which contain nanopillars of one phase embedded in a matrix of another. Because of unique strain states, uniform strain, large area of interfaces, and perfectly clean interfaces in these structures, they have been attracting a lot of interest for a wide range of functional systems. Also, VAN structures are easy to fabricate compared to planar superlattice films - they grow by self-assembly from a single target material using pulsed laser deposition, and the density of interfaces is very high with nanopillars of sizes around 10-20nm.

It is widely known that interfaces strongly influence mechanical, electrical and magnetic properties and also that at interfaces in planar heterostructures, novel functional properties often emerge. The local environment at an interface can be very different from that of the bulk material, which leads to reconstruction of the atomic and electronic structures. In VANs, the pillar-matrix nanostructure results in a large and thickness independent interface-to-volume ratio. The two phases with different structures are tightly coupled though these vertical interfaces. While theoretical and computational approaches are invaluable for studying interfaces, the atomic configurations need to be known to start with. Experimental determination of interface structures is very challenging. Although the advancement in scanning transmission electron microscopy (STEM) has allowed individual atomic columns to be imaged, determining the local structures often still requires extensive simulations and sometimes, intuition.

Recently, computational algorithms have been developed and enabled the prediction of structures for a range of materials. Ab-initio random structure searching (AIRSS) has been shown to successfully find stable structures for bulk crystals, low dimensional structures, point defects, and interfaces. Other search methods, such as those based on genetic algorithms and Bayesian optimisations, have also been reported to address structures at grain boundaries and heterostructures.

In this work, we study the interfaces in VAN films consisting of Sm-doped-CeO$_2$ (20 at.%) pillars embedded in a matrix of SrTiO$_3$ (STO). Sm-doped-CeO$_2$ has a fluorite structure and is an ionic conductor, while STO has a perovskite structure and is insulating. The former undergoes a 45-degree rotation when epitaxially grown on STO substrates such that its [110]
direction is aligned with the [100] direction of STO. A schematic of the nanostructure and crystallographic directions is shown in Figure 1d. This system and similar ones have been reported to give enhanced ionic conductivity along the out-of-plane direction \cite{6,30,31}, which makes them particularly attractive for micro solid oxide fuel cell applications. On the other hand, the roles of the vertical interfaces are still unclear. The effects of solid-solid interfaces on ionic conduction has been widely studied theoretically in planar heterostructures where the interface is between materials with the same structure \cite{32,33} or its effect is dominated by the strain \cite{34,35}. Only a few works directly addressed the interface structure \cite{27,28,36}. We are not aware of any atomic scale computational studies about the vertical interfaces in VAN films, to date. The mismatch in periodicity and the fact that two sides have different bulk structures make these interfaces rather complex. While the high crystallinity of the films (i.e. low defect concentration) has been suggested to be the key to the enhanced ionic conduction \cite{30,31}, the possibility that enhancements also occur along interfaces needs to be determined in a definitive way. Doing this experimentally is very difficult owing to the very small (sub-nm length scales) and low volumes of material involved in thin films and so theoretical approaches are very important to guide the understanding.

Using STEM images as the starting point, we determine the interface atomic configurations using random structure searching. A combination of interatomic potential and first-principles methods are used, which we will described in the next section. We found previously unknown interface structures with lower energies than that of a locally optimized hand-built model. These structures share common motifs and have a highly distorted anion lattice. The implications of the findings in the context of local ionic conduction enhancement are discussed.

II. METHODS

A. Simulation details

We choose to focus on the interfaces formed between (100) and (110) planes of SrTiO$_3$ (STO) and Sm-doped-CeO$_2$ (SDC) as electron microscopy images show the majority of them are in this orientation. They are indicated with blue lines in Figure 1b. The image is captured with a scanning transmission electron microscope in high angle annular dark field mode.
The minor STO(110)/SDC(100) type interfaces are marked by green lines. The orientation, periodicity and alignment of atomic planes of the vertical interface can be inferred from the cross-sectional STEM image shown in Figure 1a. It appears that 7 unit cells of STO match to 5 unit cells of SDC in the [001] direction, as indicated by the arrows. Figure 1c shows matching of atomic planes at the vertical interface viewed along the [001] direction. We construct a schematic of the pillar-matrix nanostructure based on the images, which is shown in Figure 1d. Crystallographic directions and imaging planes of Figure 1a-c are labelled. Note that the STO matrix has the same orientation as the substrate.

