united nations educational, scientific and cultural organization

international atomic energy agency

the **abdus salam** international centre for theoretical physics

SMR/1238-4

ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Second harmonic spectroscopy of Si surfaces with H, Ge, and B adsorbates: Experiment meets Microscopic Theory

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Adriatico Conference on
Lasers in Surface Science:
September 13, 2000

Second harmonic spectroscopy of Si surfaces with H, Ge, and B adsorbates:

Experiment meets Microscopic Theory

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D. Lim, P. Parkinson
U. Texas at Austin

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California State U.- Northridge

N. Arzate, B. S. Mendoza
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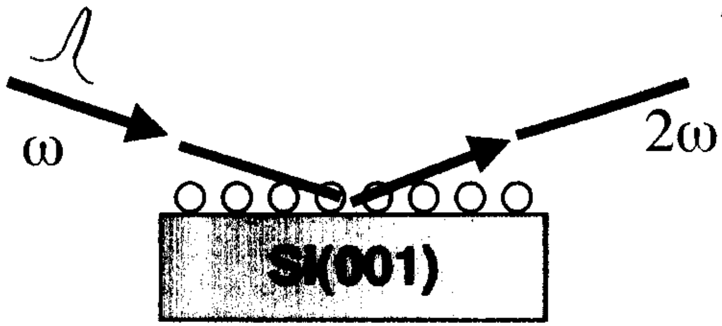
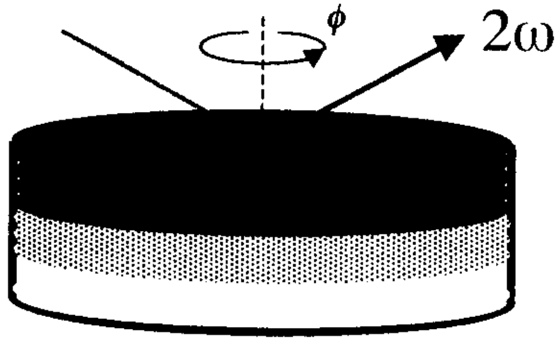
León, México



Tom *et al.*, Phys. Rev. Lett. **51**, 1983 (1983)
Aktsipetrov *et al.*, Sov. Phys. JETP **64**, 167 (1986)
Sipe *et al.*, Phys. Rev. B **35**, 1129 (1987)

MACROSCOPIC THEORY OF SHG at Si(001)

$$P_i(2\omega) = \chi_{ijk}^{(2)surf} E_j(\omega) E_k(\omega)\delta(z) + \chi_{ijkl}^{(2)bulk} E_j(\omega) \nabla_k(\omega) E_l(\omega) + \chi_{ijkz}^{(3)EFISH} E_j(\omega) E_k(\omega) \mathrm{E}_z(0)$$

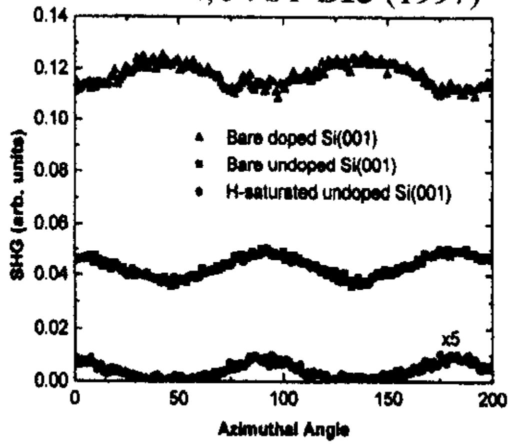


field-dependent

$$I_{PP}(2\omega) = | s_{PP}(\chi_{zzz}, \chi_{zxx}, \chi_{xzx}) + b_{PP} + b_{PP}\mathrm{E}_z(0) + b'_{PP} \cos 4\phi |^2$$
$$I_{SP}(2\omega) = | s_{SP}(\chi_{zxx}) + b_{SP} + b_{SP}\mathrm{E}_z(0) + b'_{SP} \cos 4\phi |^2$$
$$I_{QS}(2\omega) = | s_{QS}(\chi_{xzx}) + b_{QS} + b_{QS}\mathrm{E}_z(0) + b'_{QS} \cos 4\phi |^2$$

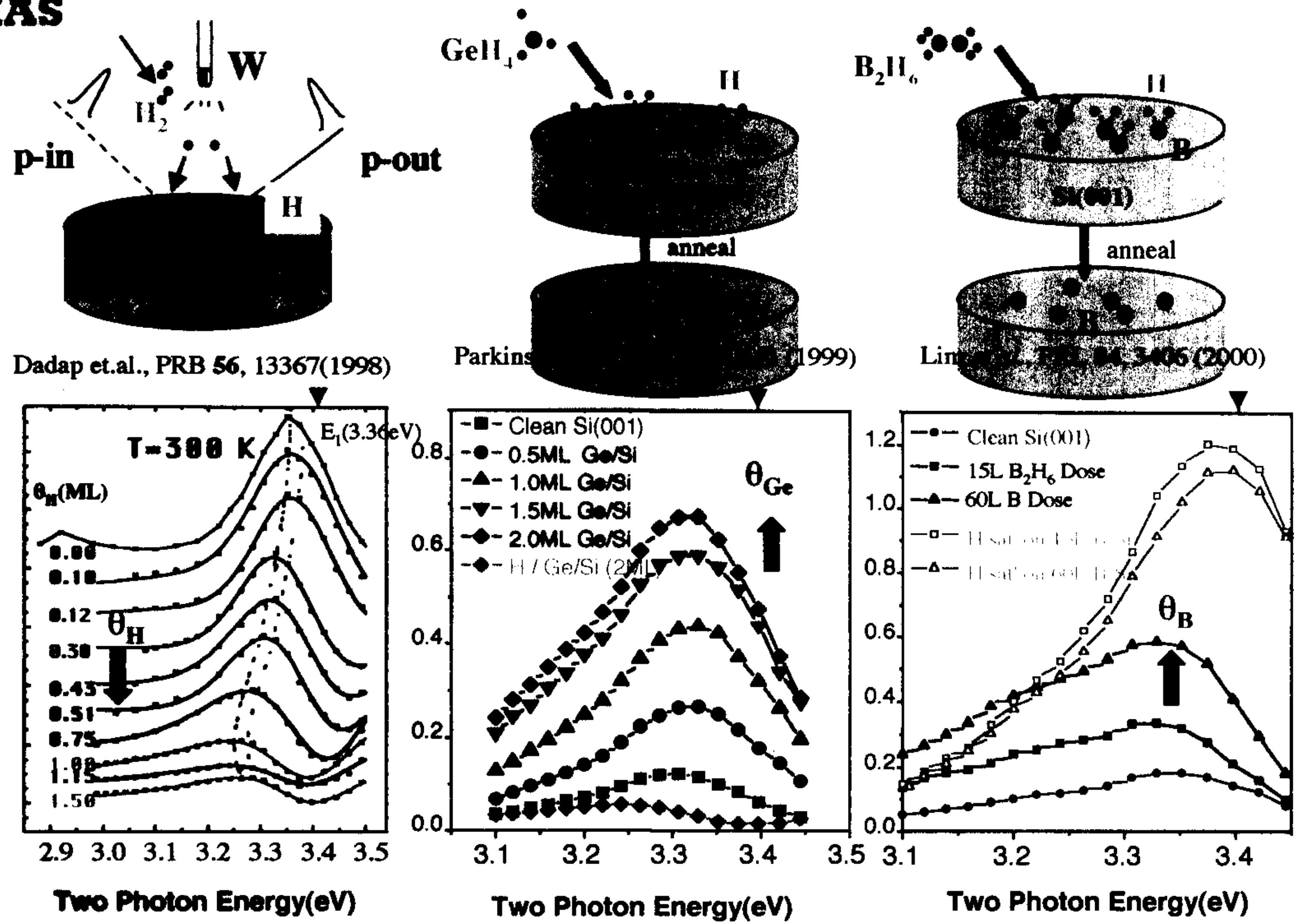
isotropic *anisotropic*

Xu *et al.*, JVST B**15** (1997)



SHG SPECTRA are ADATOM-SPECIFIC

H/Si(001) Ge/Si(001) B/Si(001)



Reasons for adsorbate-induced alterations of $\chi^{(2)}_{surface}$

STRUCTURAL

• adsorbate-induced changes in near-surface equilibrium atomic positions

&

strain gradients

CHEMICAL

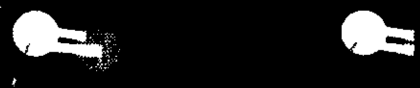
• adsorbate-induced hybrization of surface atomic orbitals

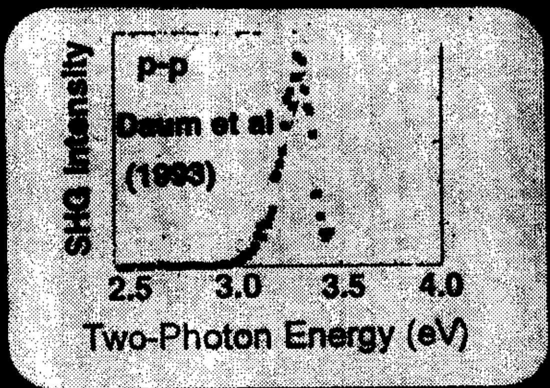
&

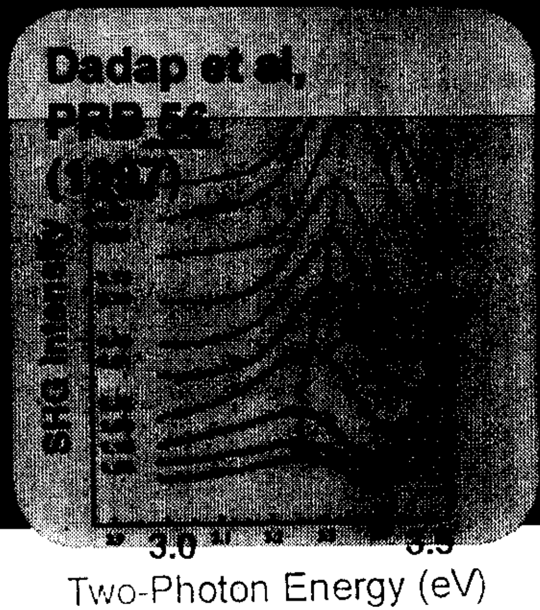
charge transfer

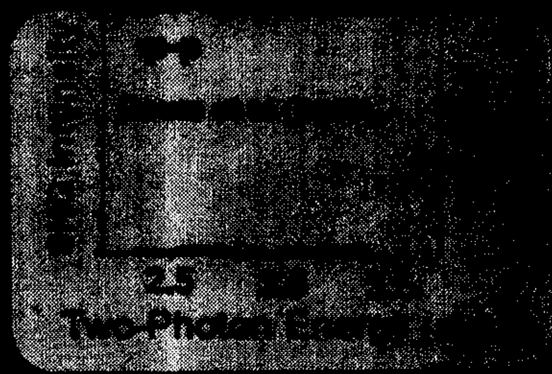
Physics of SHG at Si(001):
3 types of surfaces occur during CVD

