1D Metal Wires at Surfaces: Preparation, Phase Transitions, and Ultrafast non-Equilibrium Dynamics

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Download of presentation available at: https://www.uni-due.de/ag-hvh/

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1-dim Atom Wires on Si – why?

Dimensionality drastically changes properties of matter

3D Simple bulk (Pauli: „God made the bulk …“)

2D Surfaces are complicated – we struggle since centuries (Pauli: „…the surface was invented by the devil“)

0D Quantum dots are simple again (used in applications)

1D ?

We expect new and fascinating properties:

• Anisotropic conductivity

• 1-dim transport: Tomanaga Luttinger liquid, decouple charge and spin

• Peierls instability of atom chain

=> Playground for physicists
1-dim Atom Wires on Si

- **Si(557) – Pb:**
  - Switching Between One and Two Dimensions: Conductivity of Pb-Induced Chain Structures on Si(557)
  - Coupled Pb Chains on Si(557): Origin of One-Dimensional Conductance
  - Conductance transition and interwire ordering of Pb nanowires on Si(557)
  - Plasmons in Pb nanowire arrays on Si(557): Between one and two dimensions
  - Fermi nesting between atomic wires with strong spin-orbit coupling

- **Si(557) – Ag:**
  - One-dimensional collective excitations in Ag atomic wires grown on Si(557)
    U Krieg, C Brand, C Tegenkamp and H Pfünür

- **Si(557) – Mg:**
  - Quintuple-period Si atomic wires with alternative double and triple modulations by metal: Mg/Si(557)
1-dim Atom Wires on Si

- **Si(553) – Au:**
  - Intrinsic magnetism at silicon surfaces
    Steven C. Erwin & F.J. Himpsel
    Nature Communications 1, 58 (2010)
  - Spin-split silicon states at step edges of Si(553)-Au.
  - Spectroscopic evidence for spin-polarized edge states in graphitic Si nanowires.
  - Evidence for long-range spin order instead of a Peierls transition in Si(553)-Au chains

- **Si(553) – In:**
  - Indium-induced triple-period atomic wires on a vicinal Si(111) surface: In/Si(557)

- **Si(111)-Au (5x2)**
1-dim Atom Wires on Ge

- **Ge(001) – Au:**
  - Scanning tunneling microscopy study of self-organized Au atomic chain growth on Ge(001)
  - New Model System for a One-Dimensional Electron Liquid: Self-Organized Atomic Gold Chains on Ge(001)
  - First-principles studies of Au-induced nanowires on Ge(001)
  - Atomically controlled quantum chains hosting a Tomonaga–Luttinger liquid

- **Ge(001) – Pt:**
  - Quantum Confinement between Self-Organized Pt Nanowires on Ge(001)
  - Spatial Mapping of the Electronic States of a One-Dimensional System
  - Playing Pinball with Atoms
Si(111)-In(8x2)
Adsorbat System: Si(111)-In

Superstructures of submonolayer indium films on silicon (111)7 surfaces

M. Kawaji, S. Baba, and A. Kinbara
Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

(Received 31 October 1978; accepted for publication 22 March 1979)

Superstructures of submonolayer films of indium on a clean silicon (111)7 surface have been investigated using techniques of molecular-beam deposition and reflection high-energy electron diffraction. A two-dimensional phase diagram including four superstructures, 7x7, (3/2), (31/2), and 4x1, is presented at substrate temperatures between 300 and 600 °C.

![Phase diagram for the superstructures of two-dimensional submonolayer film of In on Si (111)7. The dots are experimental phase transition points.](image)

1 ML In @ 450 - 550 °C

M. Kawaji, S. Baba, and A. Kinbara, Appl. Phys. Lett. 34, 748 (1979)
Adsorbatsystem: Si(111)-In

- Precision-oriented (±0.1°) Si(111) sample (phosphorus doped, 0.8 Ωcm)
- Si-substrate cleaned by flash-anneal cycles up to 1200°C
- Clean Si(111) surface repeatedly checked by (7x7) superstructure spots in LEED
- Indium-deposition at elevated Si substrate temperatures
- Constant deposition rate controlled by quartz microbalance
- SPA-LEED pattern taken at 130 eV directly after rapid cooling down to ~80 K

```
\sqrt{3} \times \sqrt{3}
```

*In(\sqrt{3} \times \sqrt{3})* absorbed at ~450 °C and annealed for 180 s at ~800 °C

```
\sqrt{31} \times \sqrt{31}
```

*In(\sqrt{31} \times \sqrt{31})* absorbed ~ at 450 °C and annealed for 80 s at ~800 °C

```
\sqrt{3}\sqrt{3} / \sqrt{31}\sqrt{31} / 8x2
```

