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Interfacial radiation damage resistance in oxide thin film heterojunctions: An atomic perspective

**M. Sassi¹, T. Kaspar¹, L. Shao²,
J. Gigax³, V. Shutthanandan⁴,
K. M. Rosso¹, and S. R. Spurgeon⁵**

¹Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA

²Department of Nuclear Engineering, Texas A&M University, College Station, TX 77843, USA

³Los Alamos National Laboratory, Los Alamos, NM 87545, USA

⁴Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354, USA

⁵Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA

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Radiation-Induced Defect Formation in Oxides Impacts a Range of DOE Research Areas

Nuclear Fuel Cycle

In-Core Sensors
DOE-NE

Aerospace

Device Performance
DOE-BES

Electronics

Ion Interactions
DOE-BES

Focus on Pyrochlores ($A_2B_2O_7$)

❑ Example of use and applications:

- Oxidation catalysts
- Thermal barrier coating
- Immobilization of actinides from spent nuclear fuel

❑ Exposition to extreme environment:

- Microstructure evolution
- Phase transitions
- Degradation of physical and chemical properties

❑ Understand of the response of pyrochlores:

- Electron, ion or pulsed laser irradiation experiments

❑ Amorphization:

- Internal radiation (actinide α -decay)
- External ion-irradiation

Local Evolution of Ion-Irradiation-Induced Amorphization

□ Experimental observations upon 1 MeV Zr⁺ irradiation:

- Amorphization of film observed before the substrate
- Appearance of a crystalline band at the film/substrate interface

Local Evolution of Ion-Irradiation-Induced Amorphization

□ Focus on the interfacial changes (PACBED analysis):

Before irradiation

After irradiation at 4 dpa

- The interface remains crystalline even at 4 dpa

Evolution of Interface Composition

□ EDS analysis:

- EDS maps show a relative increase in Ti and O content at the interface with increasing dose.
- This suggests that defect migration to the interface may help promote stability.

Evolution of the Interface Structure

□ EELS analysis on LTO As-Grown:

- STO fine structure is consistent with bulk STO and LTO from the literature

Evolution of the Interface Structure

□ EELS analysis on LTO at 4 dpa:

- The irradiated STO band shows much more Ti³⁺ character

Evolution of the Interface Structure

□ Comparison of EELS analysis on LTO As-Grown and at 4 dpa:

Ti⁴⁺ to Ti³⁺ damping
Mosk *et al.* Nature 2004

- Points toward the presence of extensive oxygen vacancies

Atomic-Level Description of the Interface Configuration

$\text{La}_2\text{Ti}_2\text{O}_7$ / STO(110) interface

LaTiO_3 / STO(110) interface

Predominant interface

Relative formation energy of oxygen vacancies at the interface

$\text{La}_2\text{Ti}_2\text{O}_7$ / $\text{STO}(110)$ interface

2 nm

Predominant interface

- Less energetically favorable to have V_O at the interface
- V_O would accumulate at LTO interlayers and in bulk STO

Summary

- **STEM:** The film/substrate interface is more damage resistant than the film and substrate.
- **PACBED:** Interface remains crystalline while film and substrate are amorphous.
- **EELS:** Highlight the presence of extensive oxygen vacancies at the interface.
- ***Ab initio* Simulations:** Formation of O vacancies less favorable at the interface.
 - The energetics for O vacancy formation follow the amorphization sequence observed experimentally: film → substrate → interface.

FULL PAPER

Asymmetric Lattice Disorder Induced at Oxide Interfaces

Steven R. Spurgeon, Tiffany C. Kaspar, Vaithiyalingam Shutthanandan,
Jonathan Gigax, Lin Shao, and Michel Sassi*

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