Imaging of Point Defects in Complex Oxides Using Quantitative STEM

Honggyu Kim, Jack Zhang, and Susanne Stemmer
Materials Department, University of California, Santa Barbara, USA

Funding:

U.S. DEPARTMENT OF ENERGY
Office of Science

19th International Microscopy Congress
September 10, 2018
Sydney, Australia
Outline

- Quantitative STEM for three-dimensional imaging of dopant atoms and point defects
- Improving contrast and interpretability: variable-angle HAADF-STEM
- Vacancies and local structure relaxations around point defects
- Doping a Mott insulator
Quantitative HAADF/STEM

- Quantify atom column intensities (relative to incident probe intensity)
- Compare with simulated column intensities
- Obtain meaningful and quantifiable information from HAADF image intensities

Three-Dimensional Imaging of Individual Dopant Atoms

Quantitative STEM from a single image to:

- Determine the number of dopant atoms in each column
- Determine the dopant depth position for each dopant atom

Three-Dimensional Imaging of Individual Dopant Atoms

Gd-doped SrTiO$_3$

Column averaged intensities (insensitive to spatial incoherence)*

Haibo et al., Ultramicroscopy 133, 109 (2013)

- Thickness variations
- $I_{Sr}$ is sampled only if the standard deviation of four neighboring $I_{Ti-O}$ is 4% or less

Need to establish a visibility criterion
Three-Dimensional Imaging of Individual Dopant Atoms

\[ p_i = \frac{\text{erf}_i(t)}{\sum_{n} \text{erf}_n(t)} \]

Probability of configuration

\[ \mu = \sum_{i} z_i p_i \]

Expectation Value

\[ \sigma = \sqrt{\sum_{i} p_i (z_i - \mu)^2} \]

Uncertainty

Three-Dimensional Imaging of Individual Dopant Atoms

- Quantitative information of expectation values and dopant visibility
- Determined complete 3D configuration from a single STEM image
- Sufficiently thin TEM foils are key

Three-Dimensional Imaging of Individual Dopant Atoms

- Certain dopant atom configurations are indistinguishable
- General problem: uniquely identify a structure from the measured intensities
- How to improve contrast in STEM?

Variable Angle HAADF STEM

- Use angular resolved information
- In certain angular regions, the red dopant has a higher scattering power than the blue dopant
- Do not have a detector with angular segments
- Use two camera lengths instead

Detector 1 (60-390 mrad)  Detector 2 (47-306 mrad)

Variable Angle HAADF STEM - Experimental

- Simulate all possible dopant configurations for both detectors
- Determine standard deviation from undoped sample for both detectors

Variable Angle HAADF STEM - Simulated Configurations

All possible simulated configurations for 1 or 2 dopants

Examples

- Configuration 4,5 and 3,5 (much better with detector 2)
- Configuration 1,5 and 2,5 (better with detector 1)
- Configuration 5 (much better with detector 2)

Certain configurations are more distinguishable in one detector range but not the other

Variable Angle HAADF STEM - Simulated Configurations

All possible simulated configurations for 1 or 2 dopants

Examples

- Configuration 4,5 and 3,5 (much better with detector 2)
- Configuration 1,5 and 2,5 (better with detector 1)
- Configuration 5 (much better with detector 2)

Certain configurations are more distinguishable in one detector range but not the other

Variable Angle HAADF STEM - Simulated Configurations

All possible simulated configurations for 1 or 2 dopants

Examples

- Configuration 4,5 and 3,5 (much better with detector 2)
- Configuration 1,5 and 2,5 (better with detector 1)
- Configuration 5 (much better with detector 2)

Certain configurations are more distinguishable in one detector range but not the other

Variable Angle HAADF STEM - Simulated Configurations

All possible simulated configurations for 1 or 2 dopants

Certain configurations are more distinguishable in one detector range but not the other

One detector is *not* uniformly better than another

Determining the number of dopant atoms in a column

Some ambiguous configurations can only be determined with both detectors (2,3 and 1,3)
Combined detector information always improves accuracy

### Variable Angle HAADF STEM - Experiment

<table>
<thead>
<tr>
<th>Region 1</th>
<th>Detector 1</th>
<th>Detector 2</th>
<th>Combined</th>
<th>Detector 1</th>
<th>Detector 2</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dopants 1</td>
<td>Dopants 2</td>
<td>Combined</td>
<td>Position</td>
<td>Probability</td>
<td>Position</td>
</tr>
<tr>
<td>0</td>
<td>5.1%</td>
<td>0%</td>
<td>0%</td>
<td>5</td>
<td>0.0279</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>64.9%</td>
<td>49.5%</td>
<td>78.7%</td>
<td>4</td>
<td>0.2491</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>30.1%</td>
<td>50.5%</td>
<td>21.3%</td>
<td>3</td>
<td>0.2734</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2607</td>
<td>2</td>
<td>2</td>
<td>0.0071</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.889</td>
<td>1</td>
<td>1</td>
<td>0.0099</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Region 2</th>
<th>Detector 1</th>
<th>Detector 2</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dopants 1</td>
<td>Dopants 2</td>
<td>Combined</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1.5%</td>
<td>4.8%</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>57.3%</td>
<td>63.8%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>41.1%</td>
<td>31.3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Region 1</th>
<th>Position</th>
<th>Probability</th>
<th>2.67±1.12</th>
<th>4.34±0.67</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0692</td>
<td>5</td>
<td>5</td>
<td>0.0026</td>
</tr>
<tr>
<td>1</td>
<td>0.2978</td>
<td>4</td>
<td>4</td>
<td>0.0441</td>
</tr>
<tr>
<td>2</td>
<td>0.2970</td>
<td>2</td>
<td>2</td>
<td>0.2970</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Region 2</th>
<th>Position</th>
<th>Probability</th>
<th>2.96±1.14</th>
<th>2.21±0.92</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1267</td>
<td>1</td>
<td>1</td>
<td>0.3115</td>
</tr>
<tr>
<td>1</td>
<td>0.3489</td>
<td>3</td>
<td>3</td>
<td>0.4599</td>
</tr>
<tr>
<td>2</td>
<td>0.2970</td>
<td>2</td>
<td>2</td>
<td>0.2970</td>
</tr>
</tbody>
</table>

