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% NH_4F** solution for 6½ min followed by a short rinse in ultrapure water

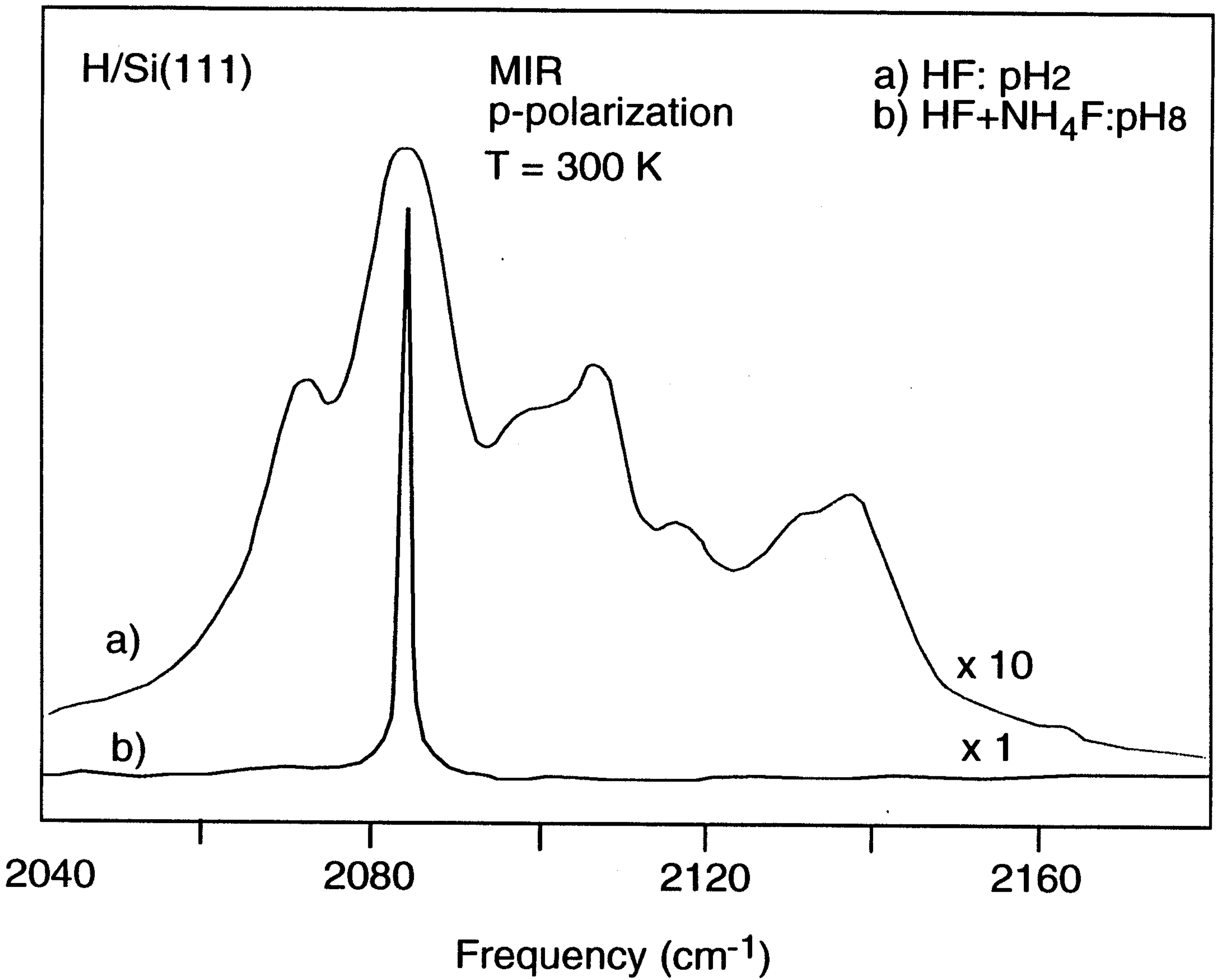
Properties:

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

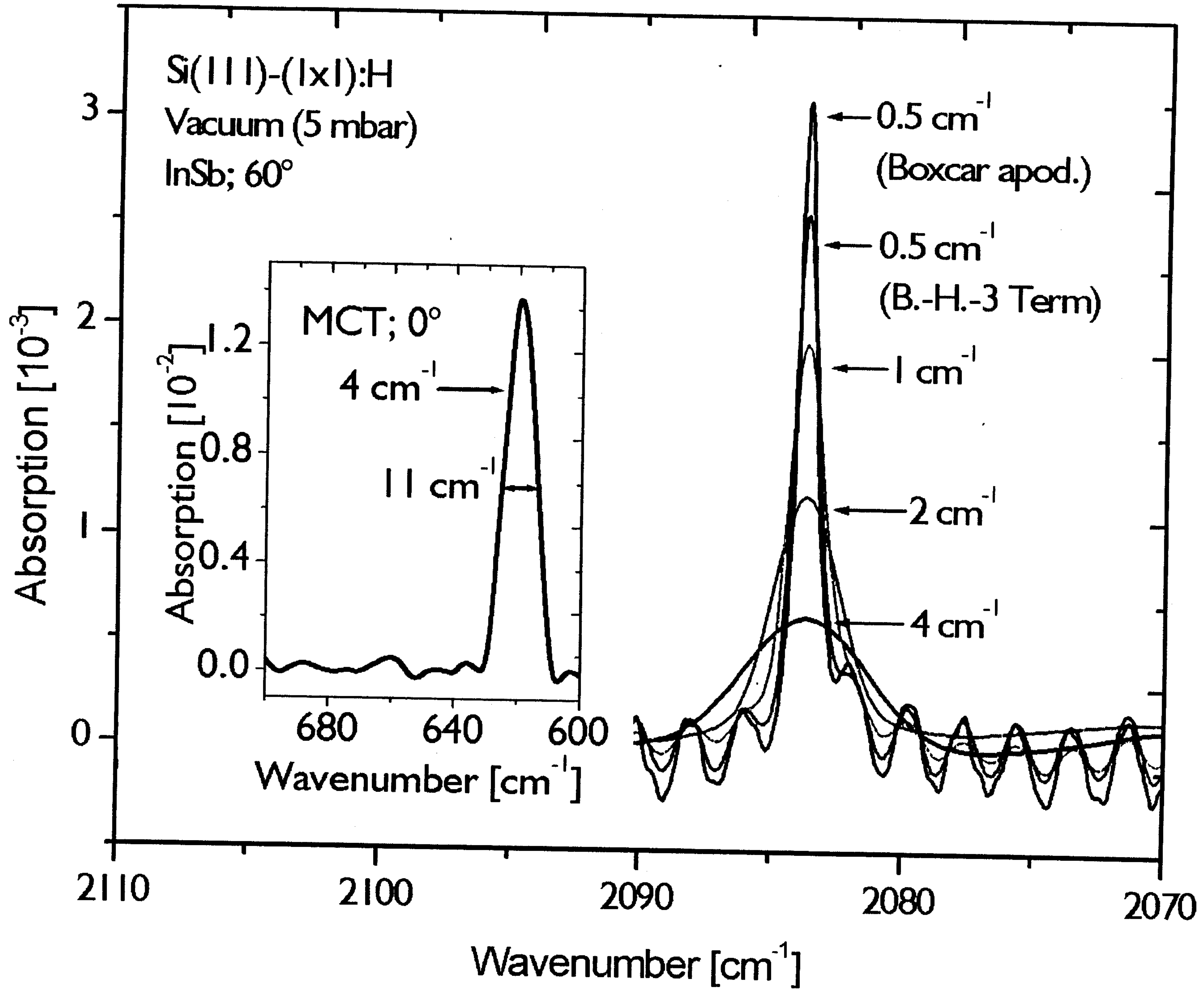
→ SiH stretching mode: **0.79 cm^{-1}**
→ SiH bending mode: ≈ **11 cm^{-1}**

