AL-Hamadany R, Goss JP, Briddon PR, Mojarad SA, O'Neill AG, Rayson MJ.
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Journal of Applied Physics 2013, 113(22), 224108-1-224108-8.

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The following article appeared in: AL-Hamadany R, Goss JP, Briddon PR, Mojarad SA, O'Neill AG, Rayson MJ. Impact of tensile strain on the oxygen vacancy migration in SrTiO₃: Density functional theory calculations. *Journal of Applied Physics* 2013, 113(22), 224108-1-224108-8 and may be found at <http://dx.doi.org/10.1063/1.4809656>

DOI link to article:

<http://dx.doi.org/10.1063/1.4809656>

Date deposited:

29/07/2014

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Citation: *J. Appl. Phys.* **113**, 224108 (2013); doi: 10.1063/1.4809656

View online: <http://dx.doi.org/10.1063/1.4809656>

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Impact of tensile strain on the oxygen vacancy migration in SrTiO₃: Density functional theory calculations

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(Received 19 April 2013; accepted 23 May 2013; published online 13 June 2013)

Strontium titanate is a promising dielectric material for device applications including capacitors and gate dielectrics. However, oxygen vacancies, which are inevitable donor defects mobile under bias at room temperature, lead to undesirable leakage current in SrTiO₃ thin films. Epitaxially grown SrTiO₃ on lattice mismatched substrates leads to strained SrTiO₃, inducing structural phase transitions from a cubosymmetric non-ferroelectric geometry to tetragonal and orthorhombic structures, depending upon the sign of the strain. In this study, density functional calculations have been performed to determine the impact of isotropic biaxial tensile strain in a (001) plane upon the phase of SrTiO₃ and the activation energy for the migration of oxygen vacancies in such strained SrTiO₃. The phase transition of the host material yields anisotropy in oxygen vacancy diffusion for diffusion within and between planes parallel to the strain. We found a general reduction in the barrier for diffusion within and normal to the plane of tensile strain. The inter-plane diffusion barrier reduces up to 25% at high values of strain. The variation in the barrier corresponding to in-plane diffusion is smaller in comparison to inter-plane diffusion. Finally, we reflect upon how the interplay between lattice strain with native defects plays a crucial role in the conduction mechanism of thin film, strained SrTiO₃. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4809656>]

I. INTRODUCTION

The miniaturization of silicon-based integrated circuit components has rendered the native oxide insufficient as a gate dielectric, and an alternative effective material has been the subject of much research. Several binary (e.g., Al₂O₃, HfO₂, and TiO₂) and ternary (e.g., BaTiO₃ and SrTiO₃) high- κ dielectrics have been proposed¹ as alternatives to SiO₂. With its high permittivity of around 300 (Ref. 2) at room temperature, perovskite SrTiO₃ is a strong candidate. It has been established as a reliable gate dielectric,³ as well as showing potential for capacitive⁴ and resistive switching applications.^{5–8} Central to the performance of SrTiO₃ in these applications is the leakage current through the thin-films, which has been the subject of many experimental and modeling studies.^{8–12} As inevitable native defects, oxygen vacancies (V_O) have had particular attention, and it is widely thought that a combination of their donor properties and the relative ease with which they migrate is responsible for the electrical conductivity.^{8,10,13–15}

Quantum chemical based simulations^{16–20} have established electrical, electronic, and thermodynamic properties of V_O , properties which are challenging to unambiguously infer from experiment. In comparison with cation vacancies, V_O has a lower formation energy under reducing conditions,²⁰ and despite the uncertainty in the precise positions of the V_O electrical levels, it seems highly likely that

conduction in SrTiO₃ corresponds to the double donor activity predicted for V_O .^{19,21,22}

Possibly the most convincing experimental evidence for the electrical levels of V_O (Ref. 23) suggests it produces a relatively shallow donor state around 0.24 eV below the conduction band. With variation probably driven by the cell size and other computational parameters, different calculations predict the V_O donor level at different depths relative to the conduction edge.²⁴

