Reconstructed surfaces of binary polar oxides: MgO(111) and ZnO(000-1)

Paul F. Lyman, S.T. King, Wei Han, K. Pradhan, S.S. Parihar, S.E. Chamberlin, C.J. Hirschmugl, and D.K. Saldin

Department of Physics and Laboratory for Surface Studies
University of Wisconsin-Milwaukee
USA
Classification of Ionic Crystal Surfaces

Type 1: Neutral
\((Q = 0; \mu = 0)\)

Type 3: Polar
\((Q \neq 0; \mu \neq 0)\)

(P. W. Tasker, J. Phys. C 12 (1979) 4977)
Bulk-Terminated Polar Oxide Surfaces

MgO (111)

Surface Oxygen
Second Layer Mg
Third Layer Oxygen

1x1 unit cell

Top view

Side View

[000-1]

ZnO (000-1)

[0001]
Bulk-Terminated Polar Oxide Surfaces

MgO (111)

- Rocksalt (fcc)
- Octahedral coordination
- Insulator (~7.8 eV)
- Centrosymmetric

Top view

Side View

1x1 unit cell

- Surface Oxygen
- Second Layer Mg
- Third Layer Oxygen
Bulk-Terminated Polar Oxide Surfaces

- Wurtzite (hexagonal)
- Tetrahedral coordination
- Wide-bandgap semiconductor (~3.4 eV)
- non-centrosymmetric
Problem in (strictly) ionic model:
- Net dipole $\mu \neq 0$;
- Surface charge $\sum q \to \infty$
$\Rightarrow$ diverging energy $E_s \to \infty$
Bulk-Terminated Polar Oxide Surfaces

MgO (111)  
ZnO (000-1)

Side View

For real polar oxide surfaces:

- Inherently high surface energy
- Lower energy by:
  - reconstruction
  - adsorption of foreign species
  - metallization
**MgO(111) and ZnO(000-1) Surfaces**

- Surface lattice similar (triangular lattice of O)
- Both can exist in (1x1) (H-stabilized?)
- Both exhibit reconstructions
  (Quite stable in air and other fluids!)
Sample Preparation

Single crystals of MgO(111) and ZnO(000-1) prepared similarly

- Commercially polished samples (Crystec, MTI)

- In tube furnace (in Al₂O₃ crucible):
  MgO or ZnO crystal liners “sandwich” the sample to protect it.

- In vacuum:
  MgO heated in tantalum boat w/ protective MgO liners. ZnO heated resistively.

![Diagram of sample preparation with Al₂O₃ crucible and Tantalum compartment]
Conventional LEED Results: MgO(111)

After 900 K Anneal
(1x1) pattern

After 1500 K Anneal
($\sqrt{3} \times \sqrt{3}$) R 30°

LEED poor: recall that MgO is an insulator
Previous Reports: MgO(111)

\[ (1 \times 1) \]

Expt:
Plass, Marks, Gajdardziska-Josifovska, PRL 1997.

\[ (\sqrt{3} \times \sqrt{3}) \text{ R}30 \]

Lazarov, Chambers, Gajdardziska PRB 2005.

\[ p(2 \times 2) \]

Theory:

\[ (2\sqrt{3} \times 2\sqrt{3}) \text{ R}30 \]

Wander, Harrison, PRB 2003.
Lazarov, Weinert PRB 2005.

(NOT an exhaustive list.)

Different times, temperatures, and atmospheres lead to different periodicities.

Many inconsistencies observed/reported.
(Kinetics may be important.)
MgO(111) Air-stable reconstructions
(Surface science without UHV is nice!)

(1x1) is stable seemingly indefinitely

$(\sqrt{3} \times \sqrt{3})R30$ is stable:
  - Yrs. in air
  - weeks in $H_2O$
  - $> minutes$ in MeOH

$p(2x2)$ is stable:
  - Months in air
  - seconds (only) in $H_2O$

Today, will focus on (1x1) and $(\sqrt{3} \times \sqrt{3})R30^\circ$. 
Conclusion: MgO(111)-(1x1) is -OH terminated.

Digression #1

fA LEED and LEED-IV

MgO is a good insulator $\Rightarrow$ charging with conventional LEED.