buckled dimer

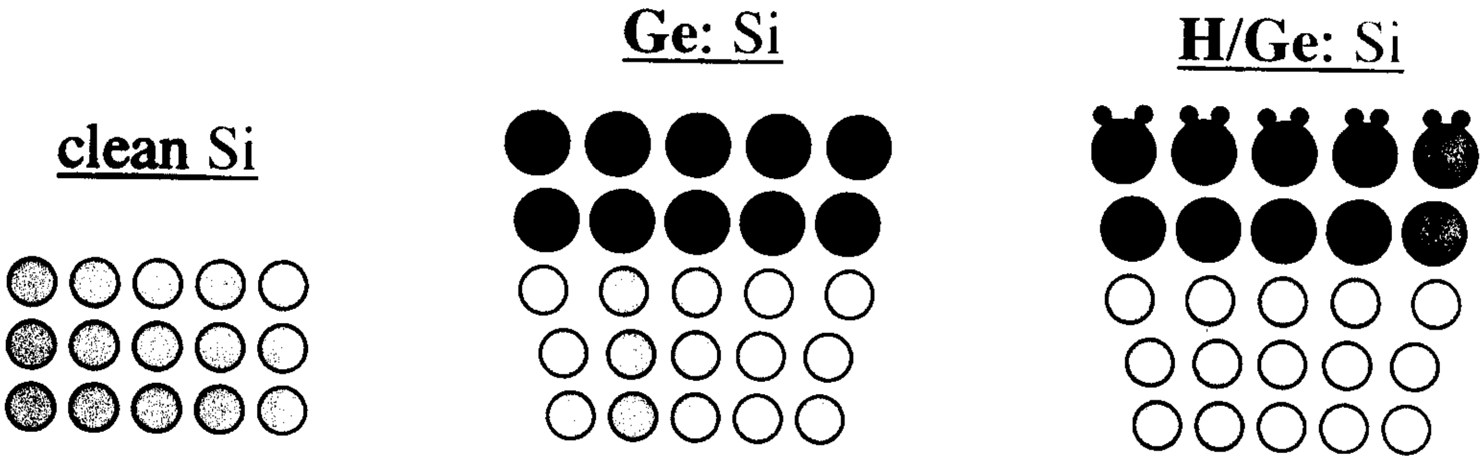


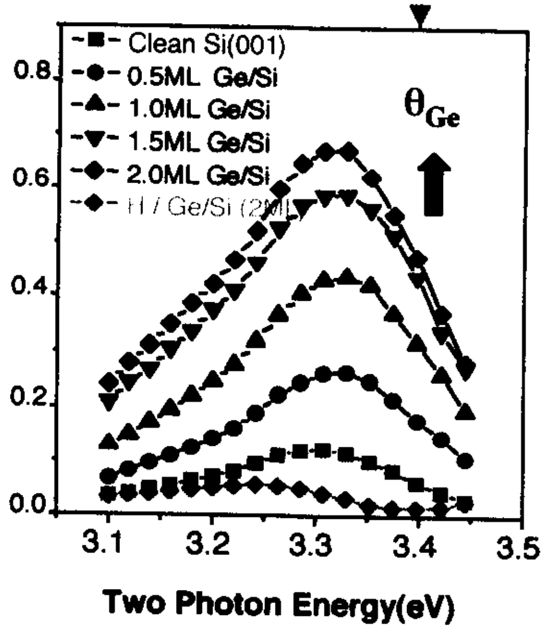






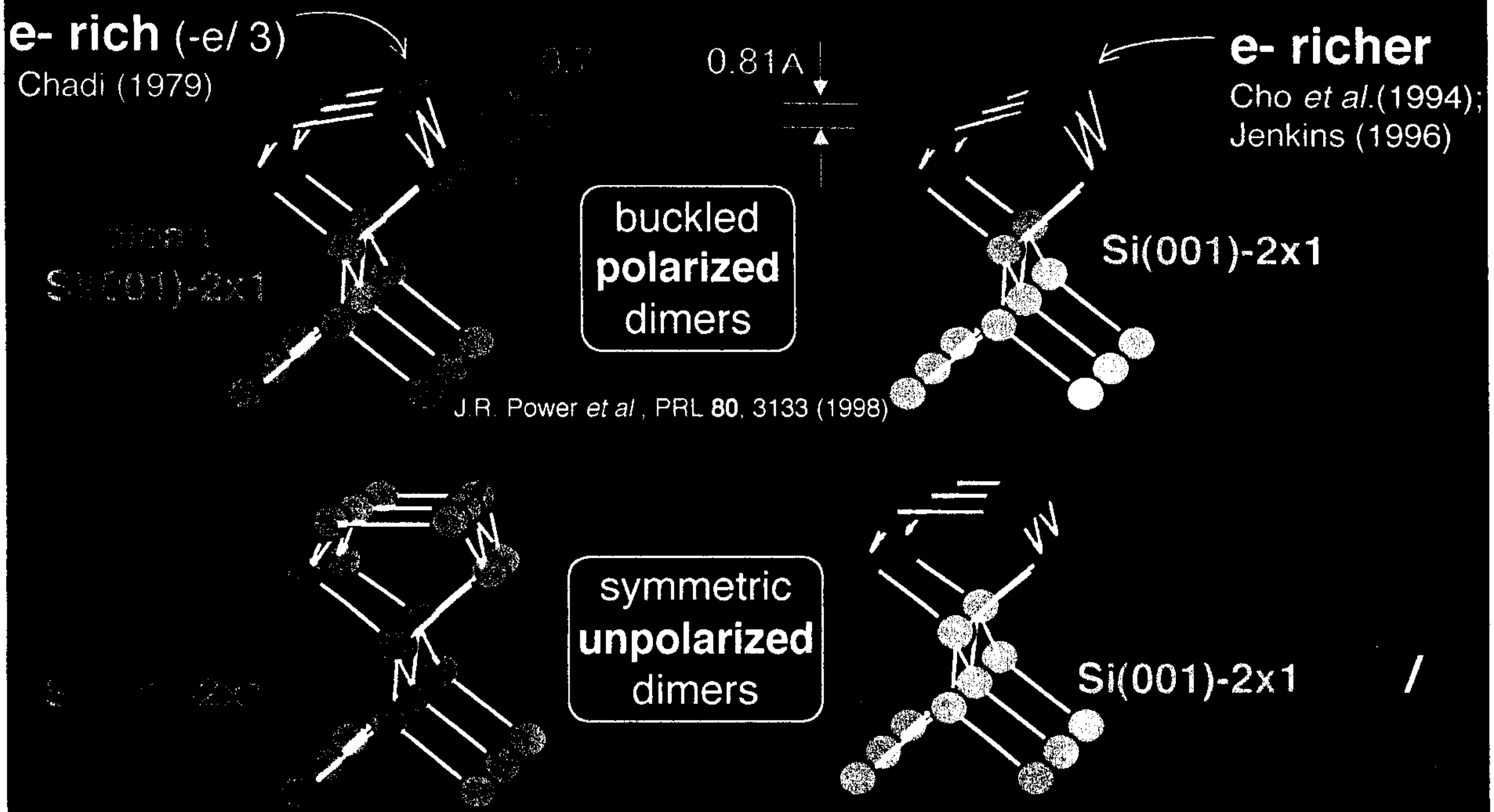
SHG trends at H/Ge: Si(001) are uncorrelated with lattice mismatch strain





Dimer is strongly POLARIZED on clean surface

Surface structures optimized for 12 ML slab,
using Molecular Dynamics with ab initio pseudopotentials



CIO - Léon

CALCULATION of SURFACE OPTICAL PROPERTIES

CSU NORTHRIDGE

INPUT: Optimized Structure

KEY QUANTITY: 2nd order surface susceptibility

$$\chi^{(2)}_{ijk}(-2\omega,\omega,\omega) = -\frac{\pi}{2}\left(\frac{e\hbar}{m}\right)^3 \sum_{g,n,n'} \left\{ \frac{(p_i)_{gn}\{(p_j)_{n,n'},(p_k)_{n'g}\}}{(2\omega-\omega_{ng}+i\Gamma_{ng})(\omega-\omega_{n'g}+i\Gamma_{n'g})} + \dots \right\}$$

TO CALCULATE $\chi^{(2)}$, ONE NEEDS: Eigen-values, -states, matrix elements

Semi-Empirical Tight Binding (SETB)

- 5-Si-orbital (sp^3s^*) basis
- no adsorbate orbitals
- $\langle s|x|p_x\rangle$,$\langle s|x|p_x\rangle$ empirical parameters derived from fits to bulk optical properties

Vogl *et al.*, JPC Solids **44**, 365 (1983)
Selloni *et al.*, PR B **33**, 8885 (1986)

...ples: DFT
...dopotentials
..., Ge, B
ad...ates

Microscopic Theory of Second Harmonic Generation at Si(100) Surfaces

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(Received 13 May 1998)