As the starting point for structure searching, we construct an idealized interface model by joining the bulk structures. We limit ourselves to TiO$_2$ terminated STO as a faint line of Ti atoms can be identified between the two lattices, shown in Figure 1a with a dotted vertical line. The orientation relationship of the two sides is set to be consistent with plan view and cross-sectional STEM images as in Figure 1a&c. The experimental lattice constant of STO is 3.905 Å and that of CeO$_2$ is 5.41 Å. In the [001] direction, we match seven unit cells of STO to five unit cells of CeO$_2$. Two unit cells of STO along its [010] direction are included with matching units of CeO$_2$. We use the experimental lattice constant for STO and adjust that of CeO$_2$ to match in the interface plane. This means that CeO$_2$ is compressively strained by 2.0% along the STO[010] direction and tensile strained by 1.0% along the STO/CeO$_2$[001] direction. We do not expect the strain to significantly affect the interface structures. As a first approximation, we neglect the Sm dopants (20 at.%) in the structure searching and hence the problem becomes finding the stable interface structure between STO (100) and CeO$_2$ (110). Including dopants would significantly increase the search space of the interface structures. The cubic $Fm\overline{3}m$ phase of CeO$_2$ is stable at low-temperature in contrast to yttria-stabilized zirconia (YSZ) where the yttria dopant plays an important role in stabilizing the cubic phase.

Interfaces are inherently non-periodic along its normal direction. There are two schemes for embedding an interface in a periodic cell. A single interface can be formed by two slabs of the material, this composite slab is then separated from its periodic images by vacuum. To mimic bulk-like boundary conditions, we add extra bulk-like layers to the exposed surfaces. These layers are internally fixed but allowed to move as a whole. An alternative scheme is to construct a cell with two identical interfaces which are mirror images of each other. This is only possible because the bulk phases both have mirror planes parallel
FIG. 1. a) A cross-sectional STEM high-angle annular dark-field (HAADF) image showing the STO(100)-SDC(110) interface viewed in the STO[010] direction. The two horizontal arrows mark the periodicity in the [001] direction. The vertical dashed line indicates the TiO$_2$ (100) termination plane of STO. b) A plan view STEM HAADF image showing bright SDC columns embedded in a darker STO matrix. The STO(100)-SDC(110) interface studied in this work is marked by the blue lines. The green lines mark the minor STO(110)-SDC(100) interfaces. c) A high magnification STEM HAADF image showing the STO-SDC vertical interface viewed along the [001] direction. The blue line marks the interface. d) A schematic of the VAN film structure. The SDC pillars are embedded in a matrix of STO with specific crystallographic matching. The image planes of a), b), and c) are labelled.

to the interface. Exposed surfaces are avoided at the price of almost doubling the number of atoms. Illustrations of the two schemes can be found in the supplementary material.

In-depth discussion of AIRSS$^{27}$ and how it can be applied to interface structure prediction has been described in previous work$^{22}$. Here, we outline only the most relevant details in this study. AIRSS relies on generating random but physically sensible structures which are subsequently relaxed. To limit the search space, we choose species-pair dependent minimum
atomic separation constraints based on the values in bulk STO and CeO$_2$. We also choose the randomized region to be within 1 or 2 atomic layers from the interface, which will be discussed later. Instead of full randomization, we displace atoms randomly from their positions in the idealized model. This avoids forming clusters of similarly charged ions, which otherwise can give rise to high electrostatic energies. Maximum displacement magnitudes of 4 Å and 2 Å are used in lateral and normal directions to the interface respectively. Random structures generated with these parameters no longer have the preexisting order at the interface as in the initial model. Periodic cells with two identical interfaces are used for searching using interatomic potentials. Selected low energy structures are converted into slab models that each includes a single interface for further DFT calculations. More details can be found in the supplementary material.

DFT calculations are exceedingly expensive to use for structure searching of systems that contain as many atoms as the interfaces require here, since even a minimal cell in the slab geometry including 4 atomic layers for each side already has 260 atoms. Hence, we choose to use empirical interatomic potentials for searching, followed by refinement DFT calculations. Buckingham potentials with long-range Coulomb interactions are used. For STO, we apply the same potentials which were used in previous structure searching works of STO grain boundaries and ZrO$_2$-STO super-lattices. The potentials chosen for CeO$_2$ were previously used for studying dopant distribution and ionic transport near edge dislocations. Details of the potentials can be found in the supplementary material. The General Utility Lattice Program (GULP) is used for relaxing random structures. The dual interface scheme described above is used. The cell size normal to the interface is allowed to relax.

