Ellipsometric Investigation of Atomically Flat Silicon Crystals

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Outline

Motivation

The Si(111)-(1×1):H Surface

- Wet-chemical preparation of silicon surfaces
- Surface bonding: FTIR spectroscopy
- Surface topography: AFM

Spectroscopic Ellipsometry

- Optical constants of Si(111)-(1×1):H
- Strength and position of $E_2$ critical point
- Optical constants of weakly degraded surfaces

Outlook
Motivation

Optical Constants:

Reflectance techniques, such as ellipsometry, do not measure the complex dielectric function directly: assumptions, modelling.

Simplest approach:

Two-phase model with ideal solid and ambient

→ Requires the preparation of an atomically flat and perfectly terminated surface with bulk properties to the top layer

Accuracy:

- Still determined by the present quality of surface preparation?
- Problems with accurate calibration of the instrument?
- The intrinsic accuracy of reflectance type measurements of 1-2% is reached

Future Goals:

→ VUV laser-induced growth of SiO$_2$
→ Formation of Ge islands on Si(111)
Si(111)-(1x1):H

Preparation:

- Wafer cleaning procedure using the RCA steps
- Oxide was stripped with ammonium fluoride etchant containing hydrofluoric acid (Merck Selectipur®)
- After reoxidation H-termination was obtained by immersion in 40% NH₄F solution for 6½ min followed by a short rinse in ultrapure water

Properties:

Theoretical linewidths detected by transmission Fourier Transform IR spectroscopy (FTIR):

→ SiH stretching mode: 0.79 cm⁻¹
→ SiH bending mode: 11 cm⁻¹

Atomically flat topography with steps was found by Atomic Force Microscopy (AFM):

→ Average terrace width: ≈100-200 nm
→ Essentially no etch pits on surface
H/Si(111)
MIR
p-polarization
T = 300 K

a) HF: pH₂
b) HF+NH₄F:pH₈

Frequency (cm⁻¹)

2040 2080 2120 2160

x 10

x 1
Si(111)-(1x1): H
InSb; 60°; UHV (6x10⁻⁸ mbar)
Resolution: 4, 2, 1, 0.5 cm⁻¹

Absorption [10⁻³]

Wavenumber [cm⁻¹]
AFM-Aufnahme einer Si(111)-H-Oberfläche
Si(111)-(1x1):H Surface Quality

Flat Terraces:

Terraces are atomically flat with perfect H-terminated domains; the step height of 3.1Å corresponds to two silicon layers ("bilayer")

→ A residual miscut of ≈ 0.2° along Si(111) creates average terrace sizes of ≈100 nm

→ A residual miscut of ≈ 0.01° along Si(111) creates average terrace sizes of ≈2000 nm

Etch Pits:

Surface holes one or several bilayers deep with triangular shape point to the next lower terrace

→ Reflect the threefold rotational symmetry of the Si(111) surface

→ Oxygen dissolved in aqueous ammonium fluoride solution initiates etch pit formation
Structure of the Si(111)-(1x1):H Surface

**Electronic Properties:**

Terminating H atoms are negatively charged due to the difference in the electronegativity between Si and H

→ Charge of - 0.74 electrons per H atom
→ The first Si layer compensates 94%

**SiH-bond length:**

The Si-H-bond length increases by 0.01Å

**Si-Lattice Relaxation:**

The first four Si layers possess alternating contracted and expanded interlayer distances

→ Contraction of the Si\textsubscript{1}-Si\textsubscript{2} interlayer
  Theory: - 0.05 Å, Experiment: - 0.073Å

→ Expansion of the Si\textsubscript{2}-Si\textsubscript{3} interlayer
  Theory: +0.007Å, Experiment: +0.013Å
Stick-and-ball representation of the slab model adopted for Si(111)\((1\times1)\)-H surface. The electron density topological analysis recovers the same bonding network.
Si(100):H; InSb; 60°
Resolution 4 cm$^{-1}$
Experimental

**Instrument:**

Spectroscopic ellipsometer (SOPRA ES4G OMA); Rotating polarizer setup with high pressure 75 W xenon arc lamp in the spectral range $1.17 - 4.72 \text{ eV}$ with $0.008 \text{ eV}$ resolution.

**Data Acquisition:**

Each spectrum consists of 512 data points between $1.2 - 4.7 \text{ eV}$, averaged about 20 times.

**Calibration:**

Calibration with two oxide covered silicon samples with a SiO$_2$ layer of 179 nm and 2.529 $\mu$m provided by SOPRA.

**Angle of Incidence:** 73.95° ± 0.05
red line: Si(111)-(1×1):H in UHV (p<10⁻⁹ mbar)
blue line: reference data of C.M. Herzinger et al. (1998)
E₂-Peak Strength

"A higher value of $E_2$ implies a more abrupt transition between bulk and ambient, and hence an improved representation of the true bulk dielectric function"

Aspnes

Experiments:

$E_2 = 47.6$:  
Oxidized epitaxial Si(001) surface

$E_2 = 48.3\pm0.1$:  
Yasuda, Aspnes (1994)  
NH₄F preparation of Si(111)-(1×1):H

$E_2 = 47.2$:  
Angermann, Henrion, Rebien, Fischer, Zettler, Röseler (1998)  
NH₄F preparation of Si(111)-(1×1):H

$E_2 = 49 \pm 1.0$:  
NH₄F preparation of Si(111)-(1×1):H
Critical Point Positions

Silicon Critical Point Energies:

E\(^0\), E\(_1\), and E\(_2\) critical point energies obtained from optical spectra are apparent not true bulk values

→ sensitive to chemical and structural surface termination

Typical Values:

(E\(^0\),E\(_1\)) transition: 3.42 eV
E\(_2\) transition: 4.24 eV

Highest Values:

(E\(^0\),E\(_1\)) transition: 3.47 eV
E\(_2\) transition: 4.28 eV

Blue Shift:

Indicates a smaller influence of surface states
Si(111)-(1x1):H

$\varepsilon_1$ (real part of dielectric function)

$\varepsilon_2$ (imaginary part of dielectric function)

- red line: Si(111)-(1x1):H after wetchemical preparation
- blue line: Si(111)-(1x1):H after immersion in HF for 30 s
- green line: Si(111)-(1x1):H after immersion in HF for 60 s

Photon energy [eV]
Si(1 1 1)-(1×1):H
60°; InSb;
Res.: 0.5 cm⁻¹

2083.8 cm⁻¹ after preparation

2083.6 cm⁻¹ after immersion in conc. HF for 30 s

after immersion in conc. HF for 60 s
Topography of silicon surfaces (AFM)
Outlook

\textit{Si(111)-(1×1):H}

- Homogeneous chemical termination (H)
- No UV-light absorption in Si-H layer
- Negligible surface roughness (atomic steps)
- Insignificant relaxation; no reconstruction

\textit{Most Ideal Solid:}

\[ \rightarrow \text{Very near "bulk optical constants"} \]

\textit{Surface Effects:}

Many changes occur on other silicon surfaces: \textit{structural, chemical, roughness, usw.}

\[ \rightarrow H \text{ termination on Si(100): SiH, SiH}_2, \text{SiH}_3 \]

\[ \rightarrow \text{Effects of residual overlays (e.g. oxide)} \]