Need extremely low currents.
The DLD-LEED System

- Low-current gun
- 3-grid retarding field analyzer
- Microchannel plates
- Pulse-counting delay-line detector

Human, Hirschmugl et al., RSI 2006.
Delay Line Construction

- A continuous wire wrapped around square frame (1 mm pitch).
- Orthogonal delay lines give 2-D imaging (75 μm resolution).
DLD- LEED Summary

- 100% Digital
- High dynamic range
- High Count Rates (MHz)
- Low Current Electron Gun ⇒ Small Source Size
- Image resolution: 75 \( \mu \text{m} \)
- Acquisition time: 60 s
- Cross artifact ⇒ 2 images
- e-dose: \( 10^4 \) X less than CCD

MgO(100)
Schematic of LEED

Get spot when \( n\lambda = D \sin \phi \)
But wave from next layer may not be in phase $\Rightarrow$ weaker signal.
Schematic of LEED

Get strong signal when \( n\lambda = C(1 + \cos \phi) \) is also satisfied \( \Rightarrow \) LEED-IV.
Conclude that MgO(111)-(1x1) is -OH terminated.

DLD-LEED MgO(111) 1x1-H terminated vacuum annealed at 625K, measured in UHV

- Experimental LEED IV - 5 beams Thick Red Lines
- Theory Thin Red Lines
- Pendry Rfac = 0.27

Theory:
OH Termination
Theory/Exp Comparison: OH Terminated

Optimum Structure
% change from bulk structure

H-O-Mg-O-Mg

<table>
<thead>
<tr>
<th>Relaxation</th>
<th>DLD/LEED</th>
<th>AED/PED</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>d1</td>
<td>-15%</td>
<td>-14%</td>
<td>-14%</td>
</tr>
<tr>
<td>d2</td>
<td>-4%</td>
<td>-0.6%</td>
<td>-0.2%</td>
</tr>
<tr>
<td>d3</td>
<td>0.1%</td>
<td>-0.3%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Rp</td>
<td>0.27</td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>
Conventional LEED Results: MgO(111)

After 900 K Anneal
(1x1) pattern

After 1500 K Anneal
($\sqrt{3} \times \sqrt{3}$) R 30°

LEED poor: recall that MgO is an insulator
Reciprocal space map: MgO(111)-($\sqrt{3} \times \sqrt{3}$)R30
MgO(111)-(\(\sqrt{3}\times\sqrt{3}\))R30°

Air-Stable Reconstruction


Nanofacet by octopolar unit to remove dipole

Plass, Marks, MGJ PRL 1998.

Cyclic ozone trimers

MgO(111) 1450°C vac (\(\sqrt{3}\times\sqrt{3}\))R30°
**MgO(111)-($\sqrt{3} \times \sqrt{3}$)R30°**

**Air-Stable Reconstruction**

Subramanian, Marks, PRL 2004.

1/3 ML Mg with charge transfer.

Ciston, Marks PRB 2009.

1/3 ML Mg + 1/3 ML H

OR

2/3 ML O + 1/3 ML H
Cyclic Ozone I-V Comparisons
Mg Vacancy I-V Comparisons

MgO(111)-\(\text{?}3\text{R}30\?)
(01) I-V Curves

MgO(111)-\(\text{?}3\text{R}30\?)
(10) I-V Curves

MgO(111)-\(\text{?}3\text{R}30\?)
(11) I-V Curves

MgO(111)-\(\text{?}3\text{R}30\?)
(\?,?) I-V Curves
O-terminated I-V Comparisons

\[ \text{MgO}(111)-?3?3\rangle \text{R30}\rangle \]

(01) I-V Curves

\[ \text{190} \quad 210 \quad 230 \quad 250 \quad 270 \]
Energy [eV]

Intensity [a.u.]

Theory
Exp.

(01) I-V Curves

\[ \text{40} \quad 90 \quad 140 \quad 190 \quad 240 \]
Energy [eV]

Intensity [a.u.]

Theory
Exp.

(10) I-V Curves

\[ \text{50} \quad 100 \quad 150 \quad 200 \quad 250 \]
Energy [eV]

Intensity [a.u.]

Theory
Exp.

(11) I-V Curves

\[ \text{190} \quad 210 \quad 230 \quad 250 \quad 270 \]
Energy [eV]

Intensity [a.u.]