Density functional theory calculations are performed using the plane-wave pseudopotential code CASTEP. Generalized gradient approximation based exchange-correlation functionals have been used in many other computational studies of STO and CeO$_2$ and were shown to give consistent results. PBEsol is used here, since it gives lattice constants closer to the experimental values for both STO and CeO$_2$. The valence states $2s^2 \ 2p^4$ for O, the $3s^2 \ 2p^6 \ 3d^2 \ 4s^2$ states for Ti, the $4s^2 \ 4p^6 \ 5s^2$ states for Sr and the $4f^1 \ 5s^2 \ 5p^6 \ 5d^1 \ 6s^2$ states for Ce are treated using on-the-fly generated core-corrected ultrasoft pseudopotentials. These pseudopotentials are soft and allow a plane wave cut off energy of 350 eV to be used. Their generation settings are tabulated in the supplementary material. A Monkhorst-Pack
grid of $1 \times 4 \times 1$ is used for sampling the Brillouin Zone. We use the slab scheme described above to embed the interface in a periodic cell. The lattice constants are fixed during the geometry optimisation.

The Atomic Simulation Environment (ASE) is used for setting up and manipulating structures. AiiDA is used to prepare, submit and parse results for DFT calculations. To distinguish and classify the structures found, Smooth Overlap of Atomic Positions (SOAP) implemented in the GAP suite is used. More details are included in the supplementary material.

### B. Experimental details

The Sm-doped-CeO$_2$/SrTiO$_3$ vertically aligned nanocomposite (VAN) film was prepared by pulsed-laser deposition (PLD) as described previously. An FEI TitanTM G2 80-200 scanning transmission electron microscope with a Cs probe corrector operated at 200 kV was used in this study. The STO/SDC interfaces were imaged by using a high-angle annular dark-field (HAADF) detector with a collection range of 60-160 mrad.

### III. RESULTS AND DISCUSSION

We first check the effectiveness of our RSS approach by searching for the bulk structures of SrTiO$_3$ (STO) and CeO$_2$ using both DFT and interatomic potentials. An $I4/mcm$ phase of STO is found to have the lowest energy using DFT for relaxation which is consistent with the low temperature phase of STO found experimentally. Using the interatomic potentials, the $Pm\bar{3}m$ cubic structure is found as the most stable one. The $Pm\bar{3}m$ phase is the high temperature phase and was found in the VAN films previously. For CeO$_2$, the $Fm\bar{3}m$ fluorite structure is the most stable one using both methods. These findings are consistent with experimental results and existing structural prediction works.

Due to the large quantity of relaxed random structures, we choose to focus on structures that have low relative energies and can be found repetitively. The relative energy for each structure is defined as:

$$E_{\text{rel}} = E_{\text{total}} - E_{\text{total}}^{\text{ref}},$$

where $E_{\text{total}}$ is the total energy and $E_{\text{total}}^{\text{ref}}$ is the total energy of the reference structure which
is chosen to be the structure with the lowest total energy. We note that the interatomic potentials can give additional local minima in its potential energy surface (PES) compared to DFT due to their fixed analytic form. Assuming a uniform sampling of the configuration space, the number of visits to the same minima is proportional to the hyper-volume of the basin it is in. These frequently visited minima are likely to represent basins that also exist in the real PES.

To check if the randomization zone is sufficiently large, we perform searches with one or two randomized atomic layers in each side of the interface. Having one extra layer shifts the distribution of the relative energies towards higher values with a broader spread. Most of the low energy structures can be found in both searches. Since none of the low energy structures is exclusively found with increased randomization zone size, we limit the number of randomized layers to be one on both sides in subsequent searches.

Due to the finite size of the search cells, interactions between an interface and its mirror images can affect the geometry optimized structures as well as their relative energies. To check the convergence of structures with respect to the number of layers included normal to the interface, we carry out searches with 4 to 10 layers. While up to 10 layers were required to converge relative energies between the unique structures, most of the structures can be found even with the lowest setting of 4 layers. This indicates interface self-interactions have a limited effect on the overall shape of the PES, despite the values of minima being shifted.