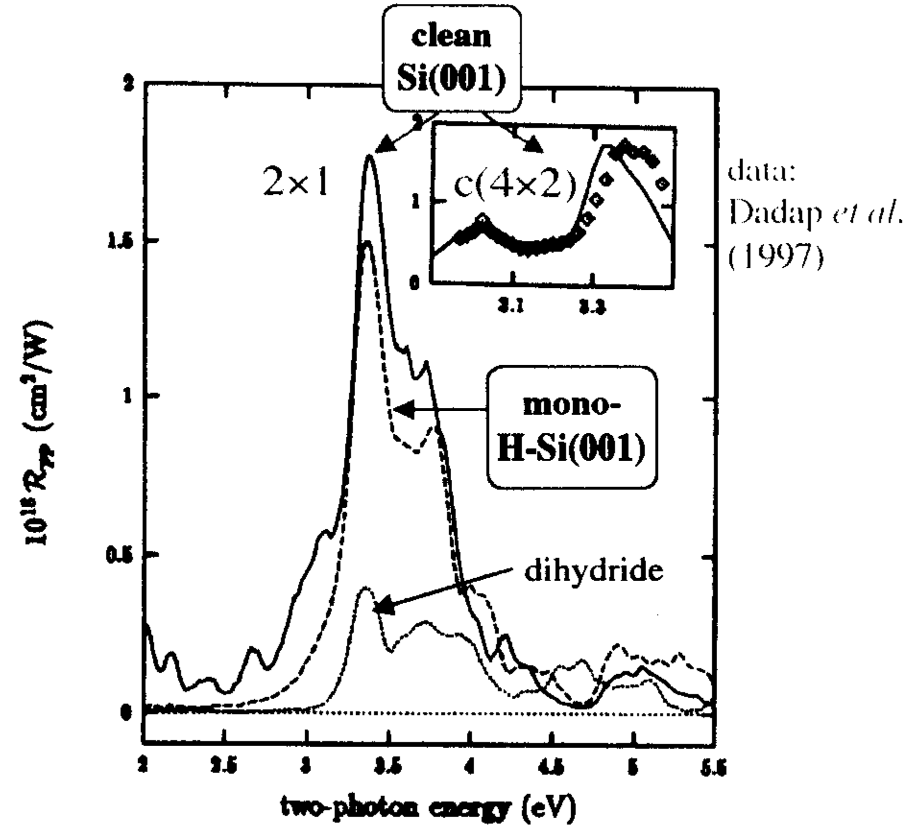
SETB with Si sp^{3}s* basis

- successful in calculating spectra of **CLEAN** Si surfaces

RDS: Noguez et al., PRL **76**, 4923 (1996)
Power et al., PRL **80**, 3133 1998)

SHG:
L. Reining *et al.*, Phys. Rev. B **50**, 8411 (1994)
Gavrilenko *et al.*, Appl. Phys. A **60**,143 (1995)
Mendoza *et al.*, PRL **81**, 3781 (1998)

- less successful in calculating **adsorbate** effects



Surface nonlinear optics is a new frontier for *ab initio* calculations

I. Ground State Properties:

Density Functional Theory ($E_{gs} \propto f[\rho(\mathbf{r})]$)

*Hohenberg & Kohn, Phys. Rev. **136**, B864 (1964)*

*Bernholc, Physics Today **52**, 30 (1999).*

predict w. few % accuracy:

- *lattice constants*
- *atomic positions*
- *elastic properties*
- *phonon frequencies*

II. Bulk Linear Optical Properties: *involve excited states*

- quasi-particle & XC corrections for excited states
- Local Field corrections (~15%)
- Excitonic effects

review of 1990's progress: *Lambrecht & Rashkeev, Phys. Stat. Sol (b) **217**, 599 (2000)*

III. Surface Nonlinear Optical Properties ($\chi^{(2)surf}$)

- No periodic BC's ⇒ finite slabs (10-50 ML) ⇒ many **k**-points, unit cells ≤ diamond
- Local Fields vary strongly across surface SHG source region ⇒ no solution yet

Absolute $\chi^{(2)surf}$ calculations not accurate yet.

⇒ settle for calculating *changes* in $\chi^{(2)surf}$

⇒ use semi-empirical approaches (e.g. SETB)

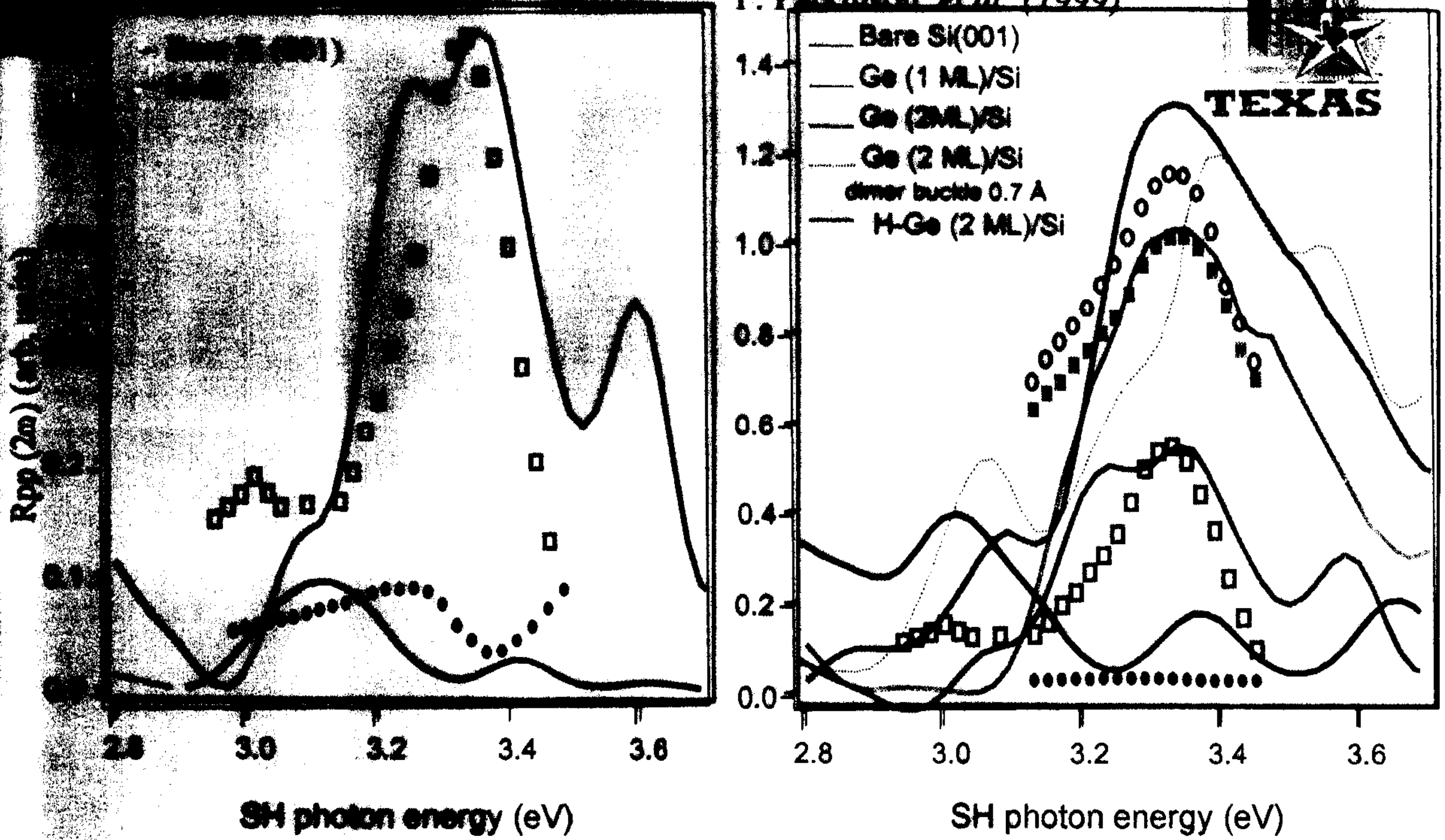
[redacted] of *ab initio* results with experiment

V. Gavrilenko and R. Q. Wu

J. Dadap *et al.* (1997)

P. Parkinson *et al.* (1999)

TEXAS



Calulated SHG <u>sensitive</u> to:

- eigenstate quality
- realistic description of charge transfer on surface
- convergence of self-consistent calculations

<u>insensitive</u> to:

- small deviations from equilibrium structure

Details of calculation

Ab initio pseudopotentials for Si, Ge, H generated by scheme of Bachelet-Hamann-Schlüter (1992)

12 ML slab

adequate for convergence

Optical calculations used:

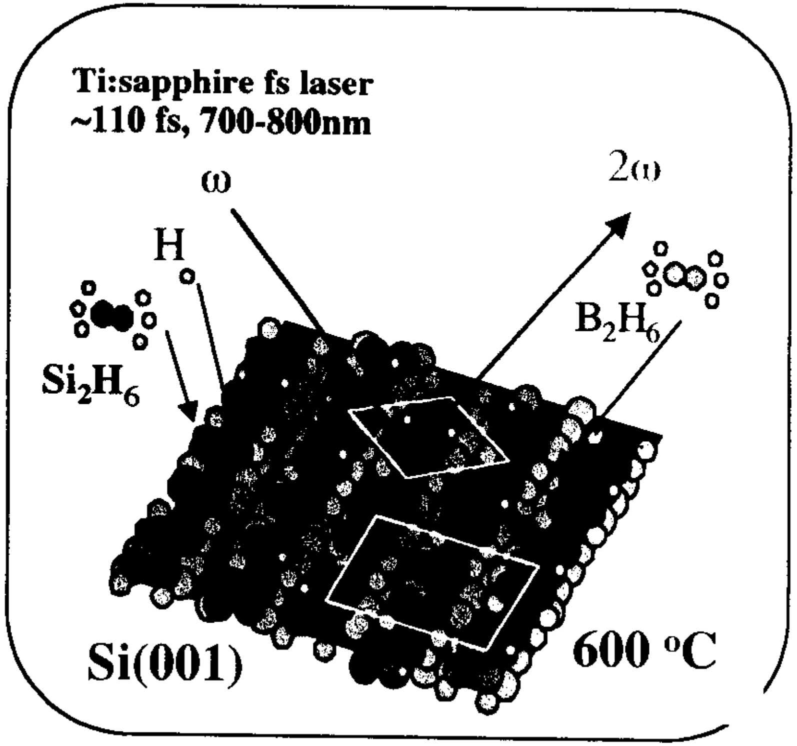
Eigen-values,-functions from direct diagonalization of Hamiltonian after full convergence of $\rho(r)$ calc^ns

