Surface reflectance spectroscopies for probing reconstructions and adsorptions on semiconductor surfaces

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- Some surface-sensitive optical techniques
  - Spectroscopic Ellipsometry
  - Reflectance Anisotropy Spectroscopy (YB, R. Del Sole)
  - Surface Differential Reflectance Spectroscopy (YB, R.DS)
  - Surface Photoabsorption
  - Electro-Reflectance
  - Second-Harmonic Generation (J. Mc Gilp, N. Tolk, L Mochan)
  - Magneto-optical techniques (T. Rasing)
  - Infra-Red Spectroscopy
  - Surface Raman Spectroscopy (W. Richter)
  - Sum (Difference) Frequency Generation (L. Mochan)

- UV-visible: electronic information
- Infra-red: vibration information
First part

1. Optical properties of semiconductor surfaces
   • Surface reconstruction
   • Bulk and Surface optical response
   • Dielectric tensor of the surface
   • Surface-sensitive optical techniques:
     • Reflectance Anisotropy Spectroscopy (RAS) (or Reflectance Difference Spectroscopy : RDS)
     • Surface Differential Reflectance Spectroscopy (SDRS)

2. Probing the reconstruction by RAS and/or SDRS
   • "Historical results" : Si(111)2x1
   • Sum rules : number of electrons involved in transitions
   • Determination of the orientation of dimers at the surface
     • "simple" cases : Si(100)2x1 and C(100)2x1
     • III-V compounds : GaAs, InAs
   • A complex surface: Si(111)7x7, well reproduced by the simple TB approach
Outline

Second part of the tutorial

3. Adsorptions on semiconductor surfaces
   • Elementary aspects of kinetics of adsorption
   • H₂ and O₂ adsorption on Si(111)7x7

4. A complete case study: Si(100)2x1
   (by combining RAS, SDRS and theoretical approaches)
   • The reconstructions of Si(100): 2x1, 2x2, c(4x2)
   • Nominal vs. vicinal single-domain surfaces
   • Contributions to the Optical Anisotropy
   • SDRS: breaking the dimers or not
   • Kinetics of adsorption on Si(100)2x1:
     ethylene; oxygen; phenylacetylene
Surface of a semiconductor: example of Silicon

Dangling bonds are energetically expensive:
Reconstruction for reducing the surface energy

Si(100)

dangling bonds

side view

Si(100)-2x1

Si dimers

[110]

LEED

Ep= 60 eV

N. Witkowski, O. Pluchery, Y. Borensztein

LEED

Si(100)2x1:H

7.68 Å

3.84 Å

1

2

[110]
Surface of a semiconductor: example of Silicon

Dangling bonds are energetically expensive:
Reconstruction for reducing the surface energy

\[ \text{Si(111)} \]
\[ \text{cleaved Si(111)-2x1} \]
\[ \text{Si(111)-7x7} \]

The Pandey \( \pi \)-bonded chain model

Coustel, YB, 2007
BULK optical response of a SC: Silicon

Si band structure

conduction bands

valence bands

Indirect transition at 1.1 eV

bulk transitions

Photon Energy (eV)

Si reflectance

(E',E)

E'

E

E2

E1

hω

Reflectance
SURFACE optical response of a SC: Silicon

(001)surface-projected Si band structure

Photon Energy (eV)

Reflectance

\( E_1 \)

\( E'_1 \)

\( (E'_o, E_1) \)

\( \hbar \omega \)

Si reflectance

Rohlfing et al, PRB 1995

surface transitions

bulk transitions

surface-to-surface transition

surface-to-bulk transition

bulk-to-surface transition
Reflectance of a bulk crystal

- Fresnel formulae at an interface

\[ r_s^o = \frac{\sqrt{\varepsilon_1 \cos \theta_1} - \sqrt{\varepsilon_{\text{bulk}}(\omega) \cos \theta_2}}{\sqrt{\varepsilon_1 \cos \theta_1} + \sqrt{\varepsilon_{\text{bulk}}(\omega) \cos \theta_2}} \]

\[ r_p^o = \frac{\sqrt{\varepsilon_{\text{bulk}}(\omega) \cos \theta_1} - \sqrt{\varepsilon_1 \cos \theta_2}}{\sqrt{\varepsilon_{\text{bulk}}(\omega) \cos \theta_1} + \sqrt{\varepsilon_1 \cos \theta_2}} \]

In normal incidence: \( r^o = \frac{1 - \sqrt{\varepsilon_{\text{bulk}}(\omega)}}{1 + \sqrt{\varepsilon_{\text{bulk}}(\omega)}} \)
Reflectance of a crystal including the surface

- **First order modification to the Fresnel formulae**

\[
\begin{align*}
    r_s &= r_s^o \left\{ 1 - 2 i \frac{\omega}{c} \cos \theta_1 \frac{\Delta \varepsilon_{yy}}{\varepsilon_{bulk} - 1} \right\} \\
    r_p &= r_p^o \left\{ 1 - 2 i \frac{\omega}{c} \cos \theta_1 \left( \frac{\varepsilon_{bulk} - \sin^2 \theta_1}{\varepsilon_{bulk} - 1} \right) \Delta \varepsilon_{xx} + \varepsilon_{bulk}^2 \sin^2 \theta_1 \Delta \varepsilon_{zz}^{-1} \right\}
\end{align*}
\]

\[\Delta \varepsilon_{xx}(\omega), \Delta \varepsilon_{yy}(\omega), \Delta \varepsilon_{zz}^{-1}(\omega)\]