The five low energy structures found in this work are shown in Figure 2. The two lowest energy structures A and B are different in oxygen positions in the last SrO layer and each has a glide plane with space group \( P_{c} \). A highly symmetric structure \( C^{*} \) is also found. It has a space group \( P_{mm2} \) and is 1.1 eV higher in energy in searches including 6 layers of material on each side. In fact, this structure can be obtained by a simple local optimization of the initial model structure. Two other structures D and E both lack any symmetry element. A common pattern emerges among these five structures as well as in many others that have low relative energies. In Figure 2, we fade out the regions where the atomic configurations are shared by different structures. This highlights where they differ from each other which is also where the oxygen sub-lattice is very different from the bulk phases.

Details of structure A are shown in Figure 3. The bulk structures of STO and CeO\(_2\) are vastly different. In perovskite-structured STO, Ti atoms are six-fold coordinated by oxygen atoms in a vertex-sharing octahedron network. The Sr atoms are twelve-fold cuboctahedron
FIG. 2. Low energy structures found using the interatomic potentials, looking down the y (STO[010]) direction to show the atomic arrangements along z (STO[001]). We include only a small section of each simulation cell along x (STO[100]) to focus on the atomic configuration at the interfaces. The regions where atomic arrangement are shared are faded out in order to highlight the differences between these structures. Note that structure C* is the result of a simple local optimization of the idealized model, and is also found during search.

coordinated, and each cuboctahedron shares faces with adjacent ones. In fluorite structured CeO₂, Ce atoms are coordinated by eight oxygen atoms and coordination cubes share their edges. At the interface where 7 units cells of STO match to 5 unit cells of CeO₂, the stacking sequence of STO (001) planes (i.e. SrO-TiO₂-SrO-TiO₂) and CeO₂ (110) planes (i.e. CeO₂-CeO₂) ends abruptly. If the sequences were not disrupted, 7 oxygen atoms would be placed in the next layer of the terminal TiO₂ plane, which continues the vertex-sharing Ti-O octahedron network. In reality, there are 10 oxygen atoms in the adjacent CeO₂(001) plane. Similarly, it would have been 10 oxygen atoms in the next layer of the terminal CeO₂ plane, but only 7 adjacent oxygen atoms are present in the TiO₂ layer of STO (Figure 3b). Hence, the Ti atoms at the interface are over-coordinated and Ce atoms are under-coordinated. The latter is shown by the missing vertices of the Ce-O cube at the interface in Figure 3c. The mismatch of the bulk structure at the interface is mostly accommodated via the rearrangement of the oxygen sub-lattice, as highlighted by the rectangles in Figure 3ab. On the other hand, there is little distortion in the cation lattice at the interface, which
FIG. 3. Illustrations of Structure A that has the space group $Pc$. a) Viewing along the STO[010] direction. The glide plane is indicated by the dashed line. b) Viewing along the [001] direction. c) Distorted Ce-O$_8$ coordination polyhedron at the interface. Some of them have corners missing. Distortions of the Ti-O$_6$ octahedra are highlighted with rectangles in a) and b).

is consistent with the STEM images (shown in Figure 1abc), where visually there is little change of the atomic arrangement at the interfaces compared to the bulk. Note that the complex distortion of the anion lattice is missing in these images due to the relatively low atomic number of O atoms. This highlights the power of performing structure searching to reveal the full lattice information. The optimized initial model (structure $C^*$) has the space group $Pmm2$. Most of the structures found do not have any symmetry present at all, apart from a few at the low energy end of the distribution. Structure A has a glide plane parallel to the (001) planes with a translation of half of the lattice vector in STO[010] direction. This is marked by the dotted line in Figure 3a.

We next carry out DFT calculations on nine candidate structures and compare their relative energies with that given by the interatomic potentials. Our checks are limited to structures with six layers of materials on each side, due to the increasing computational costs with the cell size. In Figure 4, the energy differences per unit interface area ($\sigma_{rel} = E_{rel}/A_{itf}$) from DFT and interatomic potential calculations are plotted for comparison. In addition to the low energy structures, we include six structures with higher energy and label them
FIG. 4. Comparing the energy difference per unit area given by DFT ($\sigma_{\text{rel\text{DFT}}}^d$) and interatomic potentials ($\sigma_{\text{rel\text{pot}}}^d$). Structures are labeled by their name and symmetry. A positive correlation can be seen over the plotting range, indicated by the blue fitted line. On the other hand, there is little correlation when focused on the details over a small range, as shown in the inset.