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

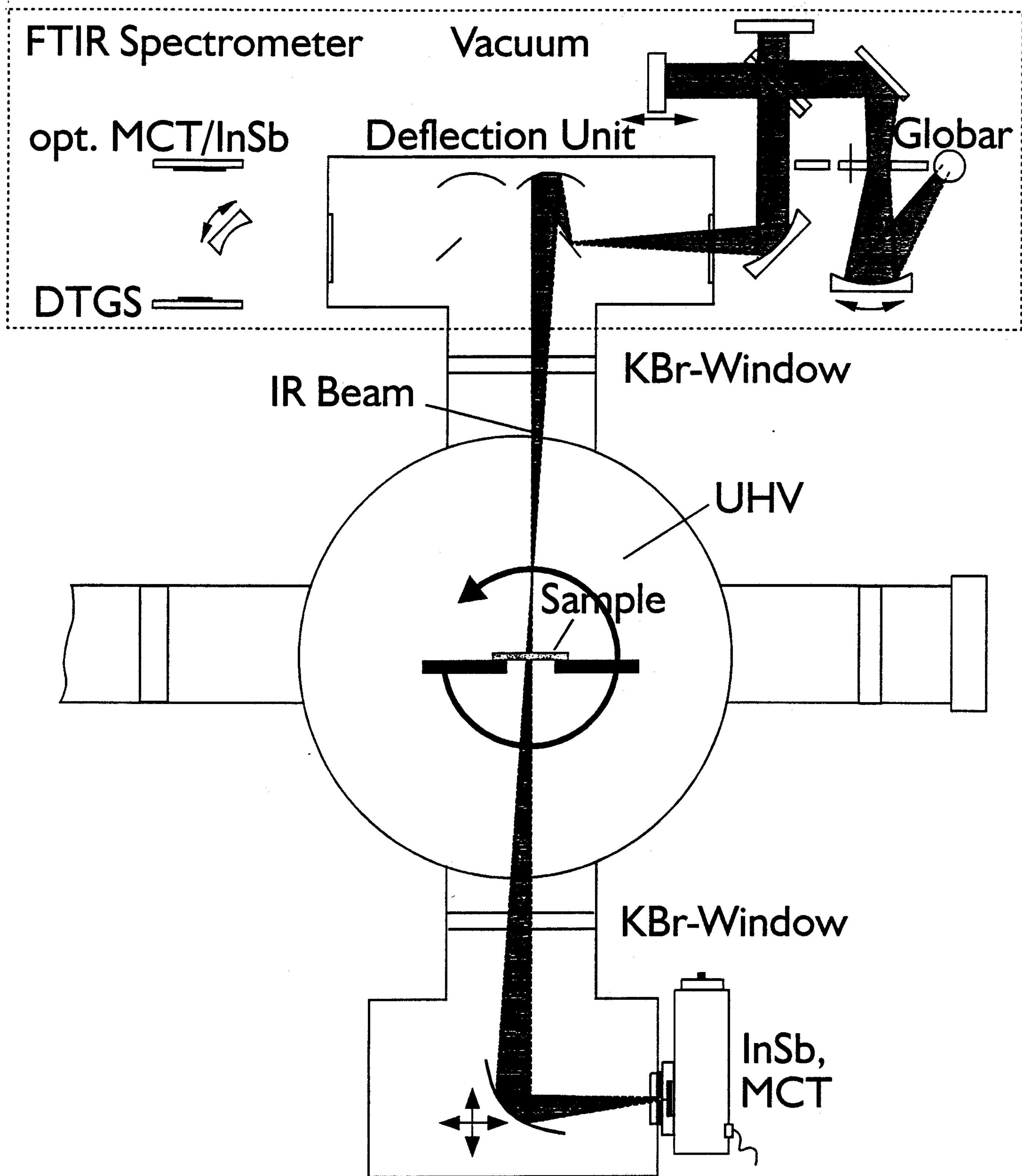
→ Average terrace width: ≈**100-200 nm**
→ Essentially no etch pits on surface