= Dielectric tensor of the surface:
- dimension of length,
- describes completely the optical response of the surface

Reflectance of a crystal including the surface

Dielectric tensor of the surface: $\Delta \varepsilon_{xx}(\omega), \Delta \varepsilon_{yy}(\omega), \Delta \varepsilon_{zz}(\omega)$

Non local relation for the dielectric displacement: 

$$\bar{D}(\vec{r}, \omega) = \iiint d\vec{r}' \bar{\varepsilon}(\vec{r}, \vec{r}'; \omega) \bar{E}(\vec{r}', \omega)$$

$\bar{\varepsilon}(\vec{r}, \vec{r}'; \omega)$ = non-local dielectric tensor of the system

Modification of $\varepsilon(\omega)$ with respect to vacuum

$$\Delta \varepsilon_{xx}(\omega) = \int_{-\infty}^{+\infty} dz \int_{-\infty}^{+\infty} dz' [\varepsilon_{xx}(z, z'; \omega) - \theta(-z)\delta(z - z') - \theta(z)\delta(z - z')\varepsilon_{\text{bulk}}(\omega)]$$

Modification of $\varepsilon(\omega)$ with respect to bulk

$$\Delta \varepsilon_{xx}(\omega) = \int_{-\infty}^{0} dz \left\{ \int_{-\infty}^{+\infty} dz' \varepsilon_{xx}(z, z'; \omega) - 1 \right\} + \int_{0}^{+\infty} dz \left\{ \int_{-\infty}^{+\infty} dz' \varepsilon_{xx}(z, z'; \omega) - \varepsilon_{\text{bulk}}(\omega) \right\}$$

$$\Delta \varepsilon_{zz}(\omega) = \int_{-\infty}^{+\infty} dz \int_{-\infty}^{+\infty} dz' [\varepsilon_{zz}^{-1}(z, z'; \omega) - \theta(-z)\delta(z - z') - \theta(z)\delta(z - z')\varepsilon_{\text{bulk}}^{-1}(\omega)]$$

$$\Delta \varepsilon_{zz}(\omega) = \int_{-\infty}^{0} dz \left\{ \int_{-\infty}^{+\infty} dz' \varepsilon_{zz}^{-1}(z, z'; \omega) - 1 \right\} + \int_{0}^{+\infty} dz \left\{ \int_{-\infty}^{+\infty} dz' \varepsilon_{zz}^{-1}(z, z'; \omega) - \varepsilon_{\text{bulk}}(\omega) \right\}$$

How to measure the optical response of the surface?

- Reflectance Anisotropy Spectroscopy: RAS (or RDS)
- Surface Differential Reflectance Spectroscopy: SDRS

Differential optical techniques to suppress the bulk contribution

Surface region ≈ 1 nm (dielectric tensor)

Surface signal

Bulk signal

≈

Surface region depth

Penetration depth

≈ a few 10⁻³

Surface region penetration depth
RAS gives the spectral dependence of the complex quantity: \[ \frac{\Delta r}{r} = \frac{r_x - r_y}{r} \]

where \( r_x \) and \( r_y \) are the reflectances of light for polarisations parallel to the two main axes of the surface.

\[ \Delta r = \frac{r_x - r_y}{r} = -2i \frac{\omega}{c} \frac{\Delta \varepsilon_{xx} - \Delta \varepsilon_{yy}}{\varepsilon_{bulk} - 1} \]

\[ RA = Re \left[ \frac{\Delta r}{r} \right] = 2 \frac{\omega}{c} Im \left[ \frac{\Delta \varepsilon_{xx} - \Delta \varepsilon_{yy}}{(\varepsilon_{bulk} - 1)} \right] \]

**Reflectance Anisotropy Spectroscopy (RAS): Principle**

(RDS: Reflectance Difference Spectroscopy)

- Bulk reflectance is isotropic in cubic crystals
- RAS originates from the surface

0.5 or 1eV - 6 eV:
electronic transitions are probed
Reflectance Anisotropy Spectroscopy (RAS) : Principle

\[
\frac{\Delta r}{r} = \frac{r_x - r_y}{\bar{r}} = -2i \frac{\omega}{c} \frac{\Delta \varepsilon_{xx} - \Delta \varepsilon_{yy}}{\varepsilon_{bulk} - 1}
\]

RAS set-up

Reflectance of a crystal including the surface

- **Reflectance Anisotropy**

  - Bulk reflectance is isotropic in cubic crystals

  \[ \Delta r = -2 i \frac{\omega}{c} \Delta \varepsilon_{xx} - \Delta \varepsilon_{yy} \]

  \[ \varepsilon_{\text{bulk}} - 1 \]

  \[ RA = \text{Re} \left[ \frac{\Delta r}{r} \right] = 2 \frac{\omega}{c} \text{Im} \left[ \frac{\Delta \varepsilon_{xx} - \Delta \varepsilon_{yy}}{(\varepsilon_{\text{bulk}} - 1)} \right] \]

- **Surface Differential Reflectance** in normal incidence

  (deviation of R with respect to Fresnel reflectance):

  \[ SDR = \frac{\Delta |r|^2}{|r|^2} = \frac{\Delta R}{R} = 4 \frac{\omega}{c} \text{Im} \left[ \frac{\Delta \varepsilon_{xx} - 1}{\varepsilon_{\text{bulk}} - 1} \right] \]

comparison between clean and, eg., completely oxidized surface

Surface Differential Reflectance Spectroscopy

- **Surface Differential Reflectance** in normal incidence (deviation of $R$ with respect to Fresnel reflectance):

$$S_D R = \frac{\Delta R}{R} = \frac{R_{\text{clean}} - R_o}{R} = 4 \frac{\omega}{c} \text{Im} \left[ \frac{\Delta \epsilon_{xx} - 1}{\epsilon_{\text{bulk}} - 1} \right]$$