as S1-6. A line is fitted to the data showing a positive correlation between the energies given by the two levels of theory over the plotting range. However, we find no correlation among the closely spaced low energy structures themselves, as shown in the inset of Figure 4. Structure E turns out to have the lowest energy given by DFT calculations, while it is 7 meVÅ⁻² higher in energy given by the interatomic potentials. In addition, A and B are two distinct structures found with the interatomic potentials, but they become the same after being optimized with DFT. It is known that empirical interatomic potentials can give more local minima. Ideally, we would like to search directly with DFT, but for a system as large as we consider here, it is prohibitively expensive to do so. The details of the PES are certainly different between these two levels of theory. Nevertheless, the trend over a relatively large energy range ($\approx 70$ meVÅ⁻²) is still captured by the interatomic potentials. The absence of correlations over a small energy range ($\approx 10$ meVÅ⁻²) means that it is necessary to refine a collection of structures with DFT calculations.

We compute the local strain for Ce atoms based on the averaged nearest neighbour
distances normalized by the mean value. The same is also done for STO using the Ti-Ti distances. In Figure 5b, each square represents a Ce column in structure E, and each triangle represents a Ti column, looking down the STO[010] direction. The sign of the strain alternates on each side of the interface going along the [001] direction. Tensile strained regions in CeO\textsubscript{2} are adjacent to compressively strained regions in STO. This strain field is quickly suppressed going into the bulk. Similar patterns also exist in other structures.

The interface can also influence the defect energy of oxygen vacancies. We calculate relative defect energies of oxygen vacancies in these structures using the interatomic potentials. A map of the relative formation energies in structure E is shown in Figure 5a. Here, oxygen sites are marked with circles, and the defect energy of bulk CeO\textsubscript{2} is chosen as the reference. All four atomic layers parallel to (010) planes of STO are included. The sizes of the circles are set according to their distances in the [010] direction, such that those further away appear smaller and may be overlapped by those in the front. A few sites at the interface have lower defect energy compared to that of the bulk, indicated by the dark green region in Figure 5a. We note that the existence of sites with very low defect energy suggests non-stoichiometric structures can become stable. However, it is challenging to perform the search with non-stoichiometric compositions since the interatomic potentials assume fixed ionic charges. The key point is that the mismatch in the crystal structure results in a complex energy landscape of the oxygen vacancies at the interface, which is likely to cause substantial trapping during vacancy migration.

We calculate the excess energy of the vertical interface using the approach of previous studies\textsuperscript{54,55}. More details can be found in the supplementary material. An excess energy of 0.91 J/m\textsuperscript{2} is found for structure E. Note that the excess energies for STO symmetrical grain boundaries vary in a range of 0.5-1.5 J/m\textsuperscript{2} depending on termination and orientation\textsuperscript{22–24}. Despite significant structural mismatch, the vertical interface is energetically similar to the grain boundaries. The variations of excess energies among the low energy structures is on the order of 3 meV/Å\textsuperscript{2} (0.05 J/m\textsuperscript{2}). The small differences mean multiple configurations are accessible at elevated temperatures, resulting in a disordered anion lattice.

Misfit dislocations are important for heterogeneous interfaces in thin films as they allow the interface strain caused by the mismatch in the lattice constants to be relaxed. In the lattice match epitaxial growth model, the growth starts with one-to-one lattice mismatching, followed by dislocation formation at the film surface. The dislocations then glide down to
FIG. 5. a) Relative defect energies of oxygen vacancies mapped in the x-z plane for structure E, viewed in the same direction as that of Figure 2. The circles represent oxygen positions. The reference is set to the oxygen vacancy energy of bulk CeO$_2$. b) Local strain of the Ce lattice in CeO$_2$ for the same view. Ce and Ti are labeled with squares and triangles respectively. The vacancy energy is related to the degree of distortion from the bulk lattice but not to the strain field. The two misfit dislocations are also marked in red at the interface.