Further to quantitative estimates of V_O energy levels, theoretical investigations produce reasonable predictions for the activation energy for diffusion, as compared to the range of values that have emerged from experiment. In SrTiO₃, the crystal structure can be viewed as containing six oxygen ions surrounding each Ti ion, and migration of V_O involves the motion of oxygen between any two of these sites, which are equivalent in unstrained SrTiO₃. Isotopic diffusion²⁵ and anelastic scattering²⁶ yield estimated V_O migration barriers of 0.60 and 0.98 eV, respectively, much lower than the estimates for the values for Ti and Sr vacancies of 3.30–4.90 eV and 2.80–4.00 eV, respectively.^{27–29} Computational estimates for V_O migration^{16,17,20,24,30,31} deliver a range 0.40–0.90 eV.

Biaxial strain imposed by the substrate is a major factor affecting the structural and electronic properties of perovskites.^{32–36} Depending upon whether the substrate has a lattice constant that is smaller or larger than SrTiO₃, the strain in the SrTiO₃ film would be either compressive or tensile, respectively. The lattice matching of a SrTiO₃ thin film to underlying substrate imposes the in-plane lattice

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parameters of the substrate upon the oxide, potentially inducing a phase transition in the thin film. For example, bi-axial tensile strains of around 2.2% (Pt),³⁷ 3.4% (Cr),³⁷ 4.4% (Au),³⁸ and 8% (TiN) (Ref. 2) might be considered. Both tensile and compressive strains alter the dielectric response and tunability of SrTiO₃.³⁹

The impact of bi-axial *compressive* strain within a (001)-plane on the diffusion of V_O has been recently documented by us, and substantial variations in the barrier relative to the value of strain were identified,³¹ in which the V_O in-plane migration barrier was found to reduce by 50%. It is important to note that the structural phase of SrTiO₃ under *tensile* strain is entirely different from that of compressive case. It is therefore essential that the impact of tensile strain upon V_O migration is established, and it is this which forms the focus of the current paper. In particular, a key aim of this study is to determine whether tensile strain has a comparable impact to that of compressive strain in terms of V_O migration in strained SrTiO₃, since that both types of strain exist in practice in SrTiO₃ thin film. We shall show in fact that the diffusion behavior of V_O in tensile strained material is quite different from that in the compressive strain regime, so that a choice of substrate might be gagged not only in terms of electronic compatibility but also in terms of the impact upon the injection or otherwise of V_O, a key electrical center.

II. COMPUTATIONAL METHOD AND MODELS

The calculations of oxygen vacancy migration in strained SrTiO₃ were executed within spin-polarized density functional theory (DFT) within the local density approximation,⁴⁰ as implemented within the AIMPRO code.^{41,42} Recent reviews for SrTiO₃ (Ref. 33) and ZnO (Ref. 43) support the use of density functional theory and the local density approximation in assessing of trends with respect to strain. Norm-conserving pseudopotentials were used to represent the core electrons,⁴⁴ where the valence sets are taken to be $4s^2 4p^6 5s^2$, $3s^2 3p^6 3d^2 4s^2$, and $2s^2 2p^4$, for Sr, Ti, and O, respectively.

Kohn-Sham eigen-states are expanded using an atom-centered Gaussian basis functions⁴⁵ as follows: Strontium is treated using five independent sets of *s*- and *p*-Gaussians, yielding 20 functions per atom. Titanium and oxygen are represented using four sets of *s*-, *p*-, and *d*-Gaussians yielding 40 functions per atom. Matrix elements of the Hamiltonian are determined using a plane wave expansion of the density and Kohn-Sham potential⁴⁶ with a cutoff of 300 Ry, which yields well converged total energies with respect to this parameter. The same approach has been successfully used to investigate⁴⁷ the impact of water adsorption on SrTiO₃.