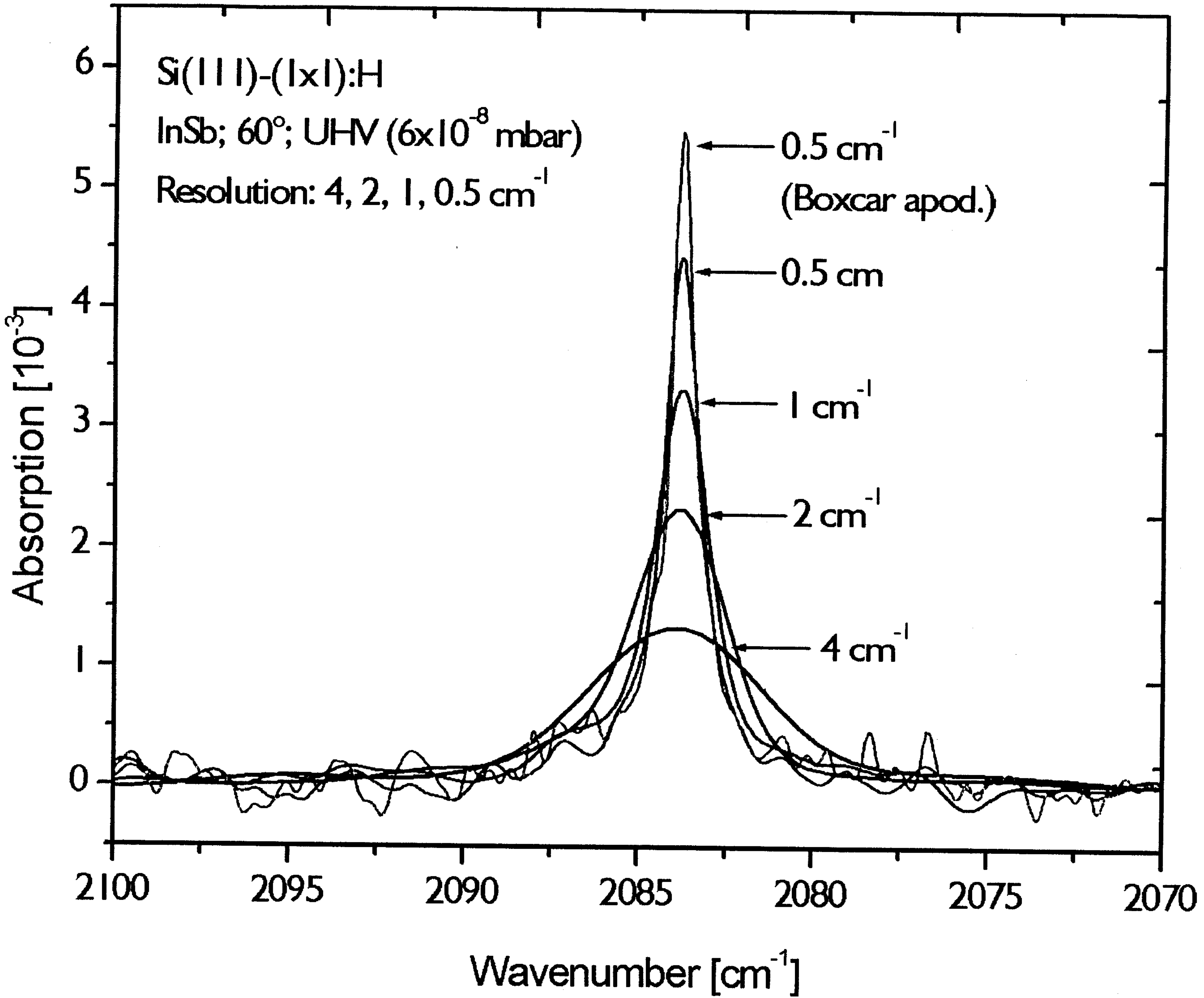


M587He



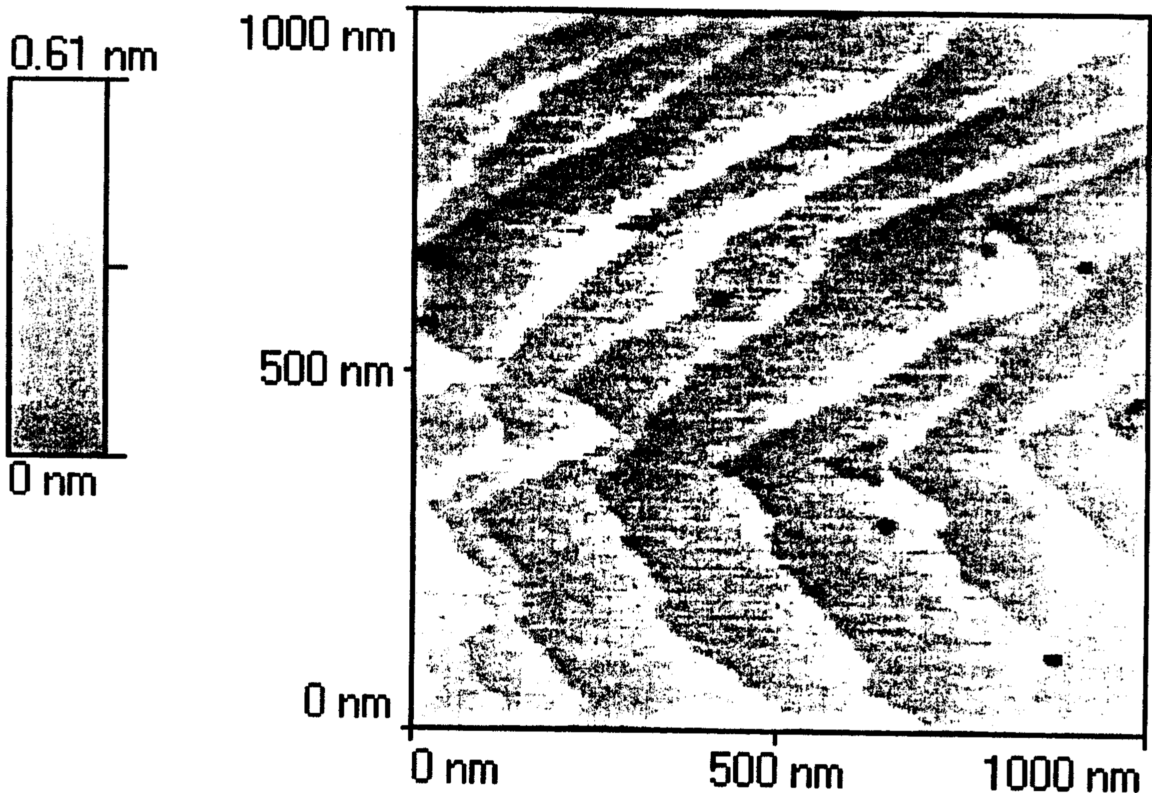
Si(111)-(1x1):H
Vacuum (5 mbar)
InSb; 60°
0.5 cm-1
(Boxcar apod.)
0.5 cm-1
(B.-H.-3 Term)
1 cm-1
2 cm-1
4 cm-1
MCT; 0°
4 cm-1
11 cm-1
Absorption [10-2]
1.2
0.8
0.4
0.0
680
640
600
Wavenumber [cm-1]
Absorption [10-3]
3
2
1
0
2110
2100
2090
2080
2070
Wavenumber [cm-1]


FTIR Spectrometer
Vacuum
opt. MCT/InSb
Deflection Unit
Globar
DTGS
KBr-Window
IR Beam
UHV
Sample
KBr-Window
InSb,
MCT



Si(111)-(1x1):H
InSb; 60°; UHV (6x10-8 mbar)
Resolution: 4, 2, 1, 0.5 cm-1
0.5 cm-1
(Boxcar apod.)
0.5 cm
1 cm-1
2 cm-1
4 cm-1
Absorption [10-3]
0
1
2
3
4
5
6
2100
2095
2090
2085
2080
2075
2070
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:

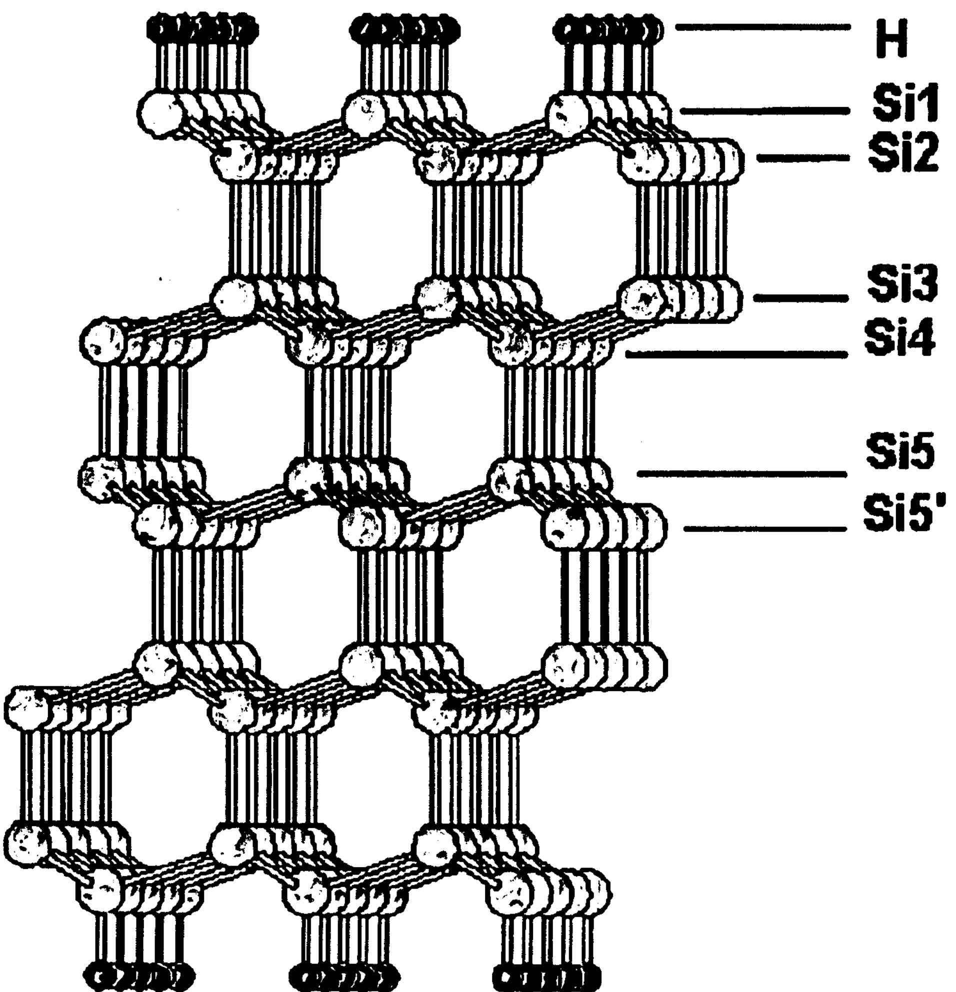
The Si-H-bond length increases by 0.01Å

Si-Lattice Relaxation:

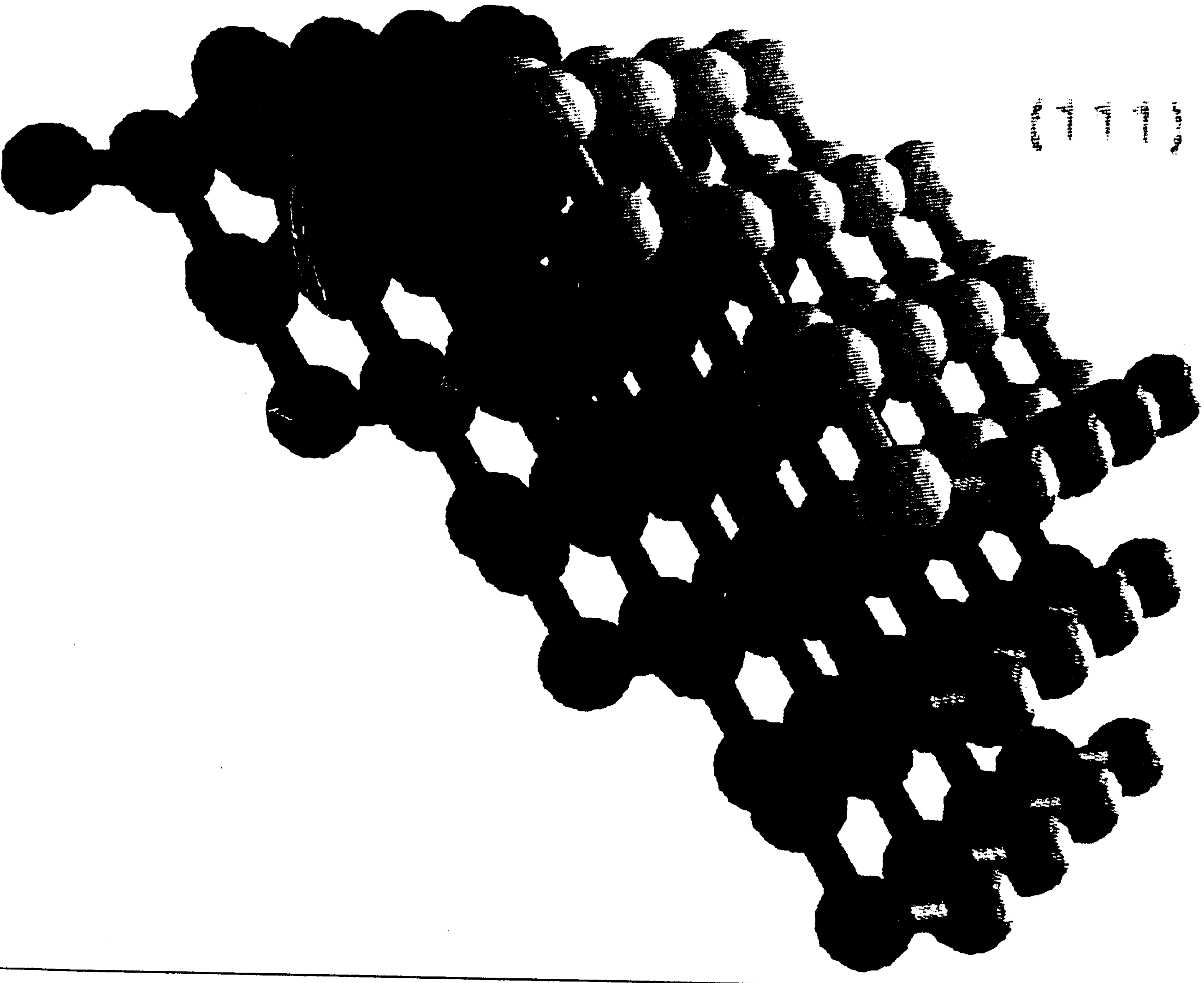
The first four Si layers possess alternating contracted and expanded interlayer distances