### Region 1:
- Detector 2 unable to distinguish number of dopants, but better at distinguishing the position!
- Combined detector converges on position

---

Variable Angle HAADF-STEM

- Three-dimensional dopant atom configurations determined by quantitative STEM
- Variable angle HAADF results in improvement in precision and accuracy in obtaining 3D dopant configurations
- One particular angular range not unilaterally better than the other
- Using multiple angle ranges and compound probabilities improve depth quantification
- Can be extended to include additional angular ranges
- Parallel data acquisition would be highly desirable
Outline

• Quantitative STEM for three-dimensional imaging of dopant atoms and point defects
• Improving contrast and interpretability: variable-angle HAADF-STEM
• Vacancies and local structure relaxations around point defects
• Doping a Mott insulator
Imaging of Point Defects in STEM

So far have considered only relatively heavy dopant atoms in lighter matrix.

Less visible defects, such as vacancies?

Structure relaxation around individual point defects

Determines “electrical activity” of a point defect

Small polaron formation: “self-trapping” of carriers by lattice distortion

Charge states of point defects

Mater. Res. Express 1 025905
So far have considered only relatively heavy dopant atoms in lighter matrix

Less visible defects, such as vacancies?

Structure relaxation around individual point defects

Determines “electrical activity” of a point defect

Combine variable angle HAADF with rigid registration
Variable Angle HAADF-STEM for Vacancy Detection

Intentionally non-stoichiometric (Sr-deficient) SrTiO$_3$ film grown by MBE

Columns containing Sr-vacancies can be identified

The number of vacancies in a column can be determined

Variable Angle HAADF-STEM of Lattice Relaxations

Column distances in stoichiometric SrTiO$_3$

Distance (Å)
Avg.: 2.76 Å
Std.: 1.5 pm
Variable Angle HAADF-STEM for Vacancy Detection

- Neighboring Ti columns move away from the Sr-vacancy containing columns
- Consistent with XRD showing lattice expansion
- Not consistent with published DFT*
- Correlation effects?


Average distance in stoichiometric SrTiO$_3$: 2.76 Å ± 1.5 pm

Outline

- Quantitative STEM for three-dimensional imaging of dopant atoms and point defects
- Improving contrast and interpretability: variable-angle HAADF-STEM
- Vacancies and local structure relaxations around point defects
- Doping a Mott insulator
What happens when the Mott gap collapses on doping is one of the most fundamental questions in condensed matter physics.

Quantitative STEM allows us to investigate the local scale (around the doping atom) and longer length scale (phase separation...).
Doping a Mott Insulator

Prototypical Mott insulators: one electron in $t_{2g}$

Filling induced MIT upon hole doping

Critical concentration for MIT depends on degree of octahedral distortions

Not consistent with ideal Mott insulator that only exists at half-filling

Disorder of the dopant atoms (i.e., Sr) localizing electrons

First order, band-width controlled MIT that requires percolation of the metallic regions*

Other?

How strongly is this MIT coupled to the lattice?

50 nm, epitaxial SmTiO$_3$ films grown by MBE and doped with Sr

Sample with ~ 5% Sr is at the MIT boundary

SmTiO$_3$ too insulating to measure

Atomic resolution STEM of octahedral distortions → how uniform?
Doping a Mott Insulator

Use STEM to quantify local octahedral distortions
Successive Sm displacements to quantify “deviation angles”

Doping a Mott Insulator

- Octahedral distortions decrease as Sr is added
- The metallic film (x = 0.1) still shows substantial octahedral distortions
- The MIT is not strongly coupled to the lattice
- Sr-doping changes the structure uniformly: there is no phase separation
- No local distortions around the dopant atoms
- Long-range structural effects

Doping a Mott Insulator

- No local distortions around the dopant atoms
- Large fraction of the image contains no Sr
- Long-range structural effects, which are uniform

Doping a Mott Insulator

- The MIT in the RTiO$_3$ is not strongly coupled to the symmetry of the lattice
- Not first order, no phase separation
- Disorder remains as a possible explanation for the large hole doping required
- However: no local distortions around Sr atoms, only global, uniform response
- Sr doping globally affects the structure and electronic properties → long range strong correlation effects drive the transition
Variable Angle HAADF-STEM of Point Defects in Oxides

- Variable angle HAADF-STEM can identify columns containing point defects with very high degree of confidence
- “Low visibility defects” such as vacancies can be identified
- Atom relaxations around the vacancies are clearly visible
- What happens around individual point defects determines their electrical activity, strong correlation physics, ...

Future developments:

- Variable angle HAADF-STEM of displacements
- Combine with low-angle data*

*J. Johnson, S. Im, W. Windl, and J. Hwang, Ultramicroscopy 172, 17 (2017).
Thank you for your attention