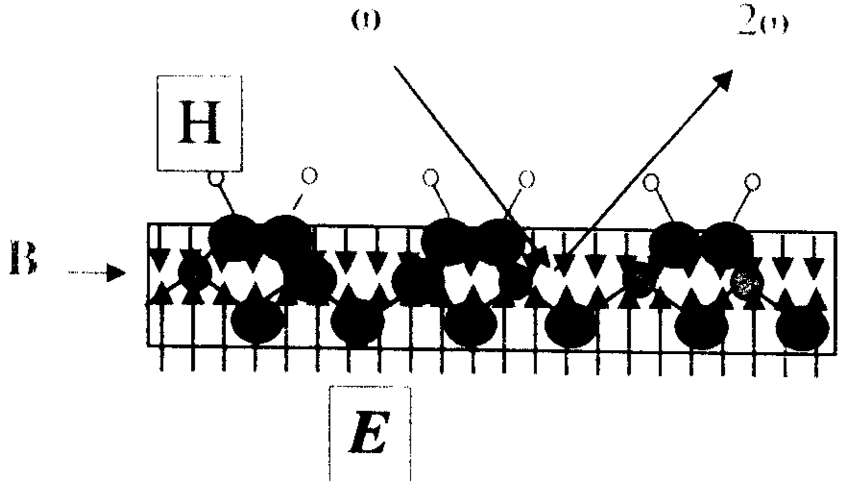
48 k-points in irreduc. 2D BZ

E_{cut} = 15 Ry

Stable 2D Boron layers can be fabricated at Si surfaces

Headrick *et al.*, PRL **63**, 1253 (1989)
Wang *et.al.*, PRL **74**, 403 (1995)



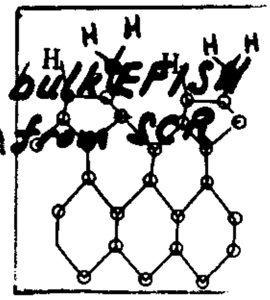


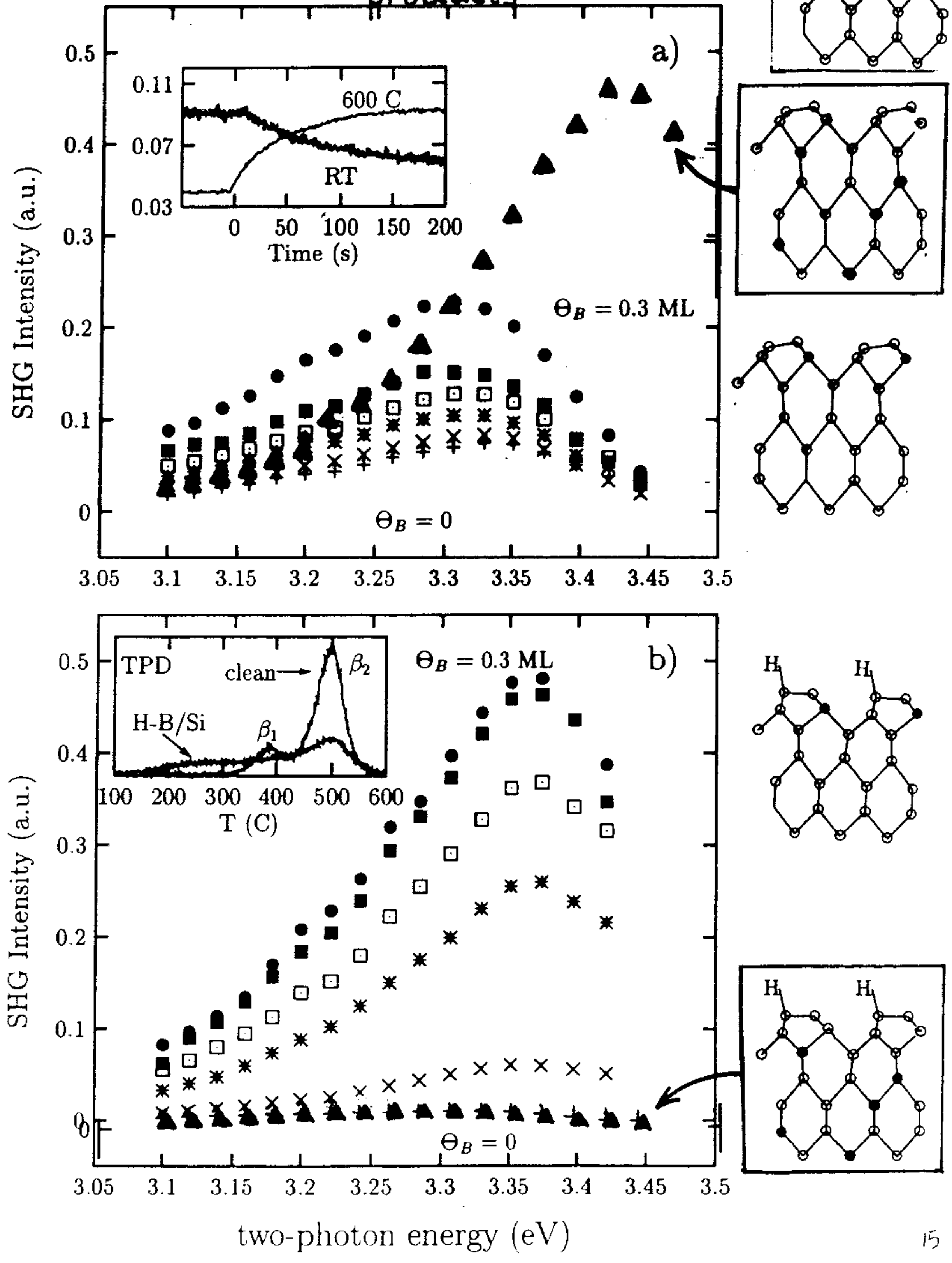
- -B occupies 2nd layer & electrically active
- - local c(4X4) reconstruction on Si(001)

D. Lim et al., PRL 84, 3406 (2000)

D. Lim et al. APL 77, 181(200

SHG response to:
1) 2nd layer B incorporation
2) bulk B doping
3) surface B_2H_6 dissociation products