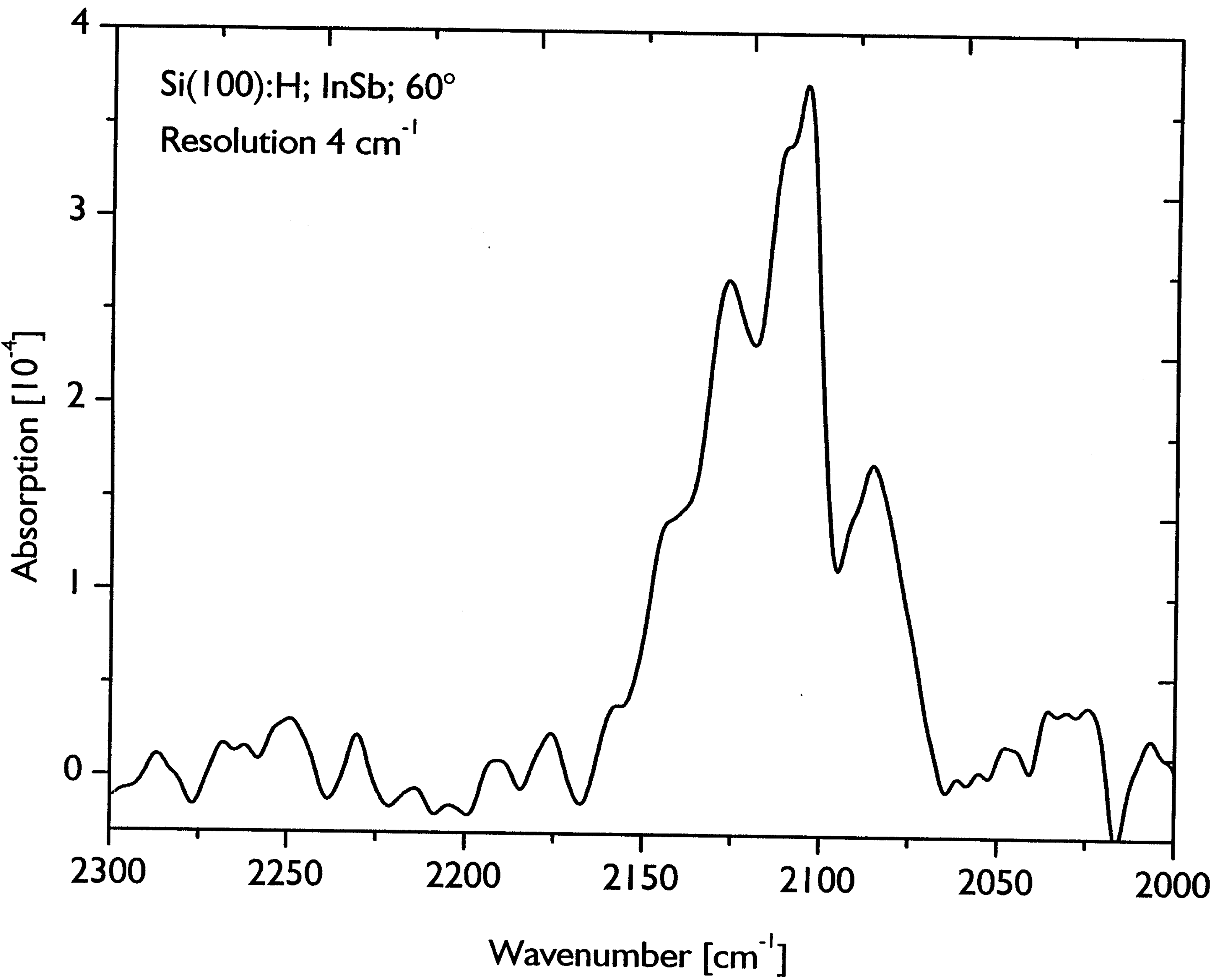
→ Contraction of the Si_1-Si_2 interlayer
Theory: - 0.05 Å, Experiment: - 0.073Å

→ Expansion of the Si_2-Si_3 interlayer
Theory: +0.007Å, Experiment: +0.013Å



Stick-and-ball representation of the slab model adopted for Si(111)(1×1)–H surface. The electron density topological analysis recovers the same bonding network.


(111)
(100)



Si(100):H; InSb; 60°
Resolution 4 cm-1
Absorption [10-4]
4
3
2
1
0
2300
2250
2200
2150
2100
2050
2000
Wavenumber [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 eV** with **0.008 eV** resolution.

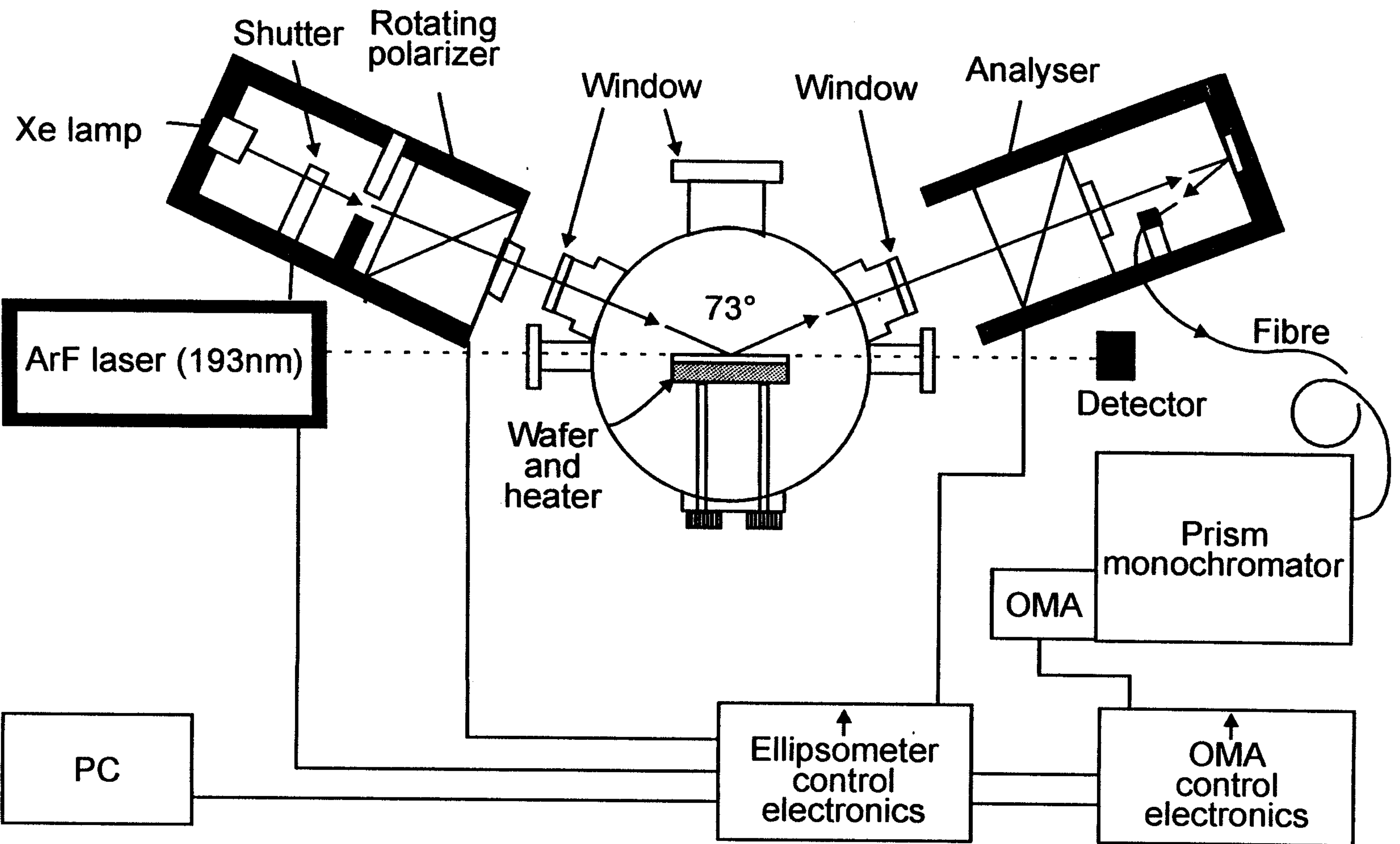
Data Aquisition:

Each spectrum consists of **512 data points** between 1.2 – 4.7 eV, averaged about 20 times.