The strained bulk SrTiO₃ has been simulated utilized a $2 \times 2 \times 2$ superlattice of the 5-atoms primitive cell. The lattice has the formula Sr₈Ti₈O₂₄ and lattice vectors of $2[a00]$, $2[0a0]$, and $2[00a]$. In the modeling of V_O, we have used supercells consisting of 32 and 64 formula units, so that for oxygen deficient structures the supercells are Sr₃₂Ti₃₂O₉₅ and Sr₆₄Ti₆₄O₁₉₁. The strained SrTiO₃ supercells used for V_O have lattice vectors of $[a\bar{a}\bar{c}]$, $[\bar{a}ac]$, and $[\bar{a}\bar{a}c]$ for the 160 atom cells, and $4[a00]$, $4[0a0]$, and $4[00c]$ for the 320 atom

cell. Here, *a* and *c* are the lattice parameters in the underlying tetragonal unit cell and $a=c$ in unstrained cubic-symmetric lattice.

Our computational approach yields an equilibrium lattice parameter for bulk (unstrained) SrTiO₃ of 3.87 Å, which is in line both with previous calculations⁴⁸ and experiment.⁴⁹

To conform to the substrates, we assume an isotropic strain so that the resulting unit cell geometry of the SrTiO₃ is tetragonal, with an in-plane lattice constant of *a* equal to that of the substrate, and a perpendicular lattice constant, *c* chosen to minimise the total energy under the in-plane constraint. Strains of up to 3% are typically simulated in SrTiO₃,^{33,39,50} but higher values are often modeled, with values exceeding 10%⁵¹ being recently analyzed. In order to cover the wide range of lattice mismatch between SrTiO₃ and typical substrate materials yielding a tensile strain, we have explored four values of bi-axial tensile strain within the (001) plane of SrTiO₃: in addition to unstrained material, values of tensile strain of 2%, 4%, 6%, and 8% have been studied. The (001) biaxial-strain breaks the symmetry of the otherwise cubic SrTiO₃, rendering different oxygen sites inequivalent. It then becomes convenient to distinguish oxygen atoms as lying in a (001) plane where the metal ions are entirely Ti or Sr. The lattice distortion also means that there are several distinct diffusion paths, all of which must be examined in order to fully characterize the diffusivity of V_O in strained SrTiO₃.

As is common practice in electronic structure calculations, the total energy is determined by sampling the Brillouin-zone,⁵² and for quantitative reliability, it is of crucial to establish convergence regarding both cell size and sampling scheme. We showed previously³¹ that zone-center sampling yields quantitatively inaccurate diffusion energies in cells as large as 64 formula units. However, sampling with a single point at the zone edge yields energies converged to 10 s of meV relative to $2 \times 2 \times 2$ meshes in both the 160 and 320 atom cells. We have therefore adopted the same approach in terms of both cell size and sampling in this study as in our previous paper.³¹

Migration barriers are estimated using climbing nudged elastic bands (NEB).^{53,54} All the energy barriers in this study were optimised until forces on each image are less than 10^{-4} a.u. A minimum of nine images was used, with the convergence of the saddle point energy with respect to the number of images being established in each case.

III. RESULTS AND DISCUSSION

In line with recent theoretical investigations,^{33,39} the structural distortion and phase transition in SrTiO₃ are found to respond sensitively to bi-axial tensile strain. As shown schematically in Fig. 1, biaxial tensile strain in a (001)-plane shifts the oxygen ions relative to the cation sub-lattices. These displacements yield a ferroelectric tetragonal phase with polarization along [110].

The structural and energetic analysis of ferroelectric polarized SrTiO₃ induced by strain is listed in Table I. The displacements of the oxygen ions along [100] and [010] ($d_{[100]}$ and $d_{[010]}$ in Fig 1(b)) are identical. The impact upon

FIG. 1. Schematics of (a) the (001) projection of centrosymmetric unstrained SrTiO₃, (b) tetragonal SrTiO₃ with bi-axial tensile strain within (001)-plane, showing the displacements $d_{[100]}$ and $d_{[010]}$ in the oxygen sub-lattice, and (c) bi-axially strained SrTiO₃ indicating the sequence of TiO₂ and SrO (001)-planes parallel to the plane of tension. The oxygen sites 1–4 are within same TiO₂ (001)-plane, and sites 5 and 6 are within the adjacent SrO (001)-plane.

the energy under strain is characterized by two values, which are also indicated in Table I: E_1 is the increase in energy per formula unit relative to the unstrained form, and E_2 is the energy reduction between the centrosymmetric and polarized structures under strain, indicating the stabilization due to the phase transition.