Comparison between clean surface and, eg., completely oxidized surface.
Surface Differential Reflectance Spectroscopy

Modification of the surface with adsorption...

\[ \frac{\Delta R}{R} = \frac{R_{\text{clean}} - R_{\text{ads}}}{R} = 4 \omega \frac{\varepsilon_{\text{bulk}} - 1}{c} \text{Im} \left[ \frac{\delta (\Delta \varepsilon_{xx})}{\varepsilon_{\text{bulk}} - 1} \right] \]

\[ \delta (\Delta \varepsilon_{xx}) \] = change of the optical response of the surface due to the adsorption

Opens the way to monitor adsorption, growth, to determine kinetics...
Surface Differential Reflectivity Spectroscopy: Set-up (1)

One-beam technique

UV and visible lamps

polarizer

Sample

gas adsorption

tungsten filament

UHV chamber

spectrograph

prism

Photodiode array

STM

LEED

computer

Fast measurements:
a spectrum every 1 or 2 seconds

Two-beam technique

Chiradia, Chiarotti, in Photonic Probes, 1995
<table>
<thead>
<tr>
<th>advantages</th>
<th>disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>- precise measurements, on well-defined surfaces</td>
<td>- works on anisotropic surfaces only (GaAs..., Si(111)2x1 ; single-domain Si(100)2x1...)</td>
</tr>
<tr>
<td>- very accurate and reproducible measurements</td>
<td>- subtle interplay of the optical responses along the two principal axis</td>
</tr>
<tr>
<td>- use of well-defined surfaces</td>
<td>- possible lose of the main surface effects, if not anisotropic</td>
</tr>
<tr>
<td>- clean surfaces, modified surfaces</td>
<td>- no or few fast spectral apparatus for monitoring real-time changes and kinetics</td>
</tr>
<tr>
<td>- isotropic defects don't modify the general shape</td>
<td></td>
</tr>
</tbody>
</table>

Both techniques are useful and can give complementary information
Outline

1. Optical properties of semiconductor surfaces

2. Probing the reconstruction by RAS and/or SDRS
   - "Historical results" : Si(111)2x1
   - Sum rules : number of electrons involved in transitions
   - Determination of the orientation of dimers at the surface
     - "simple" cases : C(100)2x1 and Si(100)2x1
     - III-V compounds : GaAs, InAs
   - A complex surface: Si(111)7x7, well reproduced by the simple TB approach

3. Adsorptions on semiconductor surfaces

4. A complete case study : Si(100)2x1
   (by combining RAS, SDRS and theoretical approaches)
First observation of a SC surface state: Si(111)2x1

- Optical detection of surface states on cleaved (111) surfaces of Ge
  G. Chiarotti, Del Signore and Nannarone, PRL 21 (1968)

- Optical Absorption of Surface States in UHV Cleaved (111) Surfaces of Ge and Si
  G. Chiarotti, S. Nannarone, Pastore, Chiaradia, PRB 4 (1971)

The ideal (111) surface

Early results in Chiarotti's group

cleaved surface in UHV, followed by complete oxidation
First observation of a SC surface state: Si(111)2x1

- Optical detection of surface states on cleaved (111) surfaces of Ge
  G. Chiarotti, Del Signore and Nannarone, PRL 21 (1968)

- Optical Absorption of Surface States in UHV Cleaved (111) Surfaces of Ge and Si
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The ideal (111) surface

Surface Differential Reflectance

Chiarotti’s group, PRB 31, 4096 (1985)
Simple (naive) explanation of the surface optical absorption

Dipolar moment related to bonds between surface atoms (dimers...)

Absorbed power: \( P_{\text{abs}} \propto \sum |\vec{E} \cdot \vec{p}_f|^2 \delta(E_{fi} - \hbar \omega) \)

- Optical absorption for polarization along the polarizable bond
- No absorption for polarization perpendicular to the polarizable bond

For optical transitions below the direct gap: peak in the reflectance spectrum

Optical measurements should permit us to determine the orientation of Si-Si bonds.

Tight-binding approach
First observation of a SC surface state: Si(111)2x1

- Optical detection of surface states on cleaved (111) surfaces of Ge
  G. Chiarotti, Del Signore and Nannarone, PRL 21 (1968)

- Optical Absorption of Surface States in UHV Cleaved (111) Surfaces of Ge and Si
  G. Chiarotti, S. Nannarone, Pastore, Chiaradia, PRB 4 (1971)
Determination of the reconstruction of Si(111)2x1: Polar dependence of the surface state transition

The ideal (111) surface

(1x1) unreconstructed symmetry

\[ \cos^2 \]

Chiarotti's group, PRB 31, 4096 (1985)
Determination of the reconstruction of Si(111)2x1: Polar dependence of the surface state

The buckling model

(2x1) reconstructed symmetry


Chiarotti’s group, PRB 31, 4096 (1985)
Determination of the reconstruction of Si(111)2x1: Polar dependence of the surface state

(2x1) reconstructed symmetry

The dimer model


Chiarotti's group, PRB 31, 4096 (1985)
Determination of the reconstruction of Si(111)2x1: Polar dependence of the surface state

