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Fundamentals of Energy Materials: A Theoretical Perspective

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Introduction

→ STO film is full of defects, especially those parallel to the growth direction

→ High density of misfit dislocations

¹M. J. Zhuo *et al.*

²Z. Bi *et al.*

³Y Zhu, C. Song, A.M. Minor, and H. Wang, *Microsc. Microanal.* **19**, 706 (2013).

⁴F. Gao, C.M. Wang, S. Maheswaran, and S. Thevuthasan, *NIM B* **207**, 63 (2003).

Motivation

Ion Irradiation Experiment

260 KeV, 0.5 dpa to 3 dpa
298 K, $1 \times 10^{15} \text{ Ne}^{++}/\text{cm}^2$ to $1 \times 10^{16} \text{ Ne}^{++}/\text{cm}^2$

→ TEM characterization of 1 dpa irradiated STO/MgO(001) sample

→ Arrows point out amorphization region on STO(011) grains

STO/MgO Interface

Experimentally observed orientations

SrO-terminated

TiO₂-terminated

Mg → Gold
Sr → Green
Ti → Blue
O → Red

→ STO (110) < 575 °C

→ 575 °C > STO (110), (100) < 750 °C

→ STO (100) > 750 °C

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Complexity with STO (110) termination*

FIG. 1. (Color online) Side view of a TiO_2 -terminated BaTiO_3 (001) surface with the definitions of the surface rumpling s and the near-surface interplanar distances d_{12} and d_{23} , respectively.

Stoichiometric STO

FIG. 2. (Color online) Side views of slab geometries used to study BaTiO_3 (011) surfaces. (a) Stoichiometric eight-layer slab with O_2 -terminated and BaTiO -terminated surfaces at top and bottom, respectively. (b) Seven-layer slab with O-terminated surfaces. (c) Seven-layer slab with TiO -terminated surfaces. (d) Seven-layer slab with Ba-terminated surfaces.

* Eglitis *et al.* Phys. Rev. B, 76, 155439, (2007).

STO (011)
MgO (001)

Stoichiometric polar surface

$\begin{pmatrix} 011 \\ 001 \end{pmatrix}$

Stoichiometric non-polar surface

$\begin{pmatrix} 011 \\ 001 \end{pmatrix}$

TiO₂ terminated

SrO terminated

Mg → Gold
Sr → Green
Ti → Blue
O → Red

Computational Methodology

- Pair potentials* of the Buckingham form used:

$$E_{ij} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

where A , ρ , and C are the potential parameters. Coulombic interactions are included.

- LAMMPS used for atomic relaxation and energy minimization
- Forces relaxed $\sim 10^{-10}$ eV/Å
- To explicitly incorporate misfit dislocations, large cells with ~ 15000 atoms used for simulations

* G. Busker, A. Chroneos, and R.W. Grimes, *J. Am. Ceram. Soc.*, **82** [6], 1553 (1999).

Results

Minimized STO/MgO Interface (SrO terminated)

32 STO units

30 MgO units

Mg Gold
Sr Green
O Red
Ti Blue

Interface layer stacking

- Mismatch $\sim 7.69\%$

- $1/\delta = a_{\text{STO}}/(a_{\text{MgO}} - a_{\text{STO}}) = 14 \text{ or } 15$
in order to ensure a completely compensated misfit and to be free from any long range strain

Disregistry

$$\Delta \mathbf{u} = \mathbf{u}^+ - \mathbf{u}^-$$

Vector comprising
relative displacements
on each side of the
slip plane

STO/MgO interface layers

Two
coherent
regions

$$d_{\text{dis}} \sim 2.7-2.8 \text{ nm}$$

Mg Gold
Sr Green
O Red (STO)
O Blue (MgO)

Top view from STO

$$d_{\text{dis}} = |b| a_{\text{sub}} / (a_{\text{film}} - a_{\text{sub}})$$

STO/MgO interface (TiO₂ terminated)

$$d_{\text{dis}} = |b| a_{\text{sub}} / (a_{\text{film}} - a_{\text{sub}})$$

$$d_{\text{dis}} \sim 2.8 \text{ nm}$$

Disregistry

STO/MgO interface layers

Two different regions

$d_{\text{dis}} \sim 2.7\text{-}2.8 \text{ nm}$

Top view from STO

Mg - Gold
O - Red (STO)
O - Green (MgO)
Ti - Blue

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Relative oxygen defect formation energy

→ Energies shifted so that 0 eV corresponds to most stable

→ Oxygen vacancies exhibit a thermodynamic preference to reside in STO as compared to MgO

→ Oxygen vacancies show stronger tendencies to exist in the vicinity of misfit dislocations

Mg
O
Sr
Ti

Relative oxygen defect energies (SrO)

Interface layer STO

Interface layer MgO

→ Residence of oxygen vacancies is contingent on different coherent regions

Relative oxygen defect energies (TiO₂)

Interface layer STO

Interface layer MgO

→ Misfit dislocations and neighborhood regions are potential sinks for oxygen vacancies

STO (100)
MgO (100)

Generalized stacking fault energy for coherent STO/MgO interface (SrO terminated)

STO (100)
MgO (100)

Generalized stacking fault energy for coherent STO/MgO interface (TiO_2 terminated)

Conclusions

- Structures of misfit dislocations at the STO/MgO interfaces are contingent not only on the orientation, but also on the termination layer of STO.
- For certain orientations, multiple stacking are possible leading to different types of coherent regions of the interface.
- Misfit dislocations and their neighborhoods could act as potential sinks for oxygen vacancies.
- Work focusing on examining defect (vacancies and interstitials) energetics at various interfaces **is in progress**.