*In(\sqrt{3}\sqrt{3} / \sqrt{31}\sqrt{31} / 8x2)* absorbed at ~450 °C, annealed for 180 s at ~450 °C

```
8x2
```

*In(8x2)* absorbed at ~500 °C and annealed for 60 s at ~500 °C

```
4 \times 1
```

*In(4 \times 1)* heated up (8x2) structure
1-dim. Indium atom wires on Si(111)

Anisotropic Conductivity

Si(111)-In (4x1) at 300 K

- Conductivity parallel to the wires 60 x larger than perpendicular

Phasetransition of In/Si(111)

In(4x1)/Si(111) – a quasi 1-dim. metallic wire system
Below $T_c \approx 130$ K structural phase transition into (8x2):
insulating phase

2-fold streaks reflect
weak interchain coupling
of 1-dim atom wires

Metallic High
Temperature Phase
(4x1) @ $T > 130$ K

Insulating Low
Temperature Phase
(8x2) @ $T < 130$ K

H.W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi,
J. Schaefer, C.M. Lee, S. D. Kevan, T. Ohta, T. Nagao,
S. Hasegawa, Phys. Rev. Lett. 82, 4898 (1999),

G. Falkenberg, R.L. Johnson, R. Feidenhans'l et al.,
C. Kumpf, O. Bunk, J.H. Zeysing, Y. Su, M. Nielsen, R.L. Johnson,
Peierls like Mechanism

(8x2): CDW
\[ \rho(r) \]
\[ 2a \]

(4x1): Without CDW
\[ \rho(r) \]
\[ a \]
Robust Hysteresis upon T-cycling

- Phase transition temperature $T_c = 130$ K
- Hysteresis width $W_H = 9$ K

F. Klasing, T. Frigge, B. Hafke, S. Wall, B. Krenzer, A. Hanisch-Blicharski, and M. Horn-von Hoegen
Figure 1.17: First order free energy $f(\phi)$ and $\phi(T)$. **Left:** Free energy $f$ as function of the order-parameter $\phi$. The red curves show the free energy for the 3 characteristic temperatures, i.e. $T_C$, $T_i$ and $T_{ii}$. Between the solid red curves, i.e. between $T = T_C$ and $T = T_{ii}$, two stable states exist one of them being meta-stable at a time. The dashed red curve marks the temperature where both states are equal in potential. **Right:** Order-parameter $\phi$ as function of the temperature $T$. Stable states, i.e. thermal equilibrium states or the global free energy minimum, are marked in red whereas meta-stable states are colored green. The shaded temperature range corresponds to the shaded area on the left hand side.
Robust Hysteresis upon T-cycling

- Phase transition temperature
  \[ T_c = 130 \text{ K} \]
- Hysteresis width \( W_H = 9 \text{ K} \)
- Proof of 1st order transition
  \( \Rightarrow \) Peierls like distortion [*]
  \( \Rightarrow \) not order-disorder transition

What else can be done?

So far equilibrium thermodynamics…

Now:

Non-equilibrium structural dynamics of this phase transition upon impulsive excitation

We will

• have (analogon of) undercooled bottles of champain on a Si surface
• will play domino day with atoms
• and answer the question how fast atoms move

We need, however, diffraction!
Ultrafast time resolved femtosecond diffraction at surfaces in Reflection High Energy Electron Diffraction (RHEED) geometry

- Laser pump & electron probe
- Re-do the experiment in stroboscopic fashion many many times
Surface Sensitivity with Electrons

Electron scattering cross section
$10^4 \ldots 10^6$ larger than x-ray
  - dominant multiple scattering
    => no simple IV-analysis

=> LEED
  - extrem surface sensitivity
  - normal incidence
  - no distortion of pattern
  - miniaturize setup to avoid huge temporal broadening of nanoseconds

Science 345, 200 (2014)
M.Gulde, S. Schäfer, C. Ropers

Electrons universal curve of mean free path

50 eV
7.3 Å$^{-1}$
Surface Sensitivity with Electrons

Electron scattering cross section
$10^4$…$10^6$ larger than x-ray
- dominant multiple scattering
  $\Rightarrow$ no simple IV-analysis

$\Rightarrow$ LEED
- extrem surface sensitivity
- normal incidence
- no distortion of pattern
- miniaturize setup to avoid huge temporal broadening of nanoseconds

$\Rightarrow$ RHEED
- grazing incidence
- distortion of pattern
- velocity mismatch
degrade temporal resolution
Pulsed RHEED Electron Gun

Electron pulses from backilluminated Au-photocathod

- via external photoeffect induced by 80 fs laser pulses at 4.6 eV
- narrow initial energy spread $\Delta E = 0.1$ eV
- 5 – 30 keV electrons
- fine-focus RHEED gun