Referring to Fig. 1(c), there are two (001)-planes for V_O diffusion, viz SrO and TiO₂ planes. The distance between adjacent sites in SrO planes (ions 5 and 6 in Fig. 1(c)) suggests diffusion entirely within these planes is unlikely. This is confirmed by calculations³¹ (unstrained SrTiO₃) which shows the V_O diffusion barrier in SrO planes is 4.18 eV, around five times greater than that in the TiO₂ planes at 0.81 eV. Based upon this observation, in-plane diffusion in this study has been confined to diffusion entirely within TiO₂ planes. The calculated migration barrier of 0.81 eV for the neutral V_O is within the range of previously reported theoretical^{17,30} and experimental⁵⁵ values. As alluded to in the introduction, V_O is understood to be a double donor, and it is predicted that there are three thermodynamically stable charge states, which may then diffuse with different activation energies.³¹ Given that V_O diffusion may be further affected by an applied electric field, such as in a capacitive device element, it is therefore imperative that all three charge state (neutral, +1 and +2) are examined explicitly. In the absence of applied strain, the activation energy for diffusion of charged V_O has also been examined, with migration

barriers of 0.74 eV and 0.77 eV for the +1 and +2 charge states, respectively. The relatively higher mobility of the ionized vacancy has support from experiment.⁵⁶

A. In-plane V_O migration

The strain-induced shift in the oxygen positions yields anisotropy in the diffusion step within a TiO₂ (001) plane. Figs. 1(c) and 2 indicate the oxygen ions can be categorised into two groups: those (ions 1 and 4) bonded to titanium ions along [010], and those (ions 2 and 3) along [100]. Despite the distortion, all oxygen atoms within the plane remain equivalent. For a complete in-plane diffusion process each oxygen vacancy should pass any consecutive pair of steps indicated in Fig. 2, where the Δ_{1-3} and Δ_{2-4} step are equivalent.

1. Path Δ_{1-2}

The V_O in-plane migration barrier along Δ_{1-2} as a function of strain is plotted in Fig. 3. There is clear reduction in the migration barrier, being 37% at 6% strain. The general trend in decreasing of the migration barrier in this step can

FIG. 2. Projection the TiO₂-(001) plane showing the V_O in-plane diffusion steps, Δ_{1-2} , Δ_{1-3} , Δ_{2-4} , and Δ_{3-4} . Δ_{1-3} and Δ_{2-4} are equivalent. Ti ions are labeled, with the remaining sites being oxygen.

TABLE I. Calculated parameters for isotropic bi-axial (001) tensile strained SrTiO₃. $d_{[100]}$ ($=d_{[010]}$) (Å) is the displacement of the oxygen ions along [100] (and [010]) relative to Ti and Sr. $(c/a)_{FD}$ is the equilibrium ratio obtained for the ferroelectric distorted structures under strain. Relative energies per formula unit (meV) are calculated relative to cubic, unstrained SrTiO₃ (E_1), and relative to biaxially strained, centro-symmetric SrTiO₃ (E_2). $(c/a)_{CS}$ is the equilibrium ratio for the cubo-symmetric phase.

Strain %	$d_{[100]}$	$(c/a)_{FD}$	E_1	E_2	$(c/a)_{CS}$
2	0.12	0.97	36	-20	0.97
4	0.19	0.94	133	-79	0.94
6	0.24	0.91	261	-196	0.92
8	0.30	0.89	295	-263	0.90

FIG. 3. In-plane V_O migration barrier as a function of isotropic, (001) biaxial tensile strain, for path Δ_{1-2} (Fig. 2), each panel showing the results for a different charge state.

be explained as resulting from the geometric changes, as follows. As the strain increases, each oxygen ion remains approximately the same distance from one of its Ti neighbors, with the distance to the other increasing commensurate with the dilation of the lattice. The interaction with the more distant Ti site weakens, so that to reach the saddle point in the Δ_{1-2} step requires the breaking of an increasingly weakened bond, reducing the barrier height with increasing strain. Above 6% strain, the change in structure was found to be offset by the increase in distance between the oxygen ions, leading to the relatively modest change in barrier height between 6% and 8% strain.

