Ab initio Study of Nitrogen Adsorption on the Cu(111) Surface

Investigating the nitrogen induced pseudo-(100) reconstruction
Nitrogen on Cu(111)

- One of a class of pseudo-(100) reconstructions of fcc metal (111) surfaces:
  - Proposed by Higgs et al. based on a LEED study.
  - Confirmed by STM imaging.
  - Proposed to have \((25 \times 7\sqrt{3})\) rectangular coincidence mesh with underlying (111) substrate.
  - MEIS study shows that only one layer is reconstructed.
Proposed Reconstruction
Motivation

- **Fundamental interest in Surface Science:**
  - Is this the most stable phase?
  - What are the driving forces behind the reconstruction?
  - Under what conditions will this phase form?

- **Interest for Possible Applications:**
  - Heterogeneous Catalysts
  - Hard or protective coatings
Method

- **Electronic Structure Calculations:**
  - Density Functional Theory
  - DMOL³ DFT implementation

- *Ab initio* atomistic thermodynamics:
  - Combine electronic structure data with thermodynamics.

- **Analyze DFT Data:**
  - DOS, difference electron density, bond-lengths
Density Functional Theory

- Theoretical Framework:
  - Hohenberg-Kohn theorems:
  - Kohn-Sham equations:

\[ f_{KS} = -\frac{1}{2} \nabla^2 + V_{\text{eff}}(n) \]  

\[ f_{KS} \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \]  

\[ n(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2 \]  

\[ V_{\text{eff}}(n) = V_{\text{el-nuc}}(n) + V_H(n) + V_{XC}(n) \]  

- Exchange-correlation potential must be approximated, typically by LDA or GGA
Ab initio Atomistic Thermodynamics

- Calculate the Gibbs free energy of adsorption, $\Delta G$
- Difference of Gibbs free energies, so approximate by the difference in total energy.
- Final expression for $\Delta G$: 
  \[ \Delta G = - \frac{N_{ad}}{A_{cell}} (E_{bind} + \Delta \mu_{ad}) \]  
  (5)
- Binding energy calculated from DFT data:
  \[ E_{bind} = \frac{1}{N} (E_{system} - E_{substrate} - NE_{gas}) \]  
  (6)
- $\Delta \mu$ and P-T phase diagram.
Example Phase Diagram

$O_2$ on Pd(100)
DMOL\textsuperscript{3} DFT Implementation

- Numerical Local Orbital Basis Set
- GGA (PBE) Functional,
- Optimized Parameters from Convergence Tests
  - Basis set: DND
  - Atom $r$-cut: 10 Bohr
  - $k$-mesh size: 12 x 12 x 1 (for 1x1 cell)
  - Slab size: 7 Cu layers
  - Vacuum region: 25 Å
Tested Surface Structures:

- fcc & hcp adsorption sites for 0.25, 0.5 and 1 ML
- Approximation to the pseudo-(100) reconstruction

(2 x √3) rectangular structure
Binding Energies

Coverage (ML)

Binding energy (eV)

-6 -4 -2 0 2 4

fcc
hcp
reconstructed
fcc (N2)
hcp (N2)
reconstructed (N2)
Phase Diagram

\[ \Delta G \ (\text{eV}/\text{Å}^2) \]

\[ \Delta \mu \ (\text{eV}) \]
Relaxed Structures
<table>
<thead>
<tr>
<th>Layer Spacing</th>
<th>$d_{N-1}$ (Å)</th>
<th>$d_{1-2}$ (Å)</th>
<th>$d_{2-3}$ (Å)</th>
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</thead>
<tbody>
<tr>
<td>fcc 1ML</td>
<td>1.213</td>
<td>2.183</td>
<td>2.097</td>
</tr>
<tr>
<td>fcc 0.5ML</td>
<td>1.108</td>
<td>2.171</td>
<td>2.082</td>
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<tr>
<td>fcc 0.25ML</td>
<td>1.069</td>
<td>2.097</td>
<td>2.094</td>
</tr>
<tr>
<td>(2 x $\sqrt{3}$)Rect. c(2x2)</td>
<td>0.478</td>
<td>2.499</td>
<td>2.093</td>
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<tr>
<td>Clean Surface</td>
<td>-</td>
<td>2.102</td>
<td>2.103</td>
</tr>
<tr>
<td>Bulk layer spacing:</td>
<td>2.103</td>
<td></td>
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</tbody>
</table>
Density of States

DOS for Nitrogen atoms on Cu surface.

0.5ML fcc

Reconstructed Surface
Difference Electron Density

0.5ML fcc

Reconstructed Surface
Conclusions and Outlook

- The pseudo-(100) reconstructed phase is the thermodynamically stable surface phase.
- The proposed \((25 \times 7\sqrt{3})\) structure may be even more favorable.
- Reconstruction most likely due to Nitrogen favoring the 4-coordinated hollow on the (100) surface.
- Future studies could verify that a single layer reconstruction in favoured over two or more.