The Pandey $\pi$-bonded chain model


(2x1) reconstructed symmetry

$\cos^2$

Si(111) - (2x1)

- Electric Field parallel to [011]
- Electric Field parallel to [211]

Chiarotti's group, PRB 31, 4096 (1985)
Determination of the reconstruction of Si(111)2x1: Comparison with tight-binding calculation

The Pandey $\pi$-bonded chain model

- Tight-binding approach
  (five-orbital basis set of atomic orbitals : $sp^3s^*$)

Selloni, Marsella, Del Sole, PRB33, 8885 (1986)
Sum rules and optical transitions (1/2)


Kramers-Kroenig relation:

\[ \varepsilon'(\omega) = 1 + \frac{2}{\pi} \varphi \int_{0}^{\infty} \frac{\omega' \varepsilon''(\omega')}{\omega'^2 - \omega^2} \, d\omega' \]

\[ \varepsilon'(\omega) = 1 - \frac{2}{\pi \omega^2} \int_{0}^{\omega_{\text{max}}} \omega' \varepsilon''(\omega') \, d\omega' \quad (\omega \gg \omega_{\text{max}}) \]

\[ \varepsilon'(\omega) = 1 - \frac{\omega_p^2}{\omega^2}, \quad \omega_p = \sqrt{\frac{4\pi e^2 N_s n_{\text{eff}}}{m}} \]

\[ \int_{0}^{\omega_{\text{max}}} \omega' \varepsilon''(\omega') \, d\omega' = \frac{\pi}{2} \omega_p^2 \]

If a group of electrons behave in a similar way (e.g. related to DBs), the interval of integration can be divided and each group of electrons considered separately

\[ n_{\text{eff}}(\omega) = \frac{m}{2\pi^2 e^2 N_0} \int_{0}^{\omega} \omega' [\varepsilon''(\omega')d] \, d\omega' \]

\[ n_{\text{eff}} \text{ shows a plateau when the oscillator strength of a given group of electrons is exhausted} \]
The Pandey $\pi$-bonded chain model

$$n_{\text{eff}}(\omega) = \frac{m}{2\pi^2e^2N_s} \int_0^\omega \omega'[\varepsilon''(\omega')d]\,d\omega'$$

Along the chain

$\mathbf{E}$

1 electron

0.5 electron
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3. Adsorptions on semiconductor surfaces

4. A complete case study : Si(100)2x1
   (by combining RAS, SDRS and theoretical approaches)
The case of C(100)2x1

Thoms et al, APL65, 2957 (1994)

2x1 reconstruction, with symmetric dimers

Bobrov, Mayne, Dujardin, Nature 413, 616 (2001)
The case of C(100)2x1

**Tight-binding approach**

![Graph showing photon energy vs. ΔR/R for symmetric and buckled dimers](image)

Gravilenko, Shkrebtii, SS 324, 226 (1995)

**DFT-LDA**

Kress, Shkrebtii, Del Sole SS 377 (1997)
Gravilenko and Bechstedt, PRB56 (1997)

**Experiment on 4°- vicinal C(100) surface**

![Graph showing RAS vs. energy for clean and monohydride](image)

The case of C(100)2x1: comparison with experiment Strong excitonic effects

GW approach

GW without excitonic effects (e-h)

GW with excitonic effects (e-h)

The case of C(100)2x1

Tight-binding approach

Kress, Shkrebtii, Del Sole SS 377 (1997)
Gravilenko and Bechstedt, PRB56 (1997)

DFT-LDA

Gravilenko, Shkrebtii, SS 324, 226 (1995)

π*

π

Fig. 2. Electron energy structure of the surface states on (001)-(2 × 1) symmetric dimer surface of diamond (filled circles). Bulk band structure has been projected on 2D Brillouin zone of the (001) surface.

GW approach

Palummo et al, PRL94 (2005)
The case of the "simple" Si(100) surface

- Nominal surface: two domains, no average anisotropy
- Dimers symmetric or buckled
- Apparent symmetric dimers because of flip-flop

N. Witkowski, O. Pluchery, Y. Borensztein
RAS of Si(100) (single-domain nominal surface)

**Tight-binding approach**

- FIG. 3. The reflection anisotropy (in %) for Si(100)2×1: (a) asymmetric-dimer model, (b) symmetric-dimer model.

- Shkrebti, Del Sole, PRL70, 26345 (1993)

**Experiment**

- Tight-binding approach, considers that the Si-Si bond is the polarizable entity:
- Fails to reproduce the experiment

- Pluchery, Witkowski and Borensztein, phys. st. sol. (b) 242, 2696 (2005)

- **π**
- **π**
- **π**
- **π**

- Shkrebti, Del Sole, PRL70, 26345 (1993)
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Reconstructions of GaAs(100)

As-rich surfaces

\(\alpha(2x4)\)

\(\beta_2(2x4)\)

\(c(4x4)\)

Ga-rich surface

\(\zeta(4x2)\)

G. Schmidt et al, phys. st. sol. (a) 188, 1401 (2001)
RAS of GaAs(100): As-rich surfaces

Optical absorption of the As dimers?

Kamiya, Aspnes et al, PR B46, 15894 (1992)
RAS of GaAs(100): As-rich surfaces

Good agreement with tight-binding calculation

Experiment (Richter’s group)

Calculation (Del Sole’s + Bechstedt groups)

Shkrebtii et al, PRL 81, 721 (1998)
RAS of GaAs(100) : from As-rich to Ga-rich surfaces

Ga dimers

As dimers

Kamiya, Aspnes et al, PR B46, 15894 (1992)

Lee et al, PRL85, 3890 (2000)

Not that simple !