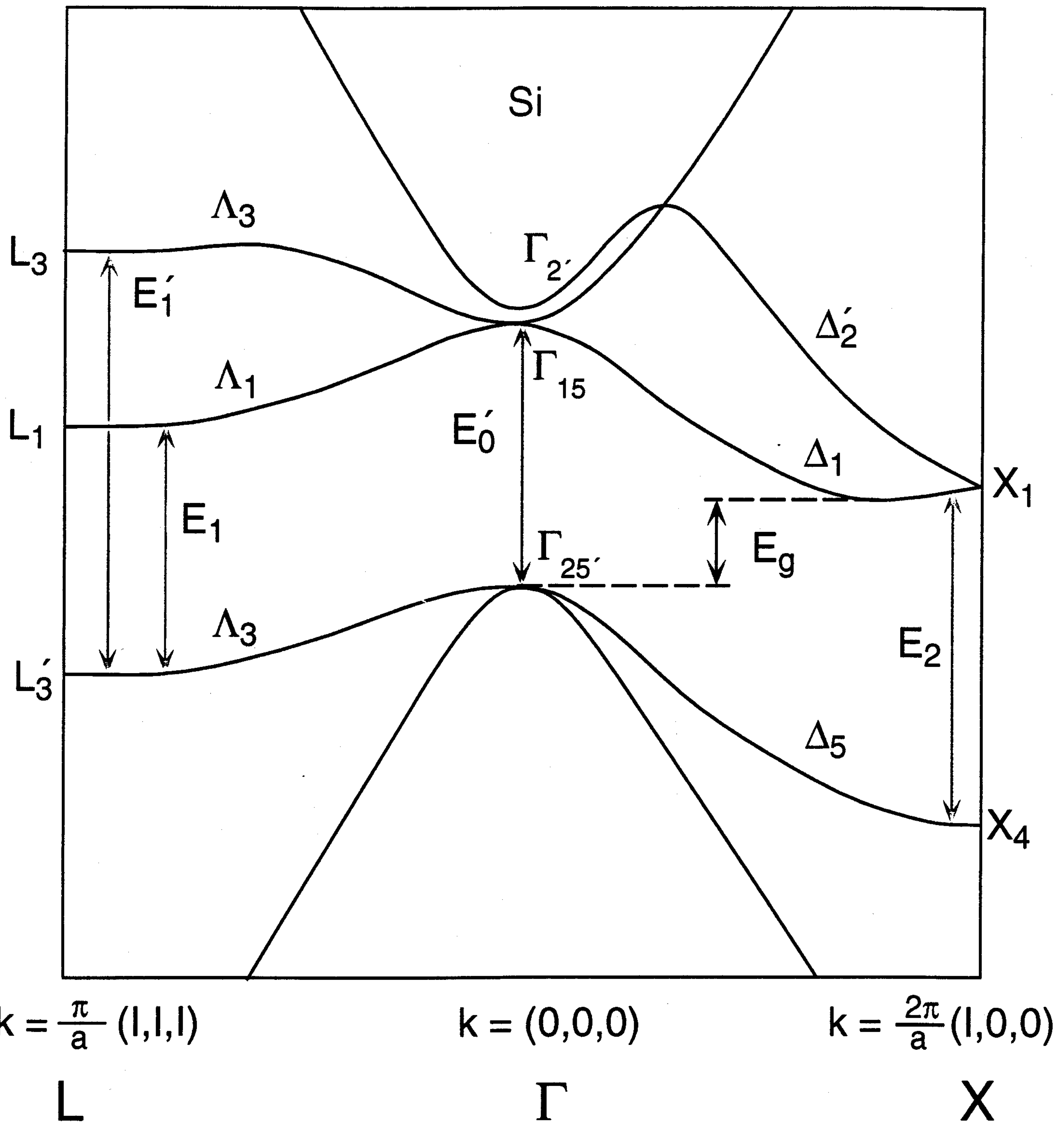
Calibration:

Calibration with two **oxide covered silicon samples** with a SiO_2 layer of **179 nm** and **2.529 µm** provided by SOPRA.

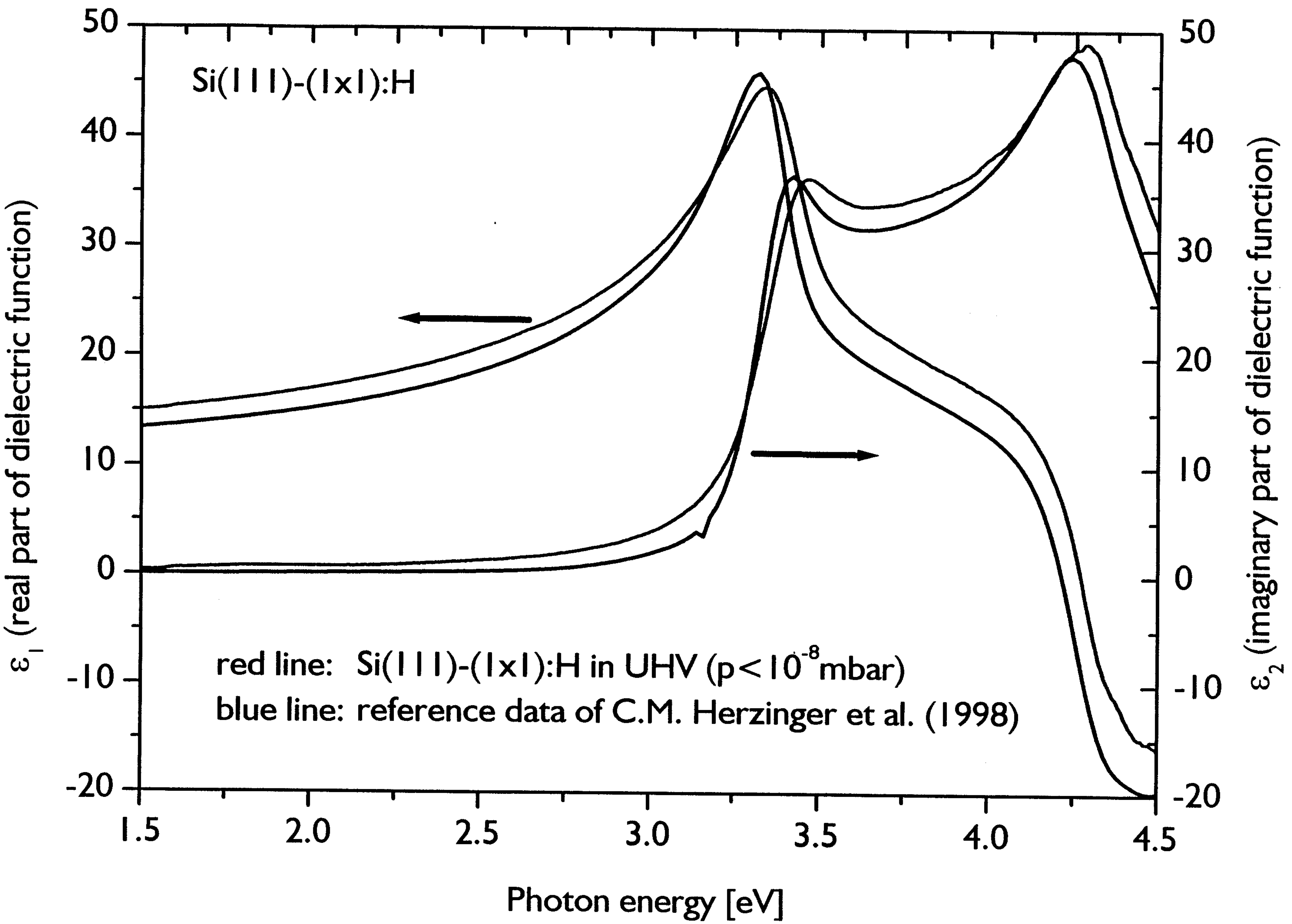
Angle of Incidence: 73.95° ± 0.05



He-027-aPı



M588HE


Si(111)-(1x1):H
red line: Si(111)-(1x1):H in UHV (p<10^-8 mbar)
blue line: reference data of C.M. Herzinger et al. (1998)
ε1 (real part of dielectric function)
ε2 (imaginary part of dielectric function)
Photon energy [eV]
50
40
30
20
10
0
-10
-20
1.5
2.0
2.5
3.0
3.5
4.0
4.5