10 nm Au/Al$_2$O$_3$

Surface Sensitivity with Electrons

Electron Diffraction
- backilluminated 10 nm Au photocathode
- fast electrons 5 - 30 keV and narrow initial energy spread $\Delta E = 0.1$ eV
  minimize temporal broadening of fs e-pulses

RHEED
- grazing incidence 2°- 6° to ensure surface sensitivity
- vertical momentum transfer $\Delta k_\perp = 4 - 10$ Å$^{-1}$
  $\Rightarrow$ huge signal in Debye Waller
- reversible surface / film system
  $\Rightarrow$ no radiation damage!
  More than $10^7$ laser pulses / experiment
- velocity mismatch limits temporal resolution to 20 ps @ 30 keV,
  (in the meantime solved that problem!)

A. Hanisch-Blicharski, A. Janzen, B. Krenzer, S. Wall, F. Klasing, A. Kalus,
Experimental Setup

**fs Laser Pulses**
- Ti-Sapphire amplifier system
- $\lambda = 800$ nm, $\hbar\omega = 1.55$ eV
- 80 fs, 1 mJ per pulse
- Fluence of up to 10 mJ/cm$^2$, i.e., $10^{12}$ W/cm$^2$
- 5 kHz repetition rate

**UHV-System**
- $p < 1 \times 10^{-10}$ mbar
- Sample 20 K – 1200 °C
- In-situ deposition of Bi, Pb, In ...

**e-Diffraction**
- RHEED 5 – 30 keV
- Image amplification by MCP
- Cooled 16 bit CCD camera
Impact excitation
through fs-laserpulse

- Base temperature 20 K << T_c = 125 K
- \( \Phi = 2.1 \text{ mJ/cm}^2 \)

- \( E = 30 \text{ kV} \)
- magnetic lense
- transversal coherence
  length of 40 nm
- 2° - 4° grazing incidence
Movie of transition – gains & losses

Intensity gain

Intensity loss

(8x2)

(4x1)
Displacive structural phase transition

- Surface at 20 K well below $T_c = 130$ K
- Confirmed that almost no heating of surface $\Delta T < 30$ K
- Photo induced, electronic (and not a thermal) excitation of phase transition

Electronic excitation:

- Laser excited electron-hole pairs
- Relaxation of hot carriers to top and bottom of bands
- Depopulation of states responsible for Peierls transition
- Lifting of (8x2) Peierls distortion, closing of bandgap, melting of CDW, and transition to (4x1) excited state

TR-RHEED: In/Si(111)

Why does the excited (4x1) phase survive that long at such low temperature?

- Life time of electronic excitations: few 10 to some 100 fs
- Here: hundreds of ps

W.G. Schmidt, S. Sanna et al., University Paderborn
Trapped in a supercooled metastable surface phase:

- 40 meV barrier hinders recovery of low temperature (8x2) groundstate
- State far away from equilibrium – unaccessible under equilibrium conditions

Hidden State of Matter!
Relaxation Dynamics

Recovery of groundstate sensitive to

- Adsorption from residual gas in UHV, most likely $\text{H}_2\text{O}$ acting as seeds
- 1-dim. atomic wire system: expect an $(\text{adsorption time})^{-1}$ behavior
Relaxation Dynamics

Recovery of groundstate sensitive to

- Adsorption from residual gas in UHV, most likely H\textsubscript{2}O acting as seeds
- 1-dim. atomic wire system: expect an \((\text{adsorption time})^{-1}\) behavior
Relaxation Dynamics

Adsorbates

(8x2)  (4x1)
Adsorbates trigger phase transition

- Adsorbates act as seed for recovery into (8x2) groundstate
- Recovery front propagates only 1-dimensionally:
  => constant velocity
- Take density of adsorbates from literature \(^1\),\(^2\) and correlate with change of \(T_c\):
- **velocity of phase front** \(\approx 100\) m/s

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Supercooled metastable surface phase:
- 40 meV barrier hinders recovery of low temperature (8x2) groundstate
- State far away from equilibrium – unaccessible under equilibrium

Adsorbates trigger phase transition
- Pre-existing adsorbates act as seed for recovery into (8x2) groundstate
- Recovery front propagates only 1-dimensionally @ 100 m/s
- Like a row of falling dominos ...