As-As dimer ?

Ga-Ga dimer ?

As-As dimer?
As-rich surfaces

\begin{align*}
\text{As} & \quad \bullet \\
\text{Ga} & \quad \bigcirc \\
\end{align*}

Ga-rich surface

\begin{align*}
\zeta(4x2) & \\
\end{align*}
GaAs: DFT-LDA and GW approaches

As-rich surfaces

Ga-rich surface

GaAs: DFT-LDA and GW approaches

As-rich surfaces

α(2x4)

β2(2x4)

Ga-rich surface

ζ(4x2)

GW

Low temp exp.

G. Schmidt et al phys. st. sol. (a) 188, 1401 (2001)
RAS of In-rich InAs(100) : effect of O$_2$ adsorption

Berkovits, Witkowski, Borensztein and Paget, PR B63, R121314 (2001)

$\zeta(4x2)$

In dimers

In-dimer absorption line

$E_0'$

$E_1+\Delta_1$

$E_1$

bulk transitions

Energie de photon (eV)

RAS (x 10$^{-2}$)

140 K

clean

1000L
RAS of In-rich InAs(100): effect of O$_2$ adsorption

Berkovits, Witkowski, Borensztein and Paget, PR B63, R121314 (2001)

In dimers

$\varsigma(4x2)$

In-dimer absorption line

$E_0'$

bulk transitions

$E_1 + \Delta_1$

$E_1$

Energie de photon (eV)

RAS (x 10^{-2})

Energie de photon (eV)

140 K

clean

1000L

8000L
Chemisorption of O\textsubscript{2} on In-rich InAs surface at 140 K

- bulk structures unchanged
- disappearance of the 1.8 eV In dimer line
- the structure is not restored after a gentle heating

⇒ oxygen molecules are chemisorbed on In dimers

Exponential law (one non-dissociated O\textsubscript{2} molecule per In dimer)

Berkovits, Witkowski, Borensztein and Paget, PR B63, R121314 (2001)
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   (by combining RAS, SDRS and theoretical approaches)
A complex surface: Si(111)-7×7

Determination of the optical response by SDRS

**Experimental method:**

- UHV preparation
- Adsorption of atomic H (at different doses and temperatures)
- Measurement of Surface Differential Reflectance
A complex surface: Si(111)-7x7
Determination of the optical response by SDRS

First step:
adsorption of H on dangling bonds

Second step:
Breaking of the backbonds

Photon energy (eV)

Si(111)7x7:H (1\textsuperscript{st} step)

Si(111)7x1:H (2\textsuperscript{nd} step)

clean Si(111)7x7
How to calculate the surface dielectric tensor? the slab approach

$$\varepsilon = 1 + 4\pi\alpha$$

$$\frac{\Delta R_i}{R} = 4 \frac{\omega}{c} \text{Im} \left[ \frac{4\pi\alpha_{ii}^{hs}(\omega)}{\varepsilon_{bulk}(\omega) - 1} \right]$$

$$\alpha_{ii}^{hs}(\omega) = \int_{-d_v/2}^{d/2} dz \int _{-\infty}^{\infty} dz' \alpha_{ii}(z, z'; \omega)$$

Slab geometry:

1. Structure of the surface
2. Band structure of the slab
3. Slab polarizability
4. Removal of the bulk contribution
5. Surface dielectric tensor

Reconstructed surface

Several layers

vacuum

F. Manghi, E. Molinari, A. Selloni, Del Sole, PRB 1990
Si(111)-7x7: Adsorption of hydrogen. Theory vs. Exp.

First step: adsorption of H on dangling bonds

- Reactive dangling bonds
- Si(111)-7x7
- 7x7
- 1x1:H

Experiment

Theory

Noguez, Beitia, Borensztein et al, PRL76, 4923 (1996)
Si(111)-7x7: Adsorption of hydrogen. Theory vs. Exp.

Second step: breaking of the backbonds and removal of the Si adatoms

Noguez, Beitia, Borensztein et al, PRL76, 4923 (1996)
Outline

Second part of the tutorial

1. Probing the reconstruction by RAS and/or SDRS
   - Remindings
   - A complex surface: Si(111)7x7, well reproduced by the simple TB approach

2. Adsorptions on semiconductor surfaces
   - Elementary aspects of kinetics of adsorption
   - H⁺ and O₂ adsorption on Si(111)7x7

3. A complete case study: Si(100)2x1
   (by combining RAS, SDRS and theoretical approaches)
Elementary aspects of kinetics of molecule/atom adsorption

1. Direct molecular adsorption (the Langmuir kinetics of chemisorption)

- adsorbates randomly occupy the sites of an adsorption checkerboard (occupancy $\theta$)
- a particle impinging an empty site adsorbs, otherwise it desorbs
- the sticking coefficient $s(\theta)$ is proportional to the product:

$$s(\theta) = s_o (1 - \theta)$$

- the kinetics equation reads:

$$\frac{d\theta}{dt} = \alpha.s_o (1 - \theta)$$

which is solved in:

$$\theta(t) = 1 - e^{-t/\tau_o}$$

where $\tau_o = 1 / (\alpha.s_o)$ is a time constant.

