In/Si(111)-(4x1)/(8x2): a fascinating model system for one-dimensional conductors

S. Wippermann, W. G. Schmidt
Model system to study (quasi) 1D physics: In-induced (4x1) surface reconstruction of Si(111) [Landers and Morrison, J. Appl. Phys. 36, 1706 (1965)]

At borderline between semiconducting low In coverage and metallic high In coverage phases

FIG. 1. Surface phase diagram of In on Si(111) for temperatures of 400–550 °C. Structures observed in STM images.

[H.W. Yeom et al., PRL 82, 4898 (1999)]

What is special about this system?
Peierls Condensation?

Temperature-induced phase transition at \( \sim 120 \text{ K} \)

Metallic RT (4x1) phase:
- structure basically understood
- real-world example for quasi-1D conductor

In 4x1 structure covered with 0.007 ML of Pb
[Hupalo et al., PRB 76, 045415 (2007)]

(presumably) semi-conducting LT (8x2) phase:
- structure not really understood
- mechanism of phase transition not really understood - Peierls instability??

[H. W. Yeom et al., PRL 95, 12601 (2005)]

[Ahn et al., PRL 93, 106401 (2004)]
Competing structural models

surface X-ray diffraction
Kumpf et al. PRB 85, 4916 (2000)

photoemission
Yeom et al. PRB 65, 241307 (2002)

DFT calculations
Cho et al. PRB 64, 235302 (2001); Tsay, PRB 71, 035207 (2005); Lopez-Lozano et al., PRB 73, 035430 (2006); Cho and Lee, PRB 76, 033405 (2007); ...

 positron diffraction

DFT calculations
Gonzalez et al. PRL 96, 136101 (2006)

...
Obtain Structure from Reflectance Anisotropy Spectroscopy

Shoulder observed experimentally at 2 eV upon cooling, signature for phase transition?

- No, reproduced by both hexagon & trimer models

Mid-infrared regime: anisotropic Drude tail replaced by two distinct peaks upon cooling

- Only hexagon model agrees with measured data

Structure determined! Now understand mechanism of phase transition

[S. Chandola, K. Hinrichs, M. Gensch, N. Esser, S. Wippermann, WGS et al., PRL 102, 226805 (2009)]
Phonon Modes: Theory vs. Experiment

<table>
<thead>
<tr>
<th>THEORY $\omega_0$ [cm$^{-1}$]</th>
<th>EXPERIMENT $\omega_0$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4x1) → (8x2)</td>
<td>(4x1) → (8x2)</td>
</tr>
<tr>
<td>22 → 20</td>
<td>31 ± 1 → 21 ± 1.6</td>
</tr>
<tr>
<td>27</td>
<td>28 ± 1.3</td>
</tr>
<tr>
<td>hexagon rotary mode</td>
<td></td>
</tr>
<tr>
<td>44 → 47</td>
<td>36 ± 2 → 41 ± 2</td>
</tr>
<tr>
<td>51 → 53</td>
<td>52 ± 0.6 → 57 ± 0.7</td>
</tr>
<tr>
<td>62 → 58, 69</td>
<td>61 ± 1.3 → 62, 69 ± 1.5</td>
</tr>
<tr>
<td>65, 68 → 70, 69, 78, 82</td>
<td>2.72 ± 3.3 → 83 ± 2.3</td>
</tr>
<tr>
<td>100, 104 → 97, 106, 113, 142</td>
<td>105 ± 1 → 100-130</td>
</tr>
<tr>
<td>129, 131 → 137, 142</td>
<td>118 ± 1 → 139 ± 1.2</td>
</tr>
<tr>
<td>143, 145 → 139, 145, 146, 147</td>
<td>2.148 ± 7 → 139, 2.154 ± 2</td>
</tr>
<tr>
<td>28 → 18, 19</td>
<td>28 ± 0.9 → 2.235 ± 0.8</td>
</tr>
</tbody>
</table>

- calculate phonon frequencies and modes
- (4x1) and (8x2) structures are well defined local minima on potential energy surface
- no soft (imaginary) modes at $T = 0$ K
- experimental spectra and assigned calculated phonon modes on backup slide

TABLE I: Calculated Γ-point frequencies for strongly surface localized A’ (upper part) and A” phonon modes (lower part) of the Si(111)-(4x1)/(8x2)-In phases in comparison with experimental data [26]. The symmetry assignment of the (8x2) modes is only approximate, due to the reduced surface symmetry.
Transition path: phonon modes show the way

- $(4 \times 1) \leftrightarrow (8 \times 2)$ transition path well-described by low energy phonon eigenvectors
- Linear combination of $(4 \times 1)$ shear and trimer modes yield $(8 \times 2)$ hexagon
- $(8 \times 2)$ shear and hexagon modes yield $(4 \times 1)$ ideal reconstruction
- Rearrangement of In atoms leads to formation of new bonds => Peierls instability?
Peierls instability

- 1D-metals *a priori* unstable
- Free energy lowered by phonon-driven metal-insulator (MI) transition

**homogeneous electron gas**

Peierls MI transition

**charge density wave (CDW) formation**

occupied & unocc. states

band gap opening

$k_F = \pi/2a$
No Peierls transition in In/Si(111) in the original sense

Follow transition path defined by soft phonon eigenvectors and calculate band structures

Formation of band-gap leads to energy gain in analogy to Peierls transition, but poor nesting and does not occur at edge of Brillouin zone

Why phase transition from semiconducting (8x2) ground state to metallic (4x1)?