The film-substrate interface. An extension of this model is domain matching epitaxy (DME) which applies when the mismatch in lattice parameter is so large that $m$ lattice planes of one side are matched to $n$ lattice planes of the other from the beginning of the growth$^{56}$, where both $m$ and $n$ are integers. In this work, 7 STO lattice planes match to 5 CeO$_2$ lattice planes along the [001] direction. This can be regarded as alternating 3/2 and 4/3 matches between the two sides, which is consistent with the DME model. We identify two misfit dislocations at the vertical interface and indicate them in Figure 5. They are consistent with the localized strain field, where CeO$_2$ is tensile strained and STO is compressively strained in the vicinity of each. However, the strongest distortion of the oxygen sub-lattice does not take place at the
cores of dislocations, but is instead located in between them. In addition, the reduction of vacancy energy can be associated with the distortion of the anion lattice, as shown in Figure 5a, rather than located at the dislocation cores as reported in other studies. One possible cause of this is that the dislocations are closely spaced (16 Å). The strongly distorted anion lattice, as we have here, is not predicted under the framework of misfit dislocations based on lattice geometry. This highlights the advantage of doing systematic structure searching for understanding heterogeneous interfaces.

We now discuss the implications of the structures we found on the ionic conductivity at the vertical interfaces. First, we found a strain field highly localized at the interface, as shown in Figure 5. The effect of strain in fluorite structured ionic conductors has been studied in previous experimental and theoretical works. The ionic conductivity is expected to increase when the lattice is subject to tensile strain due to the decrease of the migration barrier. However, these results apply to uniform or gradually decaying strain field. The situation is different here as the strain field is localized and microscopic. Furthermore, Sun et al. showed, through molecular dynamics, that the strain field caused by dislocations leads to segregation of the dopant ions in doped ceria. Dopant ions often have different ionic radii compared to the Ce$^{4+}$ ions, and by having them in the sites under local strain the elastic energy could be reduced. Both local enrichment and depletion of dopants are detrimental to the ionic conduction. The former increases the migration barrier as a result of stronger dopant-vacancy interactions, while the latter reduces the concentration of vacancies.

Second, by calculating the oxygen vacancy defect energies, sites with low relative defect energies are found at the interfaces. Once a vacancy diffuses into one of these sites, it is less likely to move out as the energy barrier of migration becomes much higher. As a result, the ionic conductivity is reduced locally. This is consistent with the work of Duholabhi et al. where the diffusivity at the STO-MgO interface was calculated using the kinetic Monte-Carlo method. It was found that vacancy mobility was lowered due to trapping sites originating from the network of misfit dislocations at the interface.

Third, the DFT energies of the low-energy structures are found to be very closely spaced. This indicates that the interface is less likely to take a single structure under a finite temperature. Such structural degeneracy mostly takes place in the anion lattice. While a disordered anion sub-lattice could lead to an enhancement in ionic conductivity, we note that for the
vertical interface this only takes place at the first interface layers of both sides. In addition, these disordered regions are confined, since they are separated by regions where atomic configurations are shared in many candidate structures, as illustrated in Figure 2. Hence, we do not expect this alone can enhance the ionic conductivity in the [001] direction.

In summary, we found a collection of lower energy structures of the STO(100)-CeO$_2$(110) vertical interfaces, including those with lower energies than that of the optimized hand-built model ($C^*$, Figure 2). A highly distorted anion lattice was determined at these interfaces arising from the structural mismatch. The excess energies of interfaces are of the same order of magnitude as high angle grain boundaries in STO. We found interface misfit dislocation models are insufficient to describe the complex landscape of vacancy defect energies and the localized strain field in the structures.

IV. CONCLUSIONS

Random structure searching is used to determine interface configurations of the SrTiO$_3$(100)-CeO$_2$(110) vertical interface which forms naturally in vertically aligned nanocomposite (VAN) thin films. Lattice information in STEM images is used to constraint the search space to interface terminations and orientations that are physically present. We find previously unknown structures with energies lower than that of a locally relaxed model built by hand ($C^*$ Figure 2). The interface excess energies of these structures are similar to that of high angle grain boundaries. We find a highly distorted oxygen anion lattices at the interfaces, while the cation lattice mostly remains similar to that of the bulk phases. The complex landscape of the defect energies is consistent with oxygen vacancies being trapped at the interface, rather than their mobility being enhanced. For the cation lattice, we find the strain field is non-uniform and is localized at the interface. Our findings provide a solid basis for further investigations on defect chemistry and migration of oxygen vacancies at the interface to reveal its effects on ionic conductivity. The structure searching approach can also be applied to other VAN systems showing a wide range of novel functionalities where the roles of vertical interfaces are not yet well understood.
V. SUPPLEMENTARY MATERIAL

See supplementary material for more details of the interatomic potentials, the pseudopotentials, interface structure searching and computing the excess energy.

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