2. Paths Δ_{1-3} and Δ_{2-4}

Fig. 4 shows plot of migration barrier as a function of strain for the two equivalent steps, Δ_{1-3} and Δ_{2-4} . Despite small variations with strain and charge state, the plot shows that for this portion of the diffusion path, the barrier varies much less than Δ_{1-2} . Perhaps more critically, the magnitude of the barriers in these steps is generally higher than along Δ_{1-2} .

3. Path Δ_{3-4}

The variation in the V_O migration barrier along Δ_{3-4} as a function of strain and charge state is plotted in Fig. 5.

FIG. 4. In-plane V_O migration barrier as a function of isotropic, (001) biaxial tensile strain, for path Δ_{1-3} (Fig. 2), each panel showing the results for a different charge state.

FIG. 5. In-plane V_O migration barrier as a function of isotropic, (001) biaxial tensile strain, for path Δ_{3-4} (Fig. 2), each panel showing the results for a different charge state.

There is general and substantial increase in barrier with increasing strain for all charge states, suggesting that diffusion along this step is rendered unfavorable under such strain conditions. The increase in barrier height most probably originates from the relatively large distance between the two sites between which the step transits.

B. Inter-plane V_O migration

For inter-plane migration, i.e., diffusion with a component of displacement perpendicular to the plane of strain, oxygen sites along [011] and [101] are involved in addition to the sites within the (001) TiO_2 planes. As a consequence of the structural distortions, V_O inter-plane migration involves two distinct steps, classified in Fig. 6. There is no distinction between migration within paths approximately within (100) or (010) planes.

As was the case previously found³¹ for compressively strained SrTiO_3 , locating V_O in a SrO plane is energetically unfavorable. The energy difference between V_O in the TiO_2 and SrO planes grows monotonically with increasing biaxial strain up to 6%, with the magnitudes showing only a very weak dependence on charge state. However, at 8% the

FIG. 6. Schematic view showing the four inter-plane migration steps labeled Δ_{3-5} , Δ_{3-6} , $\Delta_{5-3'}$, and $\Delta_{6-3'}$. Δ_{3-5} and Δ_{3-6} represent V_O diffusion from the TiO_2 (001)-plane to the adjacent SrO (001)-plane, and diffusion from the SrO (001)-plane to the next TiO_2 (001)-plane are represented by $\Delta_{5-3'}$ and $\Delta_{6-3'}$.

FIG. 7. (a) V_O inter-plane migration NEB profile for the V_O migrating along the path indicated in (b) for 4% strain. (b) shows schematic views for V_O migration between two TiO_2 -planes (sites 1 and 3) via a SrO -plane (site 2). Both diagrams represent processes indicated as Δ_{3-5} followed by $\Delta_{5-3'}$.

behavior is different, showing a marked charge dependence, which we shall return to shortly.

Based upon our calculated structures, we suggest that the variation between charge states originates from the local structural distortion the V_O in SrO (001)-plane but is a consequence of the impact of strain upon the spacing between TiO_2 (001)-planes. As strain increases, the inter-layer

separation decreases: Ti ions in (001) planes separated by a single SrO plane get closer. Then, upon removal of an oxygen ion from this SrO -plane, the nearest-neighbor Ti -ions experience an electrostatic repulsion, and they move apart. In the neutral charge state, the donor electrons partially screen this repulsion, and the distortion is weak and distributed over a number of sites. In the fully ionized form, the screening is

FIG. 8. Calculated inter-plane V_O migration barriers as a function of in-plane biaxial tensile strain for diffusion along Δ_{3-5} (diamonds) and $\Delta_{5-3'}$ (triangles), with (a), (c), and (e) representing neutral, +1, and +2 charge states, respectively. For the Δ_{3-6} (open circles) and $\Delta_{6-3'}$ (squares) the neutral, +1, and +2 charge states are plotted in (b), (d), and (f), respectively. The paths are shown in Fig. 7. In each plot, the filled circles represent the energy difference between V_O in the TiO_2 and SrO planes, equal to the difference in the forward and reverse barrier heights.

absent, and the distortion we find is larger, and more localized to the two Ti ion sites. The +1 charge state has a geometric response intermediate between the two extremes.