Theory
Exp.
Mg-terminated I-V Comparisons

MgO(111)-3°3R30°
(01) I-V Curves

MgO(111)-3°3R30°
(10) I-V Curves

MgO(111)-3°3R30°
(11) I-V Curves
Digression #2

Surface x-ray diffraction (SXRD)
SXRD geometry

2θ

α_i

α_f
SXRD geometry

\[ q \quad \alpha_f \quad \alpha_i \quad 2\theta \]
ML and Surface Diffraction

Real Space

Isolated Monolayer

Reciprocal Space

Surface of Crystal

CTR connect bulk Bragg spots.
Reciprocal space map: MgO(111)-($\sqrt{3} \times \sqrt{3}$)R30
ML and Surface Diffraction

Real Space

Reciprocal Space

Note: Reconstruction is like Isolated Monolayer. Introduces lateral length scale not found in bulk. SSR do NOT connect Bragg spots
Reciprocal space map: MgO(111)-($\sqrt{3} \times \sqrt{3}$)R30
“Reading” the depth of the reconstruction

$(1/3, 1/3, l)$ rod from $\sqrt{3}$ reconstruction

$l$ or $q_\perp$ (vary by changing incidence angle)
"Reading" the depth of the reconstruction

\((1/3, 1/3, l)\) rod from \(\sqrt{3}\) reconstruction

\(l\) or \(q_\perp\) (vary by changing incidence angle)
New reconstruction found on ZnO(000-1)

ZnO

[000-1]

O²⁻

Zn²⁺

[0001]
Metallization of ZnO Surfaces?

DFT predicts ZnO surfaces stabilize by metallization

Wander et al., PRL 2001
Reconstructed ZnO Surfaces

\[ \text{ZnO}(0001)- (\sqrt{3} \times \sqrt{3})R30^\circ \]

He-Atom Scattering – ZnO (1x3)

Margoninski et al., J. Phys C 1975

**in-situ Sample Preparation**

- ZnO (000-1) Samples obtained from MTI and Crystec
- Ar\(^+\) sputter, anneal \(\sim 650^\circ\text{C}\)
- (1x1) LEED pattern observed initially
- \((\sqrt{3} \times \sqrt{3})\)R30° reconstruction observed after several cycles
Observed LEED

Clean ZnO (1x1)

Clean ZnO ($\sqrt{3} \times \sqrt{3}$)R30°

Additional spots appear after multiple cleaning cycles
O 1s

Hydroxyl Shoulder

As Inserted
(1x1)
(\sqrt{3} \times \sqrt{3})

Intensity (arb. units)

Binding Energy (eV)
Grazing Emission XPS

Binding Energy (eV)

Hydroxyl Shoulder

Intensity (arb. units)

(1x1)

(rt3 x rt3)
Influence of Hydrogen

- H shown to stabilize MgO(111)-(1x1) surfaces
  

- Suggestion that no H-free O-polar ZnO-(1x1) exists
  
  (C. Wöll, Prog. Surf. Sci. 2007)

- Try preparing $(\sqrt{3} \times \sqrt{3})R30^\circ$ with H background
Control: No H

60eV
H- Background

$T \sim 600^\circ C$

$60 eV$
H Background

T \sim 700°C

60eV
H Background

T \sim 800^\circ C

60eV
H Background

\[ T \approx 900^\circ C \]

60eV
Removal of H Background
**ex-situ Sample Preparation**

Annealed in tube furnace at 1100°C
As Received
2 hours at 1100°C
48 hours
Tube Furnace Annealed Sample

![Graph showing O1s intensity versus binding energy for As Received and Tube Furnace Prepared samples. The graph includes a peak at 60 eV.]
ZnO(111)-($\sqrt{3} \times \sqrt{3}$) reconstruction stability

($\sqrt{3} \times \sqrt{3}$)R30 is stable:
Yrs. in air, but degrades in quality over weeks
> minutes in H$_2$O
< minute in MeOH
LEED-IV Comparison

Intensity (arb. units)

Energy (eV)

(1/3,1/3) beam

Vacuum Prepared
Tube-Furnace Prepared

(2/3,2/3) beam

(0,1) beam
LEED-IV Comparison

Curve Comparison: \( R_p \sim 0.27 \)

Energy (eV)

Intensity (arb. units)

(1/3,1/3) beam

(2/3,2/3) beam

(0,1) beam
LEED-IV Analysis

• 6 inequivalent beams
• ~20° Off normal incidence
• Total energy range ~1100 eV
LEED-IV Analysis

- Best fit model: 1/3 ML O vacancies
- \( R_p \sim 0.21 \)
Conclusions

• $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction observed on clean ZnO (000-1)

• H stabilization suggested

• LEED-IV suggests same structure for vacuum and tube-furnace prepared samples $\rightarrow$ O vacancies

• Structure? $\rightarrow$ SXRD

Funded by the U.S. Department of Energy, Office of Basic Energy Sciences