=> Calculate free energy at finite temperature

[S.Wippermann, WGS et al., PRB 84, 115416 (2011)]
Atomistic Thermodynamics

calculate **free energy** from **first principles**

\[ F(V, T) = F_{el}(V, T) + F_{vib}(V, T) \]

\[ F_{el} = E_{tot} - T S_{el} \]

approximate the total energy \( E_{tot} \) by the zero-temperature DFT value and calculate the electronic entropy \( S_{el} \) from

\[ S_{el} = k_B \int dE \ n_F [f \ln f + (1 - f) \ln(1 - f)] \]

vibrational entropy of the periodically repeated supercell with volume \( \Omega \) is calculated in harmonic approximation

\[ F_{vib} = \frac{\Omega}{8\pi^3} \int d^3k \sum_i \left( \frac{1}{2} \hbar \omega_i(k) + k_B T \ln(1 - e^{-\frac{\hbar \omega_i(k)}{k_B T}}) \right) \]
Free energy of the (4x1) and (8x2) phase ... 

... explains phase transition at 125 K (experiment: 120K)

Simple explanation possible?
Harder phonons counterbalance band structure energy gain

Hardening of phonon modes upon bond formation in (8x2) hexamer model lowers vibrational entropy...
...compared to metallic (4x1) model with soft bonds

For finite temperatures entropy contributions dominate and cause (8x2) $\rightarrow$ (4x1) phase transition

[S. Wippermann, WGS, PRL 105, 126102 (2010)]
Phase transition triggered by condensation nuclei

energetics along (4x1) -> (8x2) transition path obtained from phonon calculations

hampered by energy barrier of 20 meV per (8x2) unit cell

time-resolved electron diffraction measurements (M. Horn von Hoegen group) and ab initio molecular dynamics calculations show freezing triggered by heterogeneous nucleation of ground state at adsorbates

First order transition propagating from seeds at speed of sound (850m/s), in analogy to falling row of dominoes

[S. Wall, B. Krenzer, S. Wippermann, S. Sanna, WGS, M. Horn von Hoegen, et al., PRL 109, 186101 (2012)]
Nature of condensation nuclei?

- So far used hexagons as condensation nuclei.
- Local minimum on potential energy surface, but formation costs 40 meV per hexagon.
- Attempts to use adatoms, e.g., O, as nuclei resulted in no observable condensation.

Recent experiment by H.W. Yeom shows oxygen to facilitate phase transition, but only for pair-wise oxygen coadsorption!

=> Investigate O adatoms on In/Si(111)
Oxygen on In/Si(111)

3 dominant types of defects observed experimentally, labeled type I, II and III

Calculate adsorption energy surface, pick 3 energetically most favourable and calculate STM images

=> good agreement with measured STM images, basic adsorption understood
Oxygen reduces formation energy of seeds

- Experimentally, only type I defects with a spacing of even multiples of \( a_0 = 3.86 \text{ Å} \) observed to trigger phase transition.
- Calculate impact of O adatoms with \( x4 \) distance in type I position in (8x12) unit cell.
- O coadsorption at odd multiples of \( a_0 \) pulls trimers within hexagons apart by chemical strain, locking structure in (4x1).
- O coadsorption at even multiples of \( a_0 \) reduces energy cost for hexagon formation from 40 meV to 22 meV (same chain) or even 10 meV (opposite chain sides).
- Formation energy still positive, (4x4) hexagon still unstable contrary to experimental observation.
- 10 meV per (4x2) hexagon = 2.5 meV per In atom.
- Finite size effects, accuracy of DFT-LDA? => could try hybrid DFT with self interaction correction.
Determined structure of ground state from mid-infrared response => (8x2) hexagon

Phase transition path described by phonon eigenvectors

Transition (4x1) ➔ (8x2) is strictly NOT a Peierls transition, but energy gain due to band gap opening in analogy to Peierls transition

(8x2) ➔ (4x1) transition at finite temperatures explained as subtle interplay between lower total energy of insulating (8x2) hexagon and higher vibrational & electronic entropy of metallic and less tightly bound (4x1) zigzag chain structure

Phase transition is of first order, propagating from condensation nuclei similar to a row of falling dominoes

Condensation seeds not consisting of single adsorbates, but two adsorbates acting together (work in progress)

Acknowledgements

Thanks to my coworkers, especially to Wolf Gero Schmidt, his group, and Simone Sanna

Thanks to our collaborators Friedhelm Bechstedt, John McGilp, Norbert Esser and Han Woong Yeom
(4x1) <-> (8x2) Transition path

- Obtain transition path from linear combination of frozen-phonon eigenvectors.
- Anharmonic effects lead to fluctuation frequency of 16 cm\(^{-1}\).