Phase transition is incomplete due to weak laser excitation

- Only ~50% of (8x2) is converted into (4x1)
- Recovery time independent on adsorbate coverage and always 50-100 ps
Pattern of small (8x2) and (4x1) domains on surface

- Remnant (8x2) groundstate expands linear in time – no seeds necessary
- \( L_{8x2} = 2 \cdot v_{8x2} \cdot t \)
- (8x2) regions act as slit for electron diffraction => broadening of (8x2) spots
- FWHM \( \sim (L_{8x2})^{-1} \sim (2 \cdot v_{8x2} \cdot t)^{-1} \)
Pattern of small (8x2) and (4x1) domains on surface

- Remnant (8x2) groundstate expands linear in time
  \[ L_{8x2} = 2 \cdot v_{8x2} \cdot t \]
- (8x2) regions act as slit for electron diffraction => broadening
- FWHM $\approx (L_{8x2})^{-1}$
Transient Spot Profile Analysis

**Pattern of small (8x2) and (4x1) domains on surface**

- Remnant (8x2) groundstate expands linear in time – no seeds necessary
- \( L_{8x2} = 2 \cdot v_{8x2} \cdot t \)
- (8x2) regions act as slit for electron diffraction => broadening of (8x2) spots
- \( \text{FWHM} \sim (L_{8x2})^{-1} \sim (2 \cdot v_{8x2} \cdot t)^{-1} \)
- **Lower limit for velocity of the phase front** \( v_{8x2} > 68 \text{ m/s} \)
Recovery Dynamics
Initial Structural Dynamics ...

... requires improved Temporal Resolution!

„Tilted Pulse Front Scheme“

- Velocity mismatch of photons and electrons $v_{\text{electron, 30 keV}} = c/3$
- Matching by tilting the pulse front by $\sim 70^\circ$!

for 30 keV electron energy

\[
\begin{align*}
\text{laser pulse} & \quad \text{electron pulse} @ 30 \text{ keV} \\
& \quad \downarrow \quad \downarrow \\
& \quad \downarrow \quad \downarrow \\
& \quad \downarrow \quad \downarrow \\
& \quad \downarrow \quad \downarrow \\
\quad \Delta t = 20 \text{ ps} & \quad \Delta t < 1 \text{ ps}!
\end{align*}
\]
Tilted Pulse Fronts

„Tilted Pulse Front Scheme“
- Blazed grating
- Almost Littrow geometry
- 1:1 mapping of grating to sample

Setup realized together with group of Uwe Bovensiepen @ UDE
- Thanks to Carla Streubühr, Ping Zhou, Manuel Ligges & Dietrich von der Linde

Ultrafast fs-RHEED: Advanced Setup

**fs-Laser Amplifier**
- 800 nm, 80 fs
- 1 mJ/pulse, 5 kHz

**Diagram Details**
- Grating
- BBOs
- 266 nm
- Au-cathode
- 30 keV E-Gun
- ΔE ≤ 100 meV
- Multi Channel Plate
- CCD
Strongly driven excitation

$\tau = 350 \text{ fs}$

Data
Convolution of exponential decay and $\cos^2$

Decay Constant: 350 fs
FWHM $\cos^2$: 250 fs

T. Frigge, B. Krenzer, B. Hafke, C. Streubühr, P. Zhou, M. Ligges,
Strongly driven excitation

Potential energy landscape changes upon electronic excitation:

- Accelerated displacive transition from (8x2) ground state to (4x1) excited state in 350 fs – “slow” structural transition!
- Transition in \( \frac{1}{4} \) period of the characteristic shear and rotational soft phonon modes

\[
\begin{align*}
E &= 3.4 \text{ meV} \\
T &= 1.2 \text{ ps}
\end{align*}
\]  
\[
\begin{align*}
E &= 2.1 \text{ meV} \\
T &= 2.0 \text{ ps}
\end{align*}
\]  
\[
\begin{align*}
E &= 3.0 \text{ meV} \\
T &= 1.4 \text{ ps}
\end{align*}
\]

Wippermann et al., 
PRL 105, 126102 (2010)
Thanks to

TR-RHEED Team:

Andreas Janzen, Boris Krenzer, Anja Hanisch-Blicharski, Simone Wall, Annika Kalus, Paul Schneider, Tobias Pelka, Friedrich Klasing, Martin Kammler, Tim Frigge, Verena Tinnemann, Bernd Hafke, Tobias Witte

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Carla Streubühr, Ping Zhou, Manuel Ligges, Dietrich von der Linde, Uwe Bovensiepen

Theory Team:

Wolf Gero Schmidt¹, Simone Sanna¹, Stefan Wippermann¹ ², Andreas Lücke¹

¹ University of Paderborn
² present adress: MPI Eisenforschung, Düsseldorf

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Summary - Atomic Wires

Si(111)/In (8x2) ↔ (4x1)

Simple sample preparation

Peierls instability

1st order phase transition at 130 K
  - Ultrafast electronic excitation of phase transition in 350 fs
  - Formation of supercooled, metastable surface phase
  - Pre-existing defects trigger the 1-dim propagating recovery front, which propagates at 100m/s

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