H on Si(111)7x7 (two $\neq$ sites)

$O_2$ on InAs(110)
2. Direct dissociative molecular chemisorption

- two empty surface sites per impinging molecule are necessary
- the sticking coefficient \( s(\theta) \) is proportional to the product:

\[
( \text{impinging rate}) \times (\text{number of available sites})^2 : s(\theta) = s_o (1-\theta)^2
\]

- the kinetics equation reads:

\[
\frac{d\theta}{dt} = \alpha s_o (1-\theta)^2
\]

which is solved in:

\[
\theta(t) = \frac{t/\tau_o}{1+t/\tau_o}
\]

where \( \tau_o = 1 / (\alpha s_o) \) is a time constant

\( \theta = 0 \)

\( \theta = 5/13 = 0.38 \)

\( \text{O}_2 \text{ on Si}(111)7x7 ; \)
Elementary aspects of kinetics of molecule/atom adsorption

3. Physisorption vs. chemisorption

- A molecule (atom) can:
  1. chemisorb on an available site
  1bis. be physisorbed (precursor state)
  2. migrate on the surface
  3. chemisorb on an available chemisorption site, or desorb in the gas phase

- If the desorption rate is zero, then every impinging particle will be chemisorbed: linear kinetics

- If the desorption rate is small, the kinetics is almost linear, except at the end (H on Si(100))

- The adsorption process can be complex:
  - repulsive or attractive sites
  - different adsorption configurations and sites
  - different sticking probabilities
  - dissociative process or not...

use of a Monte Carlo approach with appropriate hypothesis can be useful
(PA and C$_2$H$_4$ on Si(100))
Si(111)-7x7:H : decomposition of SDR spectra

Two mechanisms :
- adsorption on Dangling Bonds
- adsorption on Backbonds
Each have an SDR optical signature

SDR spectra can be decomposed in both elementary spectra :

\[ S(d) = a(d) \cdot S_{DB} + b(d) \cdot S_{BB} \]

Determination of coefficients \( a(d) \) and \( b(d) \) permits us to determine the kinetics of reaction
Kinetics of adsorption of H on Si(111)7x7

Fast adsorption on DBs,
Delayed and slower adsorption on BBs

**Double Langmuir model**

\[
\frac{dx}{dt} = N_g P e^{-\frac{E_a}{kT}} (12-x) \quad (0 \leq x \leq 12)
\]

\[
\frac{dy}{dt} = N_g P e^{-\frac{E_b}{kT}} (3x-y) \quad (0 \leq y \leq 3x)
\]

\[
x(d) = 12 \left( 1 - e^{-\alpha d} \right)
\]

\[
y(d) = 36 \left( 1 - \frac{\beta}{\beta - \alpha} e^{-\alpha d} + \frac{\alpha}{\beta - \alpha} e^{-\beta d} \right)
\]

Beitia, Preyss, Del Sole, Borensztein, PRB 56 R4371 (1997)
Kinetics of adsorption of H on Si(111)7x7

Energetical scheme of H reaction with Si(111)7x7 surface

Activation barriers of both mechanisms

$E_\alpha = 3 +/- 3$ meV: no barrier for direct adsorption on DBs

$E_\beta = 20 +/- 10$ meV: Barrier for adsorption on BBs, AFTER adsorption on DBs

Beitia, Preyss, Del Sole, Borensztein, PRB 56 R4371 (1997)
Adsorption of $\text{O}_2$ on Si(111)7x7

Beitia, Borensztein, pss(a) 175, 39 (1999)
Adsorption of $\text{O}_2$ on Si(111)7x7

direct dissociative adsorption?

$$\frac{d\theta}{dt} = \alpha \cdot s_0 (1 - \theta)^2$$

$$\theta(t) = \frac{t/\tau_0}{1 + t/\tau_0}$$

Beitia, Borensztein, *pss(a)* 175, 39 (1999)
Outline

Second part of the tutorial

1. Probing the reconstruction by RAS and/or SDRS
2. Adsorptions on semiconductor surfaces
3. A complete case study : Si(100)2x1
(by combining RAS, SDRS and theoretical approaches)

- The reconstructions of Si(100): 2x1, 2x2, c(4x2)
- Nominal vs. vicinal single-domain surfaces : RAS
- Contributions to the Optical Anisotropy
- SDRS : breaking the dimers or not
- Kinetics of adsorption on Si(100)2x1:
  ethylene ; oxygen ; phenylacetylene
Different reconstructions of the Si(100) surface

Dimers - dangling bonds
Dimerisation
Buckling

p(2x1)
p(2x2)
c(4x2)

After B. Grandidier, IEMN, France
The two-domain nominal Si(100) surface

After B. Grandidier, IEMN, France
RAS on nominal vs. vicinal Si(100)2x1

- Preparation of single domain surfaces of Si(100):
  - use of a vicinal surface (4°) : pairing of steps
  - use of highly oriented surface (< 0.1°) and electromigration of surface atoms (very delicate)

- Need of very high vacuum:
  - base pressure $5 \times 10^{-11}$ mbar
  - $< 2 \times 10^{-10}$ mbar during the cleaning by direct current flow, at 1100°C
RAS on nominal vs. vicinal Si(100)2x1

Nominal surface

4° - Vicinal surface

Pluchery, Witkowski and Borensztein, phys. st. sol. (b) 242, 2696 (2005)
Reflectance Anisotropy Spectroscopy (RAS) on nominal Si(100)-2x1

- Bulk transitions modified near the surface
- No bulk transitions below 3.4 eV
Main origins of the optical anisotropy

- Transitions involving surface states:
  - $s \rightarrow s$ (case of $\pi \rightarrow \pi^*$ in C(100) and in Si(100))
  - $s \rightarrow b$
  - $b \rightarrow s$