**Shear Mode**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$(8 \times 2) \ [cm^{-1}]$</th>
<th>$\rightarrow$</th>
<th>$(4 \times 1) \ [cm^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>harmonic approx.</td>
<td>23.5 ± 0.8</td>
<td>$\rightarrow$</td>
<td>28 ± 0.9</td>
</tr>
<tr>
<td>anharmonicities</td>
<td>18, 19</td>
<td>$\rightarrow$</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$\rightarrow$</td>
<td>16</td>
</tr>
</tbody>
</table>

**Composite potential**

from shear mode + rot I + rot II + remaining modes
measurements by E. Speiser, N. Esser, ISAS Berlin
Density functional theory (DFT):

**Hohenberg-Kohn theorem:**

\[ E_{XC}[n] \approx E_{XC}^{LDA}[n] = \int n(r) e_{XC}^{hom}(n(r)) \, dr \]

\[ E_{e}[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} \, dr \, dr' + \int n(r) V(r) \, dr + E_{XC}[n] \]

[Walter Kohn, Nobel Prize for chemistry in 1998]

**Starting point:** initial geometry

\[ \left\{ -\frac{\nabla^2}{2} + \int \frac{n(r')}{|r - r'|} \, dr' + V(r) + \frac{\delta E_{XC}^{LDA}}{\delta n(r)} \right\} \psi_j(r) = \epsilon_j \psi_j(r) \]

\[ n(r) = \sum_j |\psi_j(r)|^2 \]

**Kohn-Sham self-consistent electron structure**

**interatomic forces**

**external potential**

**structurally relaxed ground-state**

**vibrational and thermal properties**

**electronic properties**

**spectroscopic and transport properties**

atomic positions
Excited states (GW/BSE)

- DFT disregards screened e⁻–e⁻ interaction and e⁻–h interaction for excited states => band gap underestimation, wrong distribution of spectral weights

- Perturbative approaches for including screening (GW) and e⁻–h interaction (Bethe-Salpeter), starting from Quantum Liouville equation

\[ i \frac{d \hat{\rho}(t)}{dt} = \left[ \hat{\mathcal{H}}(t), \hat{\rho}(t) \right] \]

\[ \rho(r, r', t) = \sum_v \phi_v^*(r, t) \phi_v(r', t) \]

- single particle occ. orbitals

\[ \int \hat{\mathcal{H}}(r, r', t) \phi(r', t) dr' = \left( -\frac{1}{2} \nabla^2 + v_H(r, t) + v_{ext}(r, t) \right) \phi(r, t) \]

\[ + \int \Sigma(r, r', t) \phi(r', t) dr' \]

- time-dep. perturbation, i.e. electromagn. field

\[ \Sigma_{COH}(r, r') = \frac{1}{2} \delta(r - r') W_p(r, r') \]

\[ \Sigma_{SEX}(r, r', t) = - \sum_v \phi_v(r, t) \phi_v^*(r', t) W(r, r') \]

- statically screened Bethe-Salpeter equation (BSE)

- screened Coulomb interaction
Excited states (GW/BSE)

To correct for DFT’s band gap underestimation, quasiparticle energies can be obtained in GW approximation from

$$\Sigma_{GW}(\mathbf{r}, \mathbf{r}'; i\omega) = \frac{1}{2\pi} \int G(\mathbf{r}, \mathbf{r}'; i(\omega - \omega')) W(\mathbf{r}, \mathbf{r}'; i\omega') d\omega'$$

Screened Coulomb interaction required (in random phase (RPA) approx.)

$$W(\mathbf{r}, \mathbf{r}') = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}'') v_c(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''$$

Bottleneck: calculation, storage & inversion of dielectric matrix is very computationally demanding, involves large sums over empty states and is hard to converge

Solution: spectral representation of RPA dielectric matrix; obtain matrix from directly calculating eigenvectors and eigenvalues

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I$$

=> no summation over empty states, no inversion, storage of eigenvector/-value pairs only!
How to calculate the screening

- Obtaining the eigenvectors/values does **NOT** require explicit knowledge of the matrix; knowledge of the **action of the matrix** on an arbitrary vector is sufficient!
- In linear response: \( (\epsilon - I) \Delta V_{SCF} = -v_c \Delta n \)
- Charge density response \( \Delta n \) to perturbation of self-consist. field \( \Delta V_{SCF} \) can be evaluated from density functional perturbation theory.
- Orthogonal iteration procedure to obtain eigenvectors/values, using \( \Delta V_{SCF} \) as trial potentials.
- In RPA fast monotonous decay of dielectric eigenvalue spectrum.
- Single parameter \( N_{eig} \) to control numerical accuracy.

\[
\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I
\]

[H. Wilson et al., PRB 79, 245106 (2009); D. Rocca et al., J. Chem. Phys. 133, 164109 (2010); H.-V. Nguyen et al., PRB 85, 081101 (2012)]