We now turn to the different diffusion paths. Starting with V_O within a TiO_2 plane, the first migration step is from one of the four in-plane sites to an oxygen site within the next SrO-plane. The second step is to any site in the next TiO_2 plane. However, care must be taken to explore all non-equivalent paths to determine the minimum energy route.

For V_O as a missing oxygen ion along [100] relative to the nearest Ti sites, the first inter-plane step is either along [101] (Δ_{3-6} in Fig. 6) or $[\bar{1}01]$ (Δ_{3-5}). The next step, i.e., the step that takes V_O to a new TiO_2 layer, may again be either of these types of step, and the equivalence of the path components means that just two barriers are required for each strain and charge state. The full migration profile for the case of 4% strain, neutral charge state is presented as an illustrative example in Fig. 7.

In detail, the processes considered are as follows. Starting with the V_O at site 3, the two possible steps are either Δ_{3-5} or Δ_{3-6} to end with V_O at site 5 or site 6. V_O may then either reverse the step (no net diffusion), step back to the initial TiO_2 plane but to a different oxygen site (representing an in-plane diffusion process), or diffuse along either $\Delta_{5-3'}$ or $\Delta_{6-3'}$ to complete full inter-plane diffusion process.

The inter-plane V_O migration barriers as a function of bi-axial (001) tensile strain and charge state are plotted in Fig. 8. From the relatively weak strain dependence of the barrier heights up to 6%, we conclude that inter-plane diffusion is not significantly impacted. However, a couple of general points may be made. First, in the neutral charge state, the diffusion barriers in the two directions (Δ_{3-5} and Δ_{3-6}) have numerically indistinguishable barriers. This arises because although the paths are symmetrically distinct, the saddle points are not. The second point is that the barriers vary more in the Δ_{3-6} direction than along Δ_{3-5} , with the former showing a general reduction of 0.1–0.2 eV over the full range of strain considered. The reason for the reduction along the Δ_{3-6} path relates to the argument made in Sec. III A 1 for the reduction in the barrier for in-plane diffusion, in that V_O is migrating between two sites most closely associated with a single Ti site. Thus, despite the Δ_{3-5} path being shorter than the Δ_{3-6} path, it is the latter that is more favorable.

We now turn to the more dramatic variation found at 8% strain. Under these conditions, even for the neutral charge state, the Δ_{3-5} and Δ_{3-6} paths are distinct. This arises from an additional delocalised structural, bulk-like, distortion stabilized by the presence of the vacancy. This distortion

combines with the geometric effects outlined above, relating to the screening of the interaction between the Ti ions where V_O lies in the intermediate SrO-plane. For the neutral charge state, the delocalized distortion at 8% stabilizes this metastable structure (a decrease in the filled circles in Fig. 8), whereas for the +2 charge state it does not, and the +1 lies somewhere between these limits.

IV. DISCUSSION AND CONCLUSIONS

In our previous study examining compressive strain, we predicted³¹ a high degree anisotropy in diffusion, with in-plane diffusion significantly enhanced, and inter-plane suppressed.

In order to determine whether a comparable effect is present in the current study of tensile strain, it is necessary to determine the most effective route both in-plane and inter-plane.

In-plane V_O diffusion process may occur entirely within a single TiO_2 (001)-plane, or as described in Sec. III B, by alternating between TiO_2 and SrO (001)-planes. The two paths are indicated in Figs. 9(a) and 9(b), with the rate limiting step indicated in each case. These are Δ_{1-3} for diffusion entirely within a TiO_2 (001)-plane and Δ_{3-5} for diffusion involving a SrO plane.