E_2-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:

$E_2 = 47.6$: *Herzinger, Johs, McGahan, Woollam, Paulson (1998)*
Oxidized epitaxial Si(001) surface

$E_2 = 48.3 \pm 0.1$: *Yasuda, Aspnes (1994)*
NH_4F preparation of Si(111)-(1×1):H

$E_2 = 47.2$: *Angermann, Henrion, Rebien, Fischer, Zettler, Röseler (1998)*
NH_4F preparation of Si(111)-(1×1):H

$E_2 = 49 \pm 1.0$: *Schmitt, Lambers, Hess (2000)*
NH_4F 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:

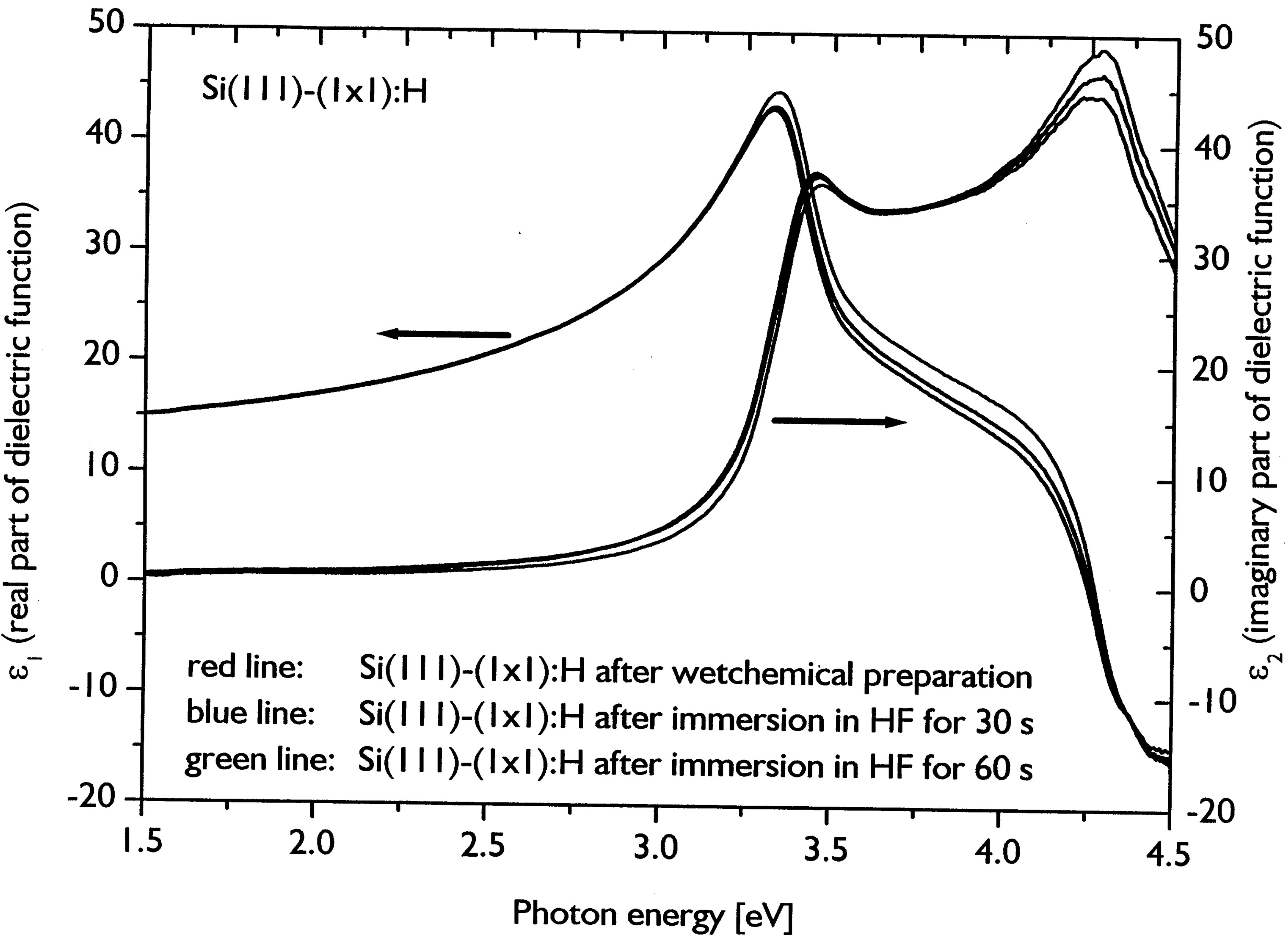
(E'_0,E_1) transition: **3.42 eV**
E_2 transition: **4.24 eV**