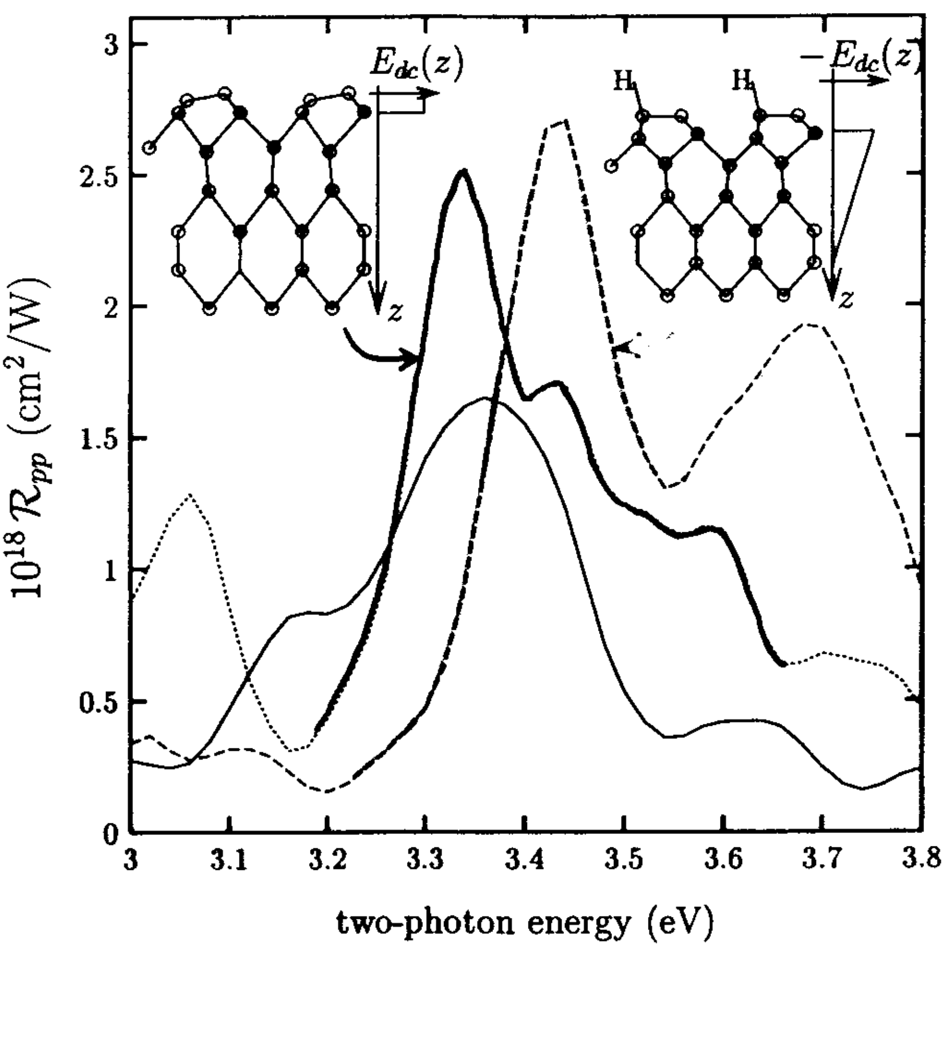




B. S. Mendoza, N. Arzate
Centro de Investigaciones en Optica
León. México

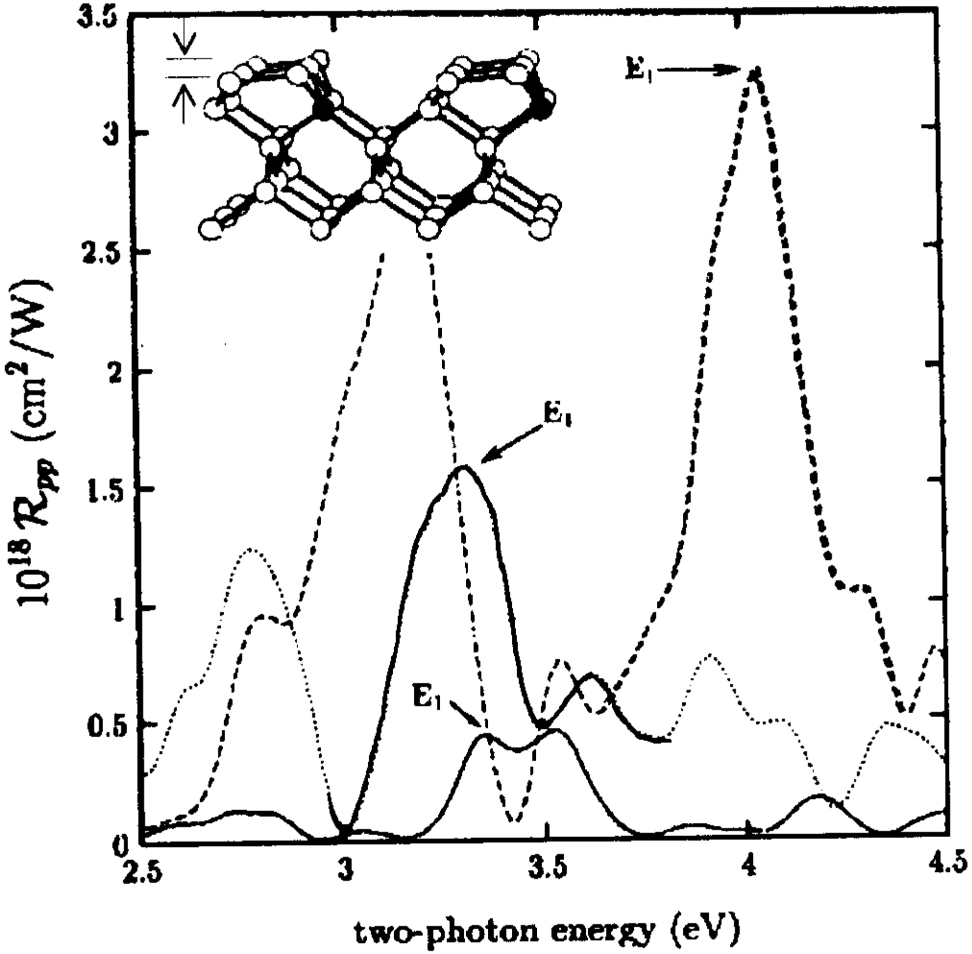
Semi-Empirical Tight Binding (SETB) Model of SHG at B-Si(001) and H-B-Si(001)

- input structure from DFT energy minimization (16 ML slab)
- replace B with Si
- account for effect of B via surface field $E_{dc}(z)$
- CB shifted by $\Delta E = 0.48$ eV



Ab initio calculation of reflected SHG for **clean**, **B-** and H-B-Si(001)

VI Gavrilenko & RQ Wu



Details of calculation

Ab initio pseudopotentials generated by schemes of

- Bachelet-Hamann-Schlüter, PRB (1982) for **Si,H**
- Troullier, Martins, PRB **43**, 1993 (1991) for **B.**

Slab of 8 atomic (001) layers

- Quantum shifts negate need for QP corrections
- E_1 occurs near 3.4 eV.

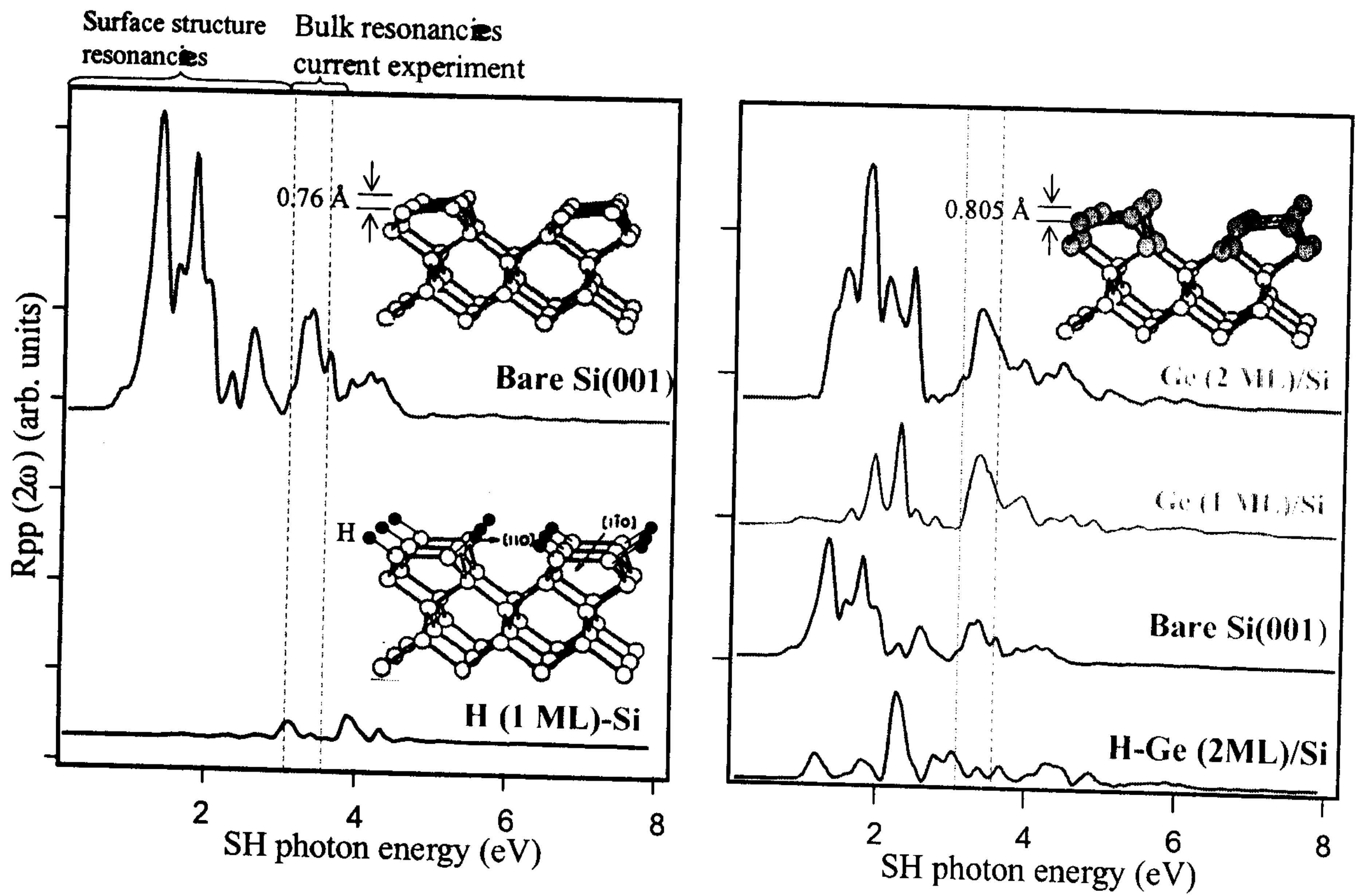
Equilibrium atomic positions

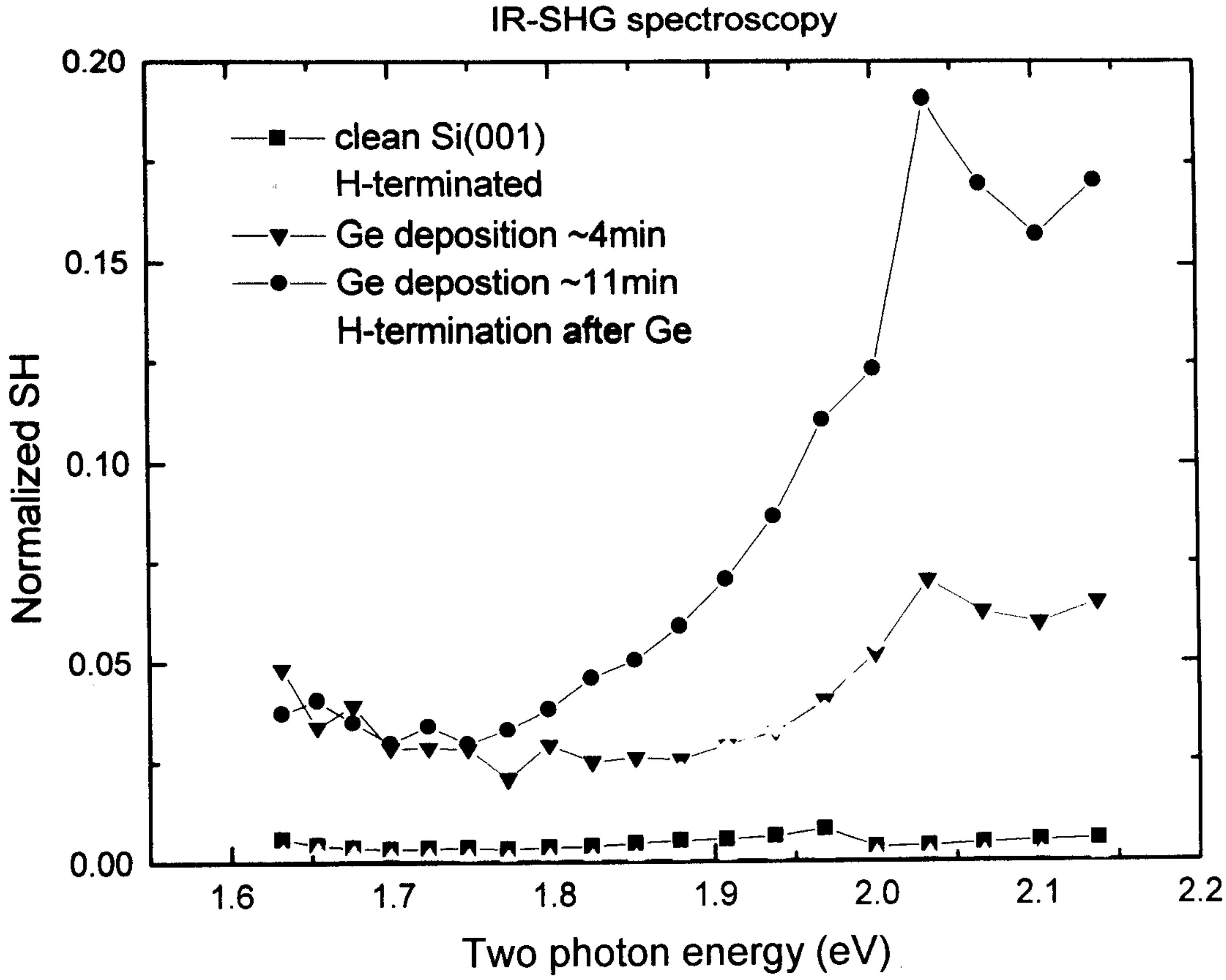
- total energy minimization using E_{cut} = 17 Ry, molecular dynamics method.
- **clean Si:** 2x1 unit cell
- **B-Si:** c(4x4), but 2x1 with one B per unit cell used to make calculation tractable