The barrier height of the rate-limiting step is listed in Table II as a function of charge and strain. For strains up to 6%, in-plane diffusion involving SrO planes is energetically more favorable, and only at 8% is diffusion entirely within TiO_2 plane dominant.

In the inter-plane diffusion, the process is less complicated as it is controlled by Δ_{3-6} as the rate limiting step, the path being indicated in Fig. 9(c). Comparing the barriers for this step with the minimum values for in-plane diffusion via either path, it can be seen that the general trend is that under bi-axial tensile strain, the V_O diffuses more readily in the direction perpendicular to the plane of tension.

One of the most significant findings to emerge from the current study is that diffusion both in-plane and inter-plane is predicted to increase under tensile strain: the barriers decrease in both directions, with the inter-plane diffusion increasing more rapidly as a function of applied strain, that is the case for in-plane diffusion.

Importantly, this behavior is quite different from the outcome of our previous study for compressively strained $SrTiO_3$.³¹ One might have assumed that the impact upon diffusion would simply be reversed when the sign of the in-plane strain is reversed, which would logically suggest that

FIG. 9. Schematic views of V_O diffusion process for (a) in-plane diffusion completely within TiO_2 (001)-plane. (b) in-plane diffusion involving both TiO_2 (001) and SrO (001) planes. (c) The inter-plane diffusion. The long Ti-O bonds along [100] and [010] directions are highlighted with yellow colors. The red arrows point to the rate limiting step for each diffusion process.

TABLE II. Diffusion barriers for the rate limiting steps for the in-plane and inter-plane paths shown in Fig. 9. For in-plane, the values in parentheses refer to path (b). For each value of strain, the value in bold face indicates which in-plane path ((a) or (b)) is lower in energy, and the underline indicates which of (a), (b), or (c) has the lowest barrier. The unstrained values are included for comparison.

Strain %	In-plane			Inter-plane		
	Neutral	+1	+2	Neutral	+1	+2
0	0.81(0.81)	0.74(0.74)	0.77(0.77)	0.81	0.74	0.77
2	0.73(0.71)	0.78(0.77)	0.85(0.78)	<u>0.71</u>	<u>0.72</u>	<u>0.70</u>
4	0.69(0.68)	0.75(0.70)	0.78(0.73)	0.69	<u>0.66</u>	<u>0.64</u>
6	0.72(0.71)	0.75(0.73)	0.79(0.74)	0.72	<u>0.69</u>	<u>0.63</u>
8	0.69 (0.75)	0.75 (0.78)	0.73 (0.80)	<u>0.63</u>	<u>0.63</u>	<u>0.58</u>

in-plane diffusion under tensile strain might be suppressed. However, this is not the case. Most likely due to the change of phase under tensile strain, in-plane diffusion is predicted to increase under both tensile and compressive strains!

In summary, as a key factor leading to resistive switching and undesirable leakage current mechanisms in SrTiO₃ thin films, V_O migration under interfacial (001) bi-axial tensile strain has been investigated utilizing density functional theory calculations. Structural distortion in the underlying crystal structure of SrTiO₃ driven by the biaxial strain has been included. The subsequent phase transition involving displacement of oxygen sub-lattice relative to the Ti and Sr sub-lattices yields anisotropy in both in-plane and inter-plane V_O diffusion trajectories.

A modest reduction in the barrier has been found in comparison to that determined for compressive strain.³¹ The barrier for diffusion exhibits a general decrease with increasing tensile strain, with inter-plane diffusion decreasing more rapidly than in-plane. In contrast to the findings for compressive strain³¹ where the diffusion barriers significantly diverge between in-plane and inter-plane, under (001)-biaxial tensile-strain the diffusion of V_O is predicted to increase in all directions, albeit more so in the direction perpendicular to the plane of strain.

Finally, based upon the predicted impact of both compressive and tensile bi-axial strain within (001) plane upon V_O diffusion in epitaxial SrTiO₃ films, we conclude that compressive strain is a potential route for limiting injection of electrically active V_O centers, whereas tensile strain enhances diffusion in this direction, which may be advantageous in resistive switching devices.

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