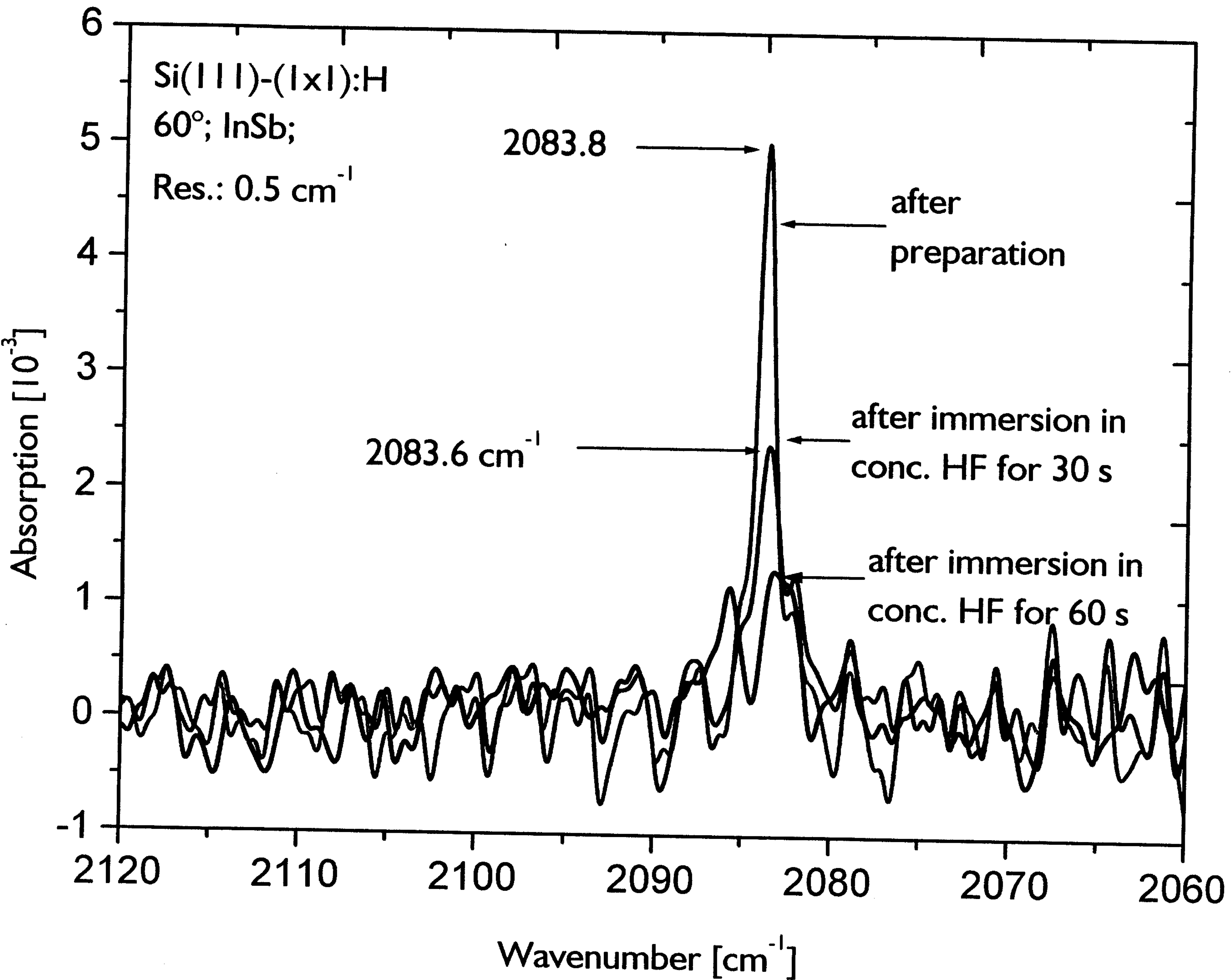
Highest Values:

(E'_0,E_1) transition: **3.47 eV**
E_2 transition: **4.28 eV**

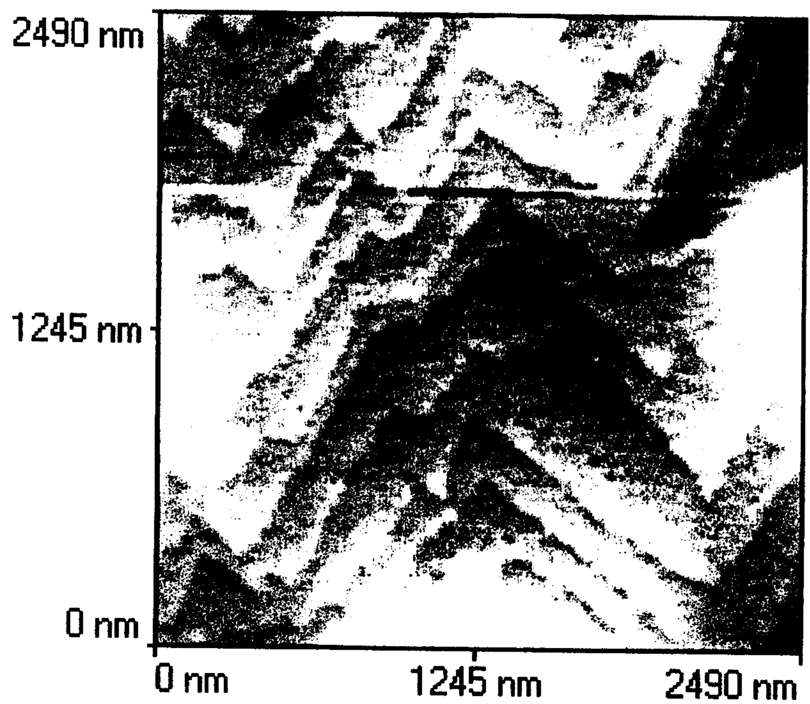
Blue Shift:

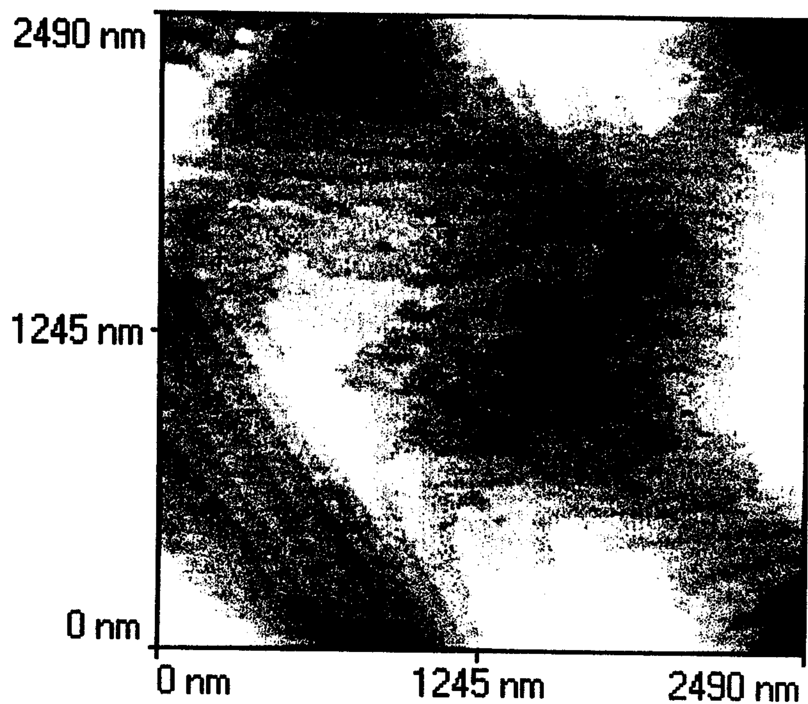
Indicates a smaller influence of **surface states**


Si(111)-(1x1):H
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
ε1 (real part of dielectric function)
ε2 (imaginary part of dielectric function)
Photon energy [eV]
50
40
30
20
10
0
-10
-20
1.5
2.0
2.5
3.0
3.5
4.0
4.5


Si(111)-(1x1):H
60°; InSb;
Res.: 0.5 cm-1
2083.8
after
preparation
2083.6 cm-1
after immersion in
conc. HF for 30 s
after immersion in
conc. HF for 60 s
Absorption [10-3]
Wavenumber [cm-1]
6
5
4
3
2
1
0
-1
2120
2110
2100
2090
2080
2070
2060

Topography of silicon surfaces (AFM)





Outlook

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

Most Ideal Solid:

→ **Very near "bulk optical constants"**

Surface Effects:

Many changes occur on other silicon surfaces:
structural, chemical, roughness, usw.

→ H termination on **Si(100)**: SiH, SiH_2, SiH_3

→ Effects of residual overlayers (e.g. **oxide**)