  = Fingerprints of the surface reconstruction

- Surface-perturbed bulk transitions
  - folding of the Brillouin zone
  - stress-induced optical anisotropy (piezo-optic effect)
  - Franz-Kelddish effect (opto-electric effect, or electroreflectance)

- Additional surface features (steps, defects...)
Reflectance Anisotropy Spectroscopy (RAS) on nominal Si(100)-2x1

- **Surface-to-bulk** transitions
- **Bulk-to-surface** transitions

**Surface-to-surface transition** ($\pi \rightarrow \pi^*$), delocalized along the dimer row

- **Bulk transitions modified by the surface**
- **No bulk transitions below 3.4 eV**

Incze, Del Sole, Onida, PRB71, 035350 (2005)
Reflectance Anisotropy Spectroscopy (RAS) on nominal Si(100)-2x1

- Good agreement between experiment and GW + excitonic effects

Palummo, Borensztein et al, to be published
Contribution of steps in RAS of vicinal Si(100)

Nominal single-domain surface

Vicinal single-domain surface

Jaloviär et al, PRL 82, 791 (1999)

step contribution
Contribution of steps in RAS of vicinal Si(100)

G. Schmidt et al, PRB 63, 045322 (2001)
RAS on nominal vs. vicinal Si(100)2x1

Nominal surface

4° - Vicinal surface

Pluchery, Witkowski and Borensztein, phys. st. sol. (b) 242, 2696 (2005)
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   - SDRS: breaking the dimers or not
   - Kinetics of adsorption on Si(100)2x1:
     ethylene; oxygen; phenylacetylene
Optical monitoring of H adsorption on Si(100) by SDRS

H\textsubscript{at} adsorption at 300 °C

H\textsubscript{at} adsorption at 25 °C

(First step)

\begin{align*}
\Delta R/R &= R\text{\textsubscript{clean}} - R\text{\textsubscript{H}} \\
\Delta r/r\text{\textsubscript{10}} &= \text{Optical "fingerprint"}
\end{align*}

Advertisment on dangling bonds, Dimers unbroken

First step: dimers unbroken

Borensztein, Pluchery and Witkowski, PRL 95, 117402 (2005)
Optical monitoring of H adsorption on Si(100) by SDRS

H$_{at}$ adsorption at 300 °C

H$_{at}$ adsorption at 25 °C

(Second step)

Mono-hydride

Di-hydride

Optical "fingerprint"

Adsorption on dangling bonds, Dimers unbroken

First step: Dimers unbroken

Second step: Dimers are broken

Borensztein, Pluchery and Witkowski, PRL 95, 117402 (2005)
H$_{at}$ on Si(100): good agreement experiment / theory

\[ \frac{\Delta R}{R} = \frac{R_{\text{clean}} - R_H}{R} \]

Experiment

0.2 eV shift due to the different temperatures

Theory

GW with e-h

GW without e-h

Palummo, Del Sole, Pluchery, Witkowski, Borensztein, to be published
$H_{\text{at}}$ on Si(100): good agreement experiment / theory

$$\frac{\Delta R}{R} = \frac{R_{\text{clean}} - R_{H}}{R}$$

- **experiment**

**dihydride**

**monohydride**

0.2 eV shift due to the different temperatures
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   • SDRS: breaking the dimers or not
   • Kinetics of adsorption on Si(100)2x1:
     • H₂
     • ethylene; oxygen; phenylacetylene
Adsorption of ethylene on Si(100)

Binding energy $E_b$ (in eV) per adsorbed ethylene molecule

<table>
<thead>
<tr>
<th></th>
<th>0.5 ML on-top</th>
<th>0.5 ML bridge</th>
<th>1 ML on-top</th>
<th>1 ML bridge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_4$</td>
<td>2.06</td>
<td>1.94</td>
<td>1.98</td>
<td>2.10</td>
</tr>
<tr>
<td>$C_2H_4^{13}$</td>
<td>1.94</td>
<td>1.82</td>
<td>1.91</td>
<td>2.01</td>
</tr>
<tr>
<td>$C_2H_4^9$</td>
<td>2.10</td>
<td>1.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_4^{12}$</td>
<td>1.93</td>
<td></td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>$C_2H_4^{31}$</td>
<td>1.57</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Marsili, Witkowski, Pulci, Pluchery, Silvestrelli, Del Sole, Borensztein, PRB77, 125337 (2008)
Adsorption of ethylene on Si(100)

- Good agreement for the clean surface
- 0.5 ML: No clear distinction between the on-top and bridge configurations
- 1 ML: Better agreement for the on-top configuration than for the bridge one
- Energy barrier to be crossed for going to the more stable on-top configuration at 0.5 ML to the more stable bridge one at 1 ML
Native oxide formation

- **Here**: very initial adsorption process at room temperature:
  - first Si layer only

- Dissociative process: $\text{O}_2 \rightarrow \text{O}^- + \text{O}^-$
- No energy barrier
- Oxidation of first Si layer: incomplete but fast
- Complete oxidation of first Si layer: much slower
- Oxidation of deeper Si layers not possible at RT
Adsorption of oxygen molecules at RT

- Numerous possible geometries

![Diagram showing various oxygen molecule geometries at RT](image)
Adsorption of oxygen molecules at RT

From Differential Reflectance

- Initial effect of RT adsorption of $O_2$:
  - breaking of the dimers
  - no adsorption on the dangling bonds

- Large exposure needed to completely oxidize the surface
  (much more than 300 L)