CeO₂/SrTiO₃ film

- Significant research efforts have been focused on ceramic oxides and ceramic-ceramic composites to identify materials that have the potential to mitigate radiation damage
- Ceramic oxides that can inherently accommodate lattice disorder are prime candidates for radiation tolerant materials as they show improved amorphization resistance¹
- Applications not limited to radiation tolerant materials
- Perovskite-fluorite composites are used as advanced cathodes in SOFCs and oxygen separation membranes. Here, the perovskite-fluorite interfaces are pathways for fast oxygen diffusion²
- Used as buffer layer for thin film deposition (superconductors³, TWC⁴, microwave applications⁵ etc.

¹ Sickafus et al. *Nat. Mater.* **6**, 217 (2007).

² Sadykov et al. *J. Euro. Ceram. Soc.* **33**, 2241 (2013).

³ Fabbri et al. *Sci. Technol. Adv. Mater.* **11**, 054503 (2010).

⁴ Overbury et al. *J. Vac. Sci. Technol. A* **15**, 1647 (1997).

⁵ Petrov et al. *J. Appl. Phys.* **84**, 3134 (1998).

Computation methodology (DFT)

- DFT+ U calculations performed using Vienna Ab initio Simulation Package (VASP)
 - + U accounts for localization of f and d orbitals
 - $U_{\text{eff}} = 5$ eV for Ce (4 f electrons in Ce)*
 - $U_{\text{eff}} = 4.2$ eV for Ti (3 d electrons in Ti)**
 - Plane wave cut-off energy = 400 eV
 - The configurations of Ce 5 s 5 p 6 s 5 d 4 f , O 2 s 2 p , Ti 3 d 4 s and Sr 4 s 4 p 5 s are treated as valence electrons

* P. P. Dholabhai, J. B. Adams, P. A. Crozier, and R. Sharma, *J. Chem. Phys.* **132**, 094104 (2010).

** Z. Hu and H. Metiu, *J. Phys. Chem. C* **115**, 5841 (2011).

CeO₂/STO interface minimized using DFT+U

- O_{vac} in STO favorable by ~1.5 eV as compared to CeO₂

Interface structure

O_{vac} in STO

O_{vac} in CeO₂

Minimized CeO_2 /STO interface (Atomistics)

CeO_2 →

STO →

CeO_2 →

Stepped interface
(mixed termination)

TiO_2 -terminated

SrO-terminated

Ce → Yellow	O → Red
Sr → Green	Ti → Blue

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TiO₂-terminated interface

SrO-terminated interface

Relative O_{vac} formation energy

Electrostatic potential (mixed termination)

Mixed
termination

Data shifted so that
the lowest potential
site is at 0 V

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Relative Ce, Sr, and Ti vacancy formation energy

- Energies shifted $\rightarrow 0$ eV = most stable
- Ce_{vac} , Sr_{vac} , and Ti_{vac} formation near the the steps is favorable than bulk

attraction

Relative O_{vac} formation energy

Energy (eV)

Side view

Distance (Å)

repulsion

- O_{vac} prefers STO over CeO_2
- Thermodynamic preference of O_{vac} to reside in STO is verified by DFT+U
- O_{vac} are attracted near one step, whereas repelled at the other (electrostatic effects and different strain near the steps)

Behavior of vacancies

CeO_2
 SrO
 TiO_2

Ce_{vac}
 O_{vac}
 Sr_{vac}
 Ti_{vac}

- Black line represents the stepped interface
- Short arrows indicate the flow of "**vacancies**" near the stepped interface
- Long arrows indicate the flow from one phase to other

- O_{vac} are attracted towards Steps 1 and 2 whereas they repel from Steps 3 and 4
- Ce_{vac} , Sr_{vac} , and Ti_{vac} are attracted towards Steps 3 and 4 whereas they repel from Steps 1 and 2

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Relative energies of interstitials

attraction

- Energies shifted $\rightarrow 0$ eV = least stable
- Ce_{int} and O_{int} are more favorable near the the steps compared to bulk
- Ce_{int} prefer STO, whereas O_{int} prefer CeO_2

Relative energies of interstitials

attraction

- Sr_{int} and Ti_{int} are more favorable near the steps compared to bulk
- Sr_{int} and Ti_{int} prefer STO

Behavior of interstitials

CeO_2
 SrO
 TiO_2

Ce_{int}
 O_{int}
 Sr_{int}
 Ti_{int}

- O_{int} are attracted towards Steps 1 and 2 whereas they repel from Steps 3 and 4
- Ce_{int} , Sr_{int} , and Ti_{int} are attracted towards Steps 3 and 4 whereas they repel from Steps 1 and 2
- Ce_{int} , Sr_{int} , and Ti_{int} prefer STO, whereas O_{int} prefer CeO_2

Implications for radiation damage evolution

- Two key factors: (i) Interaction of isolated point defects with the interface (ii) Defect mobilities
- Thermodynamic preference of the respective defect to exist in either CeO_2 or STO, however defects can only flow from one phase to another if the defect kinetics are fast
- Interstitials are more mobile than vacancies at most T. Hence, at low T, interstitials that reach the interface will not recombine with vacancies leading to defect accumulation at the interface
- For the present case, the Sr_{int} and Ti_{int} prefer STO phase. Irrespective of Sr_{int} and Ti_{int} diffusion towards the interface, if Sr_{vac} and Ti_{vac} cannot reach fast enough, recombination may not occur
- Previously, for titanate perovskites, amorphization has been attributed to the defect pileup at the interface