Optical calculations

- used E_{cut} = 31 Ry

Ab initio results: 1. Predictions for future experiments



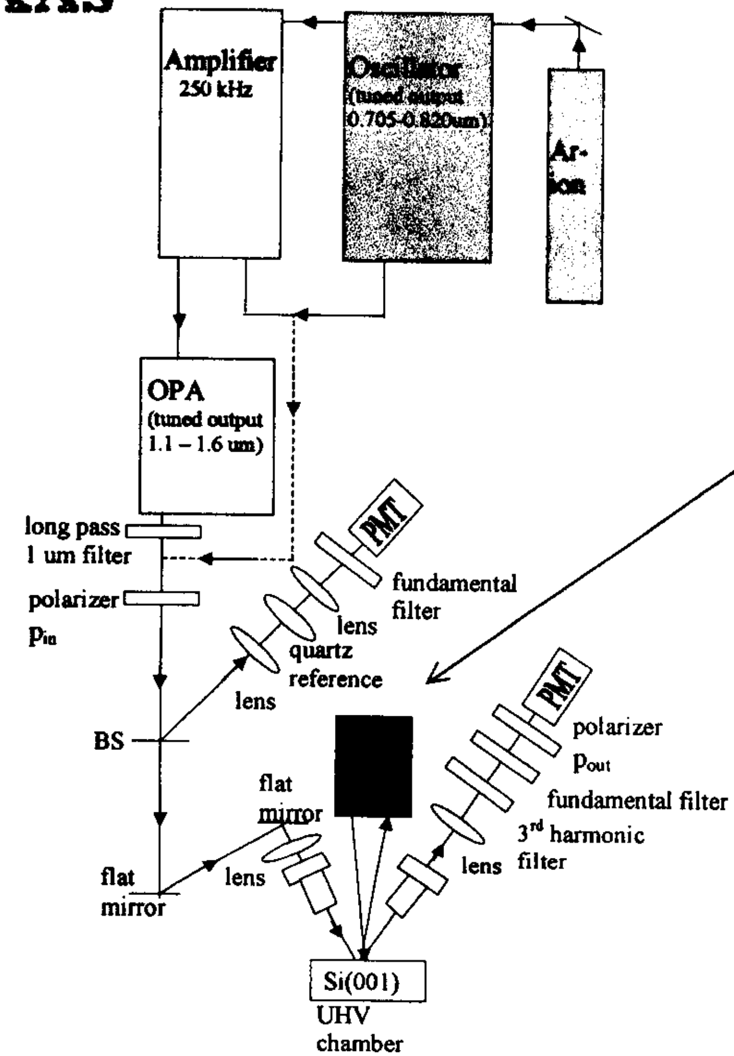


IR-SHG spectroscopy
clean Si(001)
H-terminated
Ge deposition ~4min
Ge depostion ~11min
H-termination after Ge
Normalized SH
0.20
0.15
0.10
0.05
0.00
1.6
1.7
1.8
1.9
2.0
2.1
2.2
Two photon energy (eV)

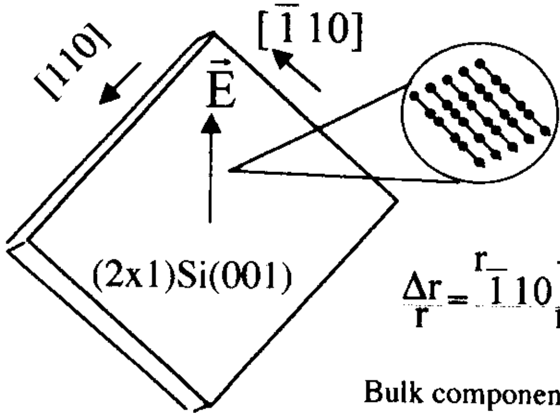
Simultaneous spectroscopic SHG and Reflectance-Difference Spectroscopy (RDS)

Experimental setup

L. Mantese, D. Lim



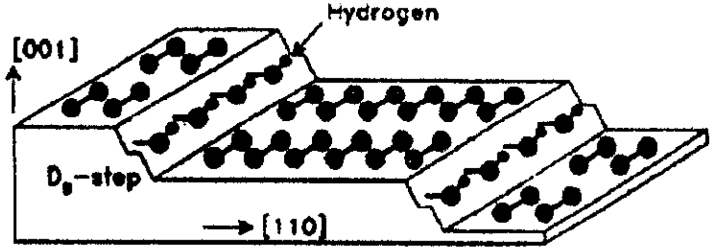
RDS is highly surface-sensitive



$$\frac{\Delta r}{r} = \frac{r_{\bar{1}10} - r_{110}}{r}$$

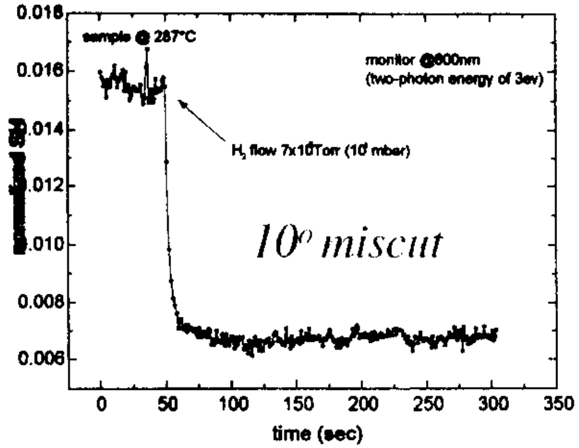
Bulk component optically isotropic

SHG vs. RDS response to H_2 adsorption on vicinal Si(001)



H_2 adsorbs selectively on D_B steps

I. SHG



Kratzer *et al.*, PRL **81**, 5596 (1998)

Raschke & Höfer, PRB **59**, 2783 (1999)

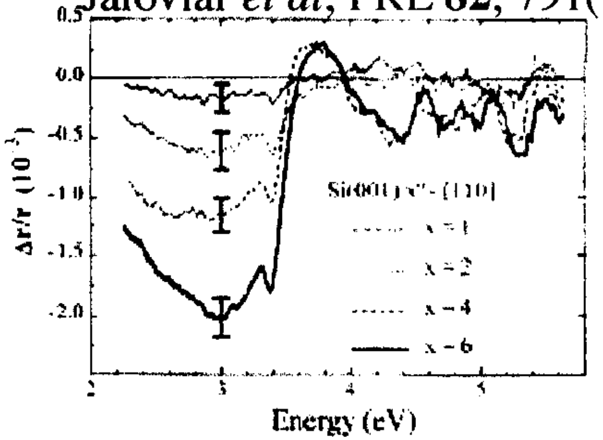
strong step-induced SHG contribution

quenched by H_2 adsorption

II. RDS

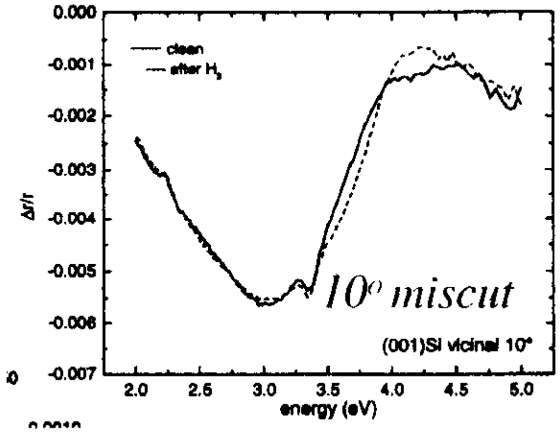
strong step-induced optical anisotropy

Jaloviar *et al*, PRL **82**, 791(1999)

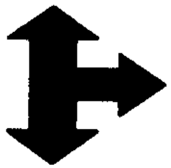


<u>YET</u> only slightly perturbed by H_2 adsorption

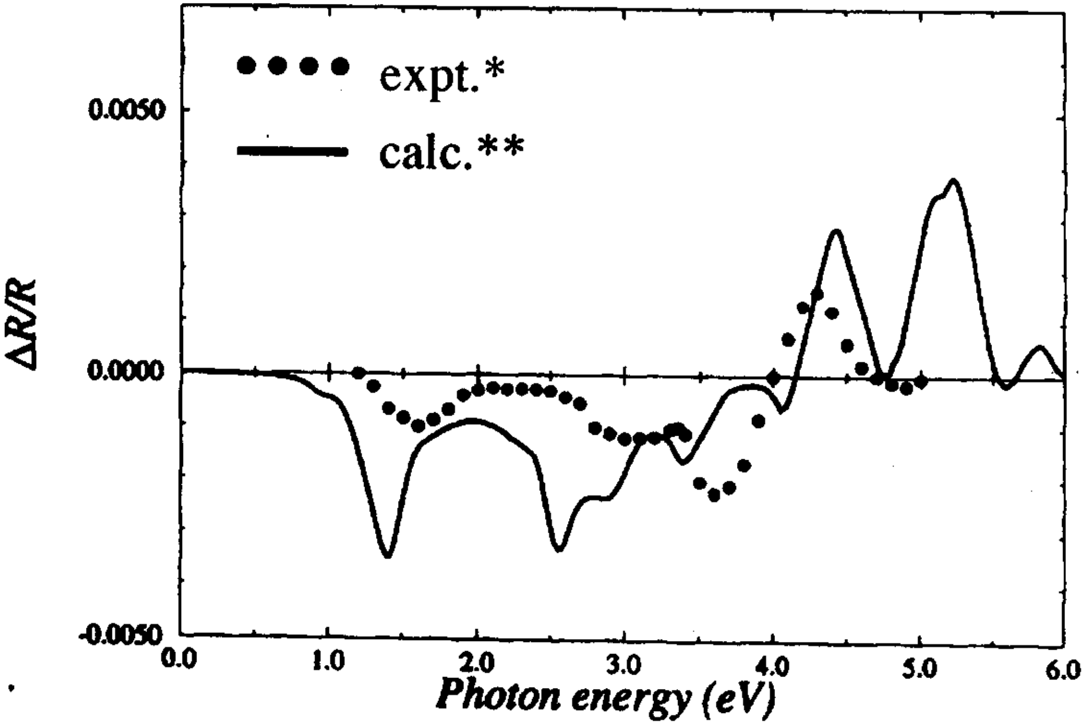
L. Mantese (2000)



RDS of single-domain Si(001)(2x1): experiment* & calculation**



$$\frac{\Delta R(\omega)}{R_0} = \frac{R[110] - R[1\bar{1}0]}{R_0}$$



Calculated RDS converges only for $N_{sl} > 12$

(vs. $N_{sl} < 8$ for SHG)

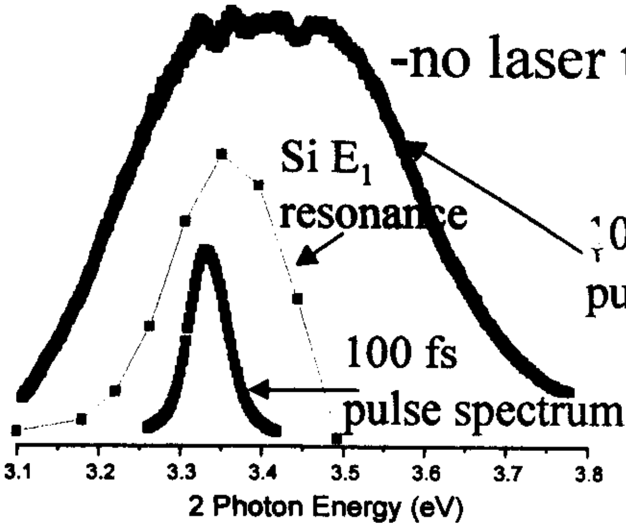
- 64 k-points in irreducible BZ
- E_{cutoff} = 15 Ry

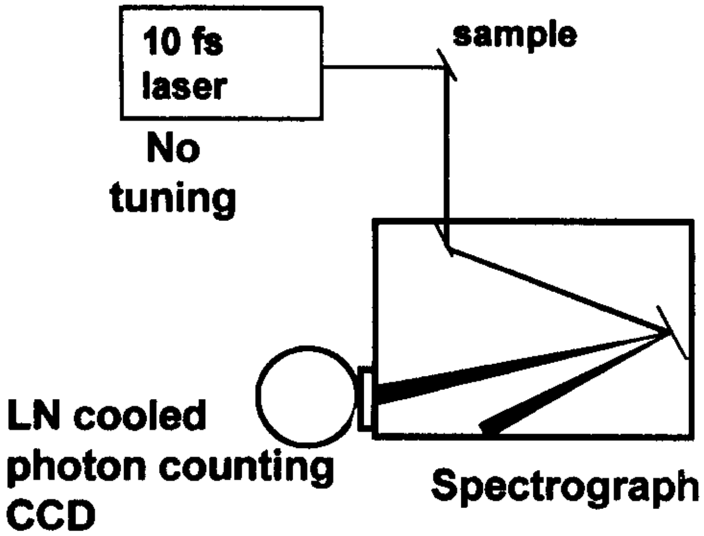
* R. Shioda & J. van der Weide, PRB **57**, R6823 (1998).
** V. Gavrilenko & R. Q. Wu (2000).

4. SHG in a Box

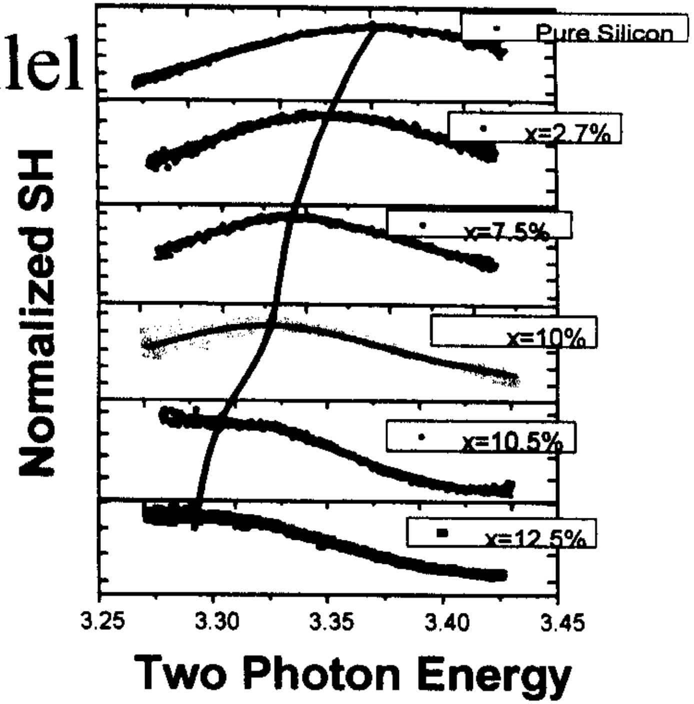
Broadband Real-time parallel Harmonic spectroscopy

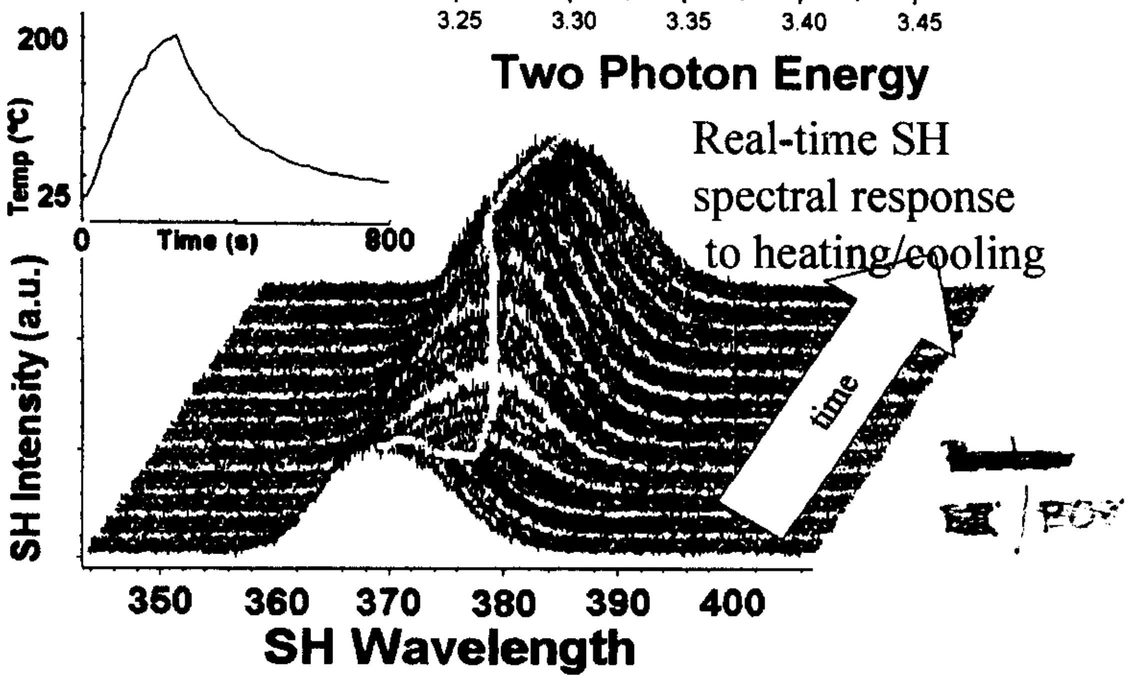
-no laser tuning required-





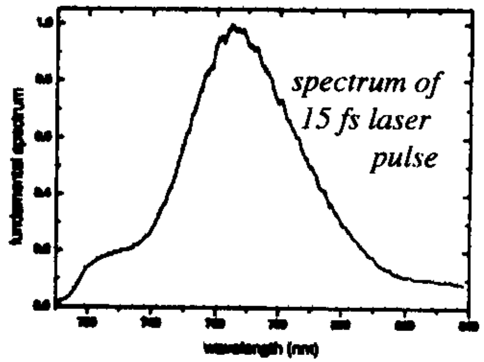
$Si_{1-x}Ge_x$ alloys





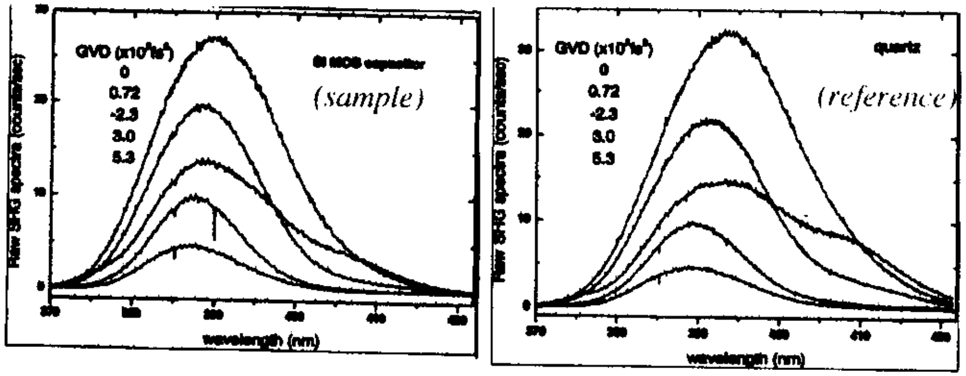
Real-time SH spectral response to heating/cooling

P. T. Wilson, Y. Jiang, O. A. Aktsipetrov, E. D. Mishina M. C. Downer, ~~submitted to~~ Optics Letters(1999) 24, 496

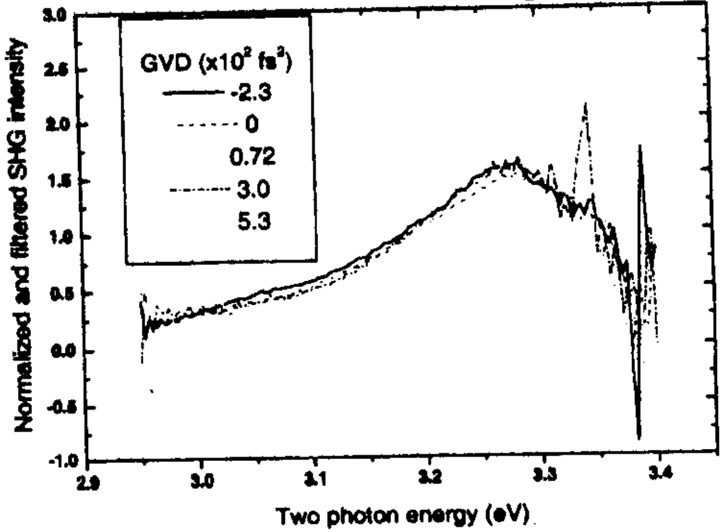


Normalized SHG intensity spectra are chirp-independent

Chirp-dependent raw SHG spectra



Normalized SHG spectrum



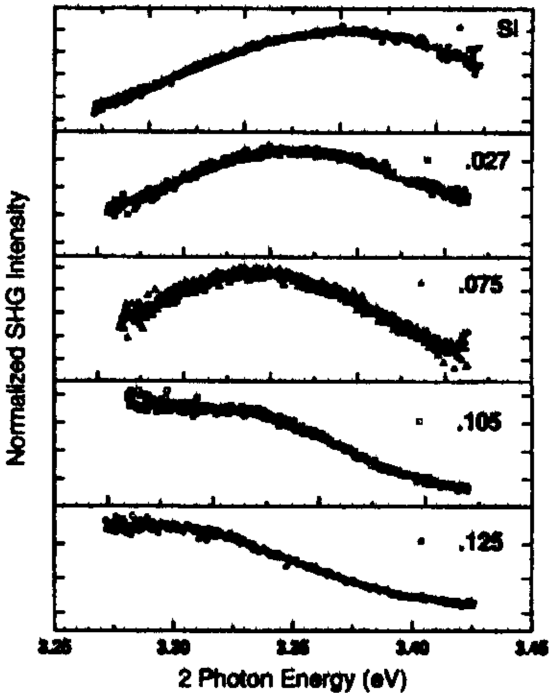
- **Pulse chirp varied by adding glass to beam path**
- **Raw spectra change drastically with chirp**

- Normalized spectra agree quantitatively in shape and amplitude

The reference sample must be spectrally flat

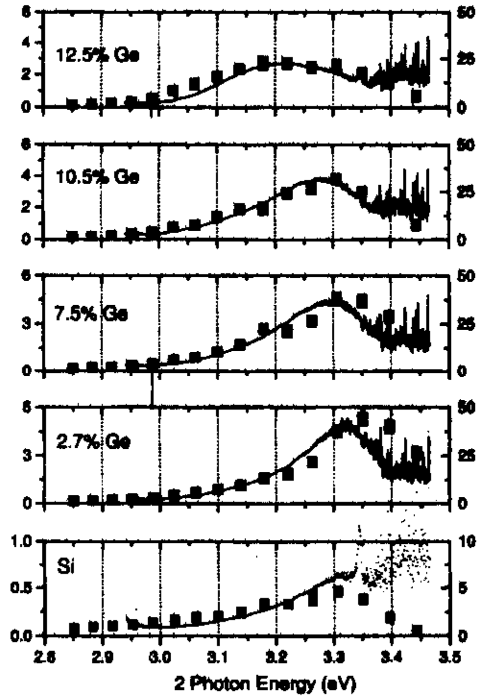
Chemical shifts of SiGe E_1 peak

Broadband SHG spectra of $Si_{1-x}Ge_x$ normalized to GaAs

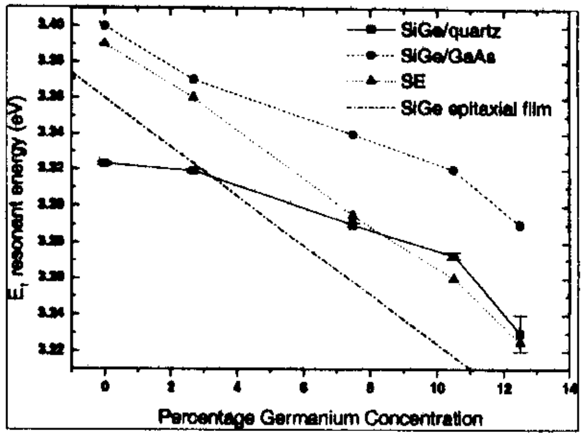


—*Same normalized to* ***quartz***

■ ■ ■ *conventional SHG spectrum*



E_1 peak position



- *Accurate normalization enables quantitative measurement of material properties*

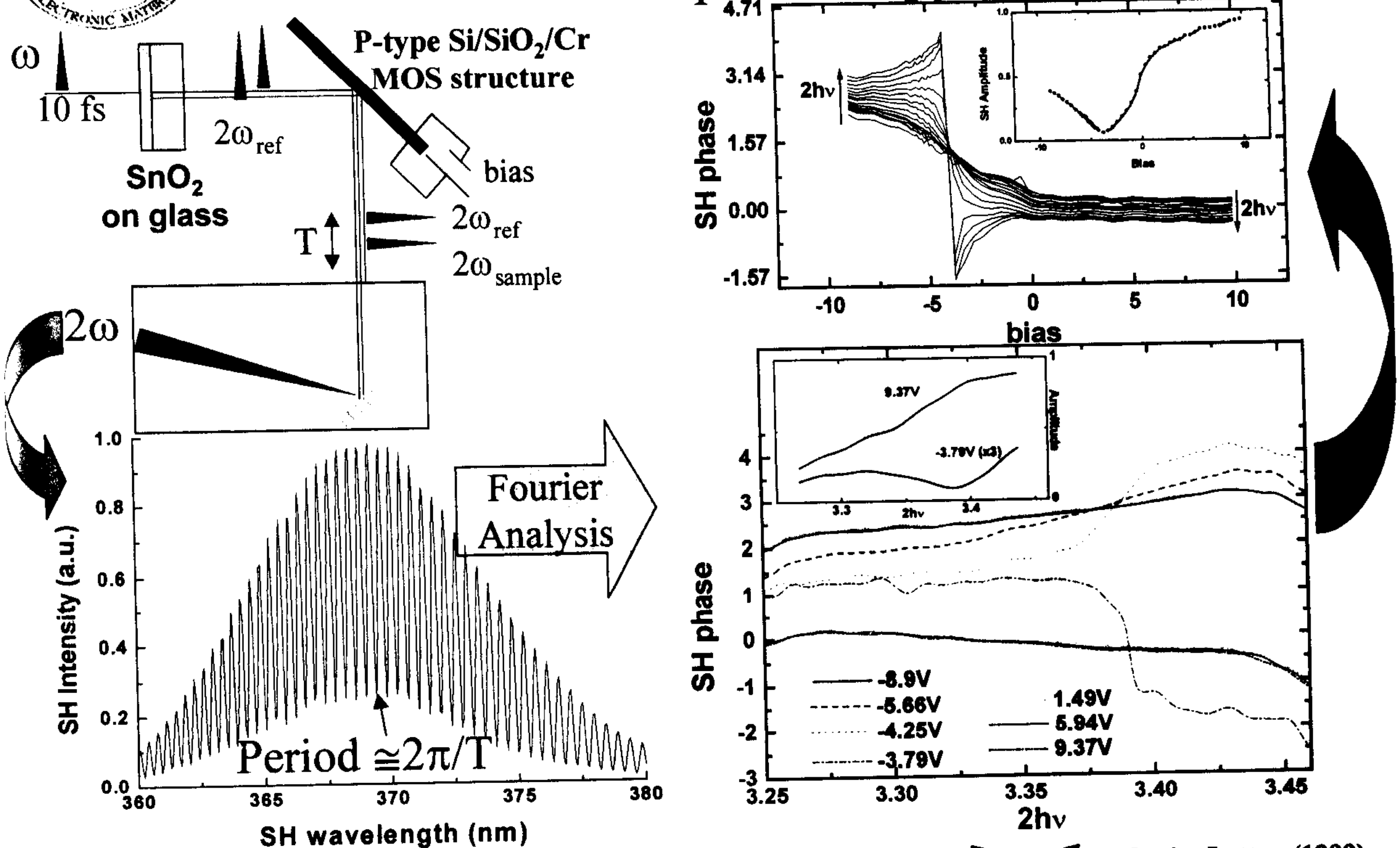
- *Broadband & conventional spectra agree quantitatively*
- *Broadband spectra more robust in middle of range, noisier at extremes*

SHG phase measurements

- Phase of SHG is sensitive to polar orientations (Kemnitz, 1986), and can be necessary for distinguishing resonant and background contributions (Stolle, 1996).
- Time-domain measurements require narrow bandwidth tuning and delay variation
- Kramers-Kronig relations allow better lineshape fitting as in spectroscopic ellipsometry

4. SHG in a Box

Frequency Domain Interferometric Second Harmonic Spectroscopy

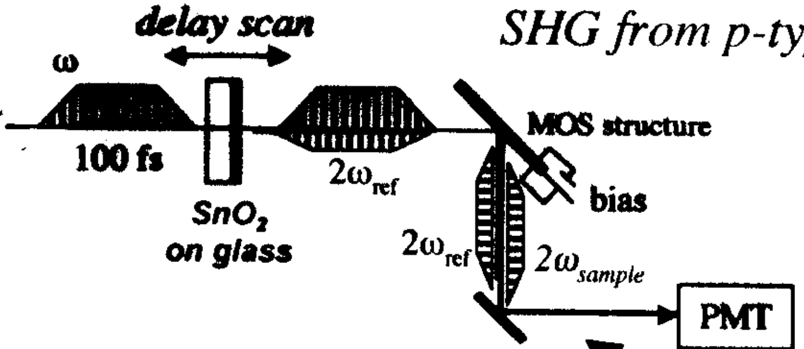


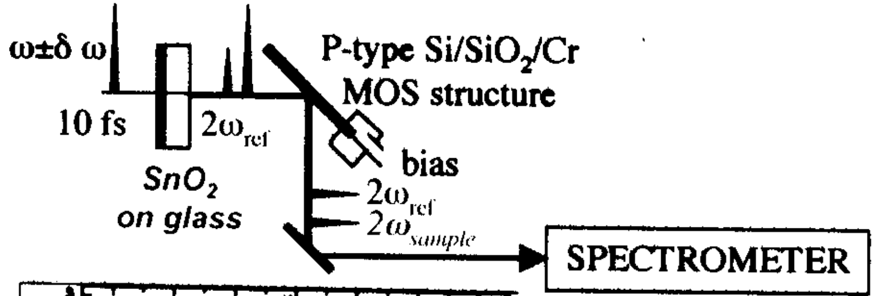
P. T. Wilson, Y. Jiang, O. A. Aktsipetrov, E. D. Mishina M. C. Downer, ~~submitted~~ accepted to Optics Letters(1999)