From Reflectance Anistropy

- RAS very sensitive to the adsorption structure
- Comparison experiments / calculations for different configurations
Adsorption of oxygen molecules at RT

RAS calculations for the more stable structures at 0.5 ML coverage (Bechstedt, Del Sole, Onida groups)

C1

Dimer-Backbond

C2

Backbond-Backbond

1E

Backbond-Backbond

1D

Dimer-Dimer

Witkowski, Pluchery, Borensztein, Gaal-Nagy, Incze, Onida, Fuchs, Bechsdedt, Del Sole, submitted
Adsorption of oxygen molecules at RT

RAS calculations for the more stable structures at 0.5 ML coverage (Bechstedt, Del Sole, Onida groups)

π → π* transition

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RAS calculations for the more stable structures at 0.5 ML coverage (Bechstedt, Del Sole, Onida groups)

$\pi \rightarrow \pi^*$ transition

Witkowski, Pluchery, Borensztein, Gaal-Nagy, Incze, Onida, Fuchs, Bechstedt, Del Sole, submitted
Adsorption of oxygen molecules at RT

**Calculated RAS for 0.5 ML**

- Good agreement for clean surface
- No calculated RAS can reproduced experimental one for $\approx 0.5$ ML
- Close adsorption energies: combination of different adsorption configurations
- C2 and 1E give similar spectra; 1E has a smaller energy

**Experimental RAS for increasing amount of $O_2$**
Adsorption of oxygen molecules at RT

Coexistence of different configurations at the surface: C1, 1D, 1E, clean, with respective weights: $x_c$, $x_D$, $x_E$, $(1-x_c-x_D-x_E)$

Witkowski, Pluchery, Borenszteim, Gaal-Nagy, Incze, Onida, Fuchs, Bechsdedt, Del Sole, submitted
Adsorption of oxygen molecules at RT

Calculated RAS for 0.5 ML

Linear combination of clean, C1, 1D, 1E for reproducing the exp RAS

\[
\frac{\Delta r}{r} = x_D \cdot \frac{\Delta r}{r}(1D) + x_E \cdot \frac{\Delta r}{r}(1E) + x_C \cdot \frac{\Delta r}{r}(C1) \\
+ (1 - x_D - x_E - x_C) \cdot \frac{\Delta r}{r}(\text{clean})
\]
Adsorption of oxygen molecules at RT

- Experimental fitting
- Clean
- Coverage
- Photon Energy (eV)

- 1E
- 1D
- C1
- C2
Adsorption of oxygen molecules at RT

Langmuirian kinetics model
- $x_D$ and $x_E$ = proportion of 1D and 1E sites
- two adsorption probabilities $p_E$ and $p_D$

\[
\frac{dx_D}{dt} = p_D (1 - x_D - x_E)
\]
\[
\frac{dx_E}{dt} = p_E (1 - x_D - x_E)
\]

\[
x_{D,E}(t) = p_{D,E} \left(1 - e^{-t/\tau}\right)
\]

$p_D = 0.42$ ; $p_E = 0.58$

exponential parameter : $\delta = 2.2$ L
Adsorption of oxygen molecules at RT

- What about larger coverage?
  - more complicated local configurations:
    - disordering of the surface, which removes the optical response of Si(100)
  - First-principle molecular dynamic calculation

Ciacchi and Payne, PRL95,196101 (2005)
Phenylacetylene on Si(100)

Ordering of the molecules on a reconstructed Si(100)2x1 surface?

- conductivity properties
- optical properties (dichroism...)

phenylacetylene

parallel charge transfer

conjugated molecule
Phenylacetylene on Si(100)

Numerous possible configurations

The most probable:

Phenylacetylene on Si(100) : first stage


ratio of both configurations:

L (large spot): 45%
S (small spot): 55%
Large spot

Small spot

depression

L = Large spot
A = (coordinate)
B = (coordinate)
C = (coordinate)
D = (coordinate)

S = Small spot
S = (coordinate)
S = (coordinate)

Molecular structures:
Left side:
- Benzene ring
- Other structural elements

Right side:
- Molecular structure with additional elements
- Comparison with large spot
Large amounts of phenylacetylene: STM fails

LEED (57 eV)

Si(100)-2x1

Clean

Saturated with PA

Saturation

0.15 ML

6.2 nm
SDRS of PA on Si(100)2x1: comparison with H

1. Same spectrum as for monohydride-Si: dimers are not broken
2. Intensity reduced by 0.65: 65% of the dangling bonds are affected by PA adsorption

possibly optical absorption (in phenylacetylene or in styrene-like)

Kinetics of PA adsorption

- Doesn't follow Langmuir kinetics
- Linear increase: precursor (physisorbed) state

Kinetic equations
1. every impinging molecule is physisorbed
2. a precursor can chemisorb or desorb
3. probability of chemisorption depends on the coverage

Monte Carlo approach

- at the beginning: 45% of L, 55% of S
- probability of chemisorption: \( f(\theta) \approx 1 - \frac{\theta}{0.65} \)

Final coverage: 65% of the dangling bonds are bound to PA

Alternative possibilities:
- only L configuration: coverage of 78%
- only S configuration: coverage of 50%
Monte Carlo approach

- at the beginning: 45% of L, 55% of S
- probability of chemisorption: \( f(\theta) \approx 1 - \frac{\theta}{0.65} \)

Final coverage: 65% of the dangling bonds are bound to PA
**Kinetics of PA adsorption**

At the end

- 71% of L
- 29% of S

RAS : a "chemical" probe of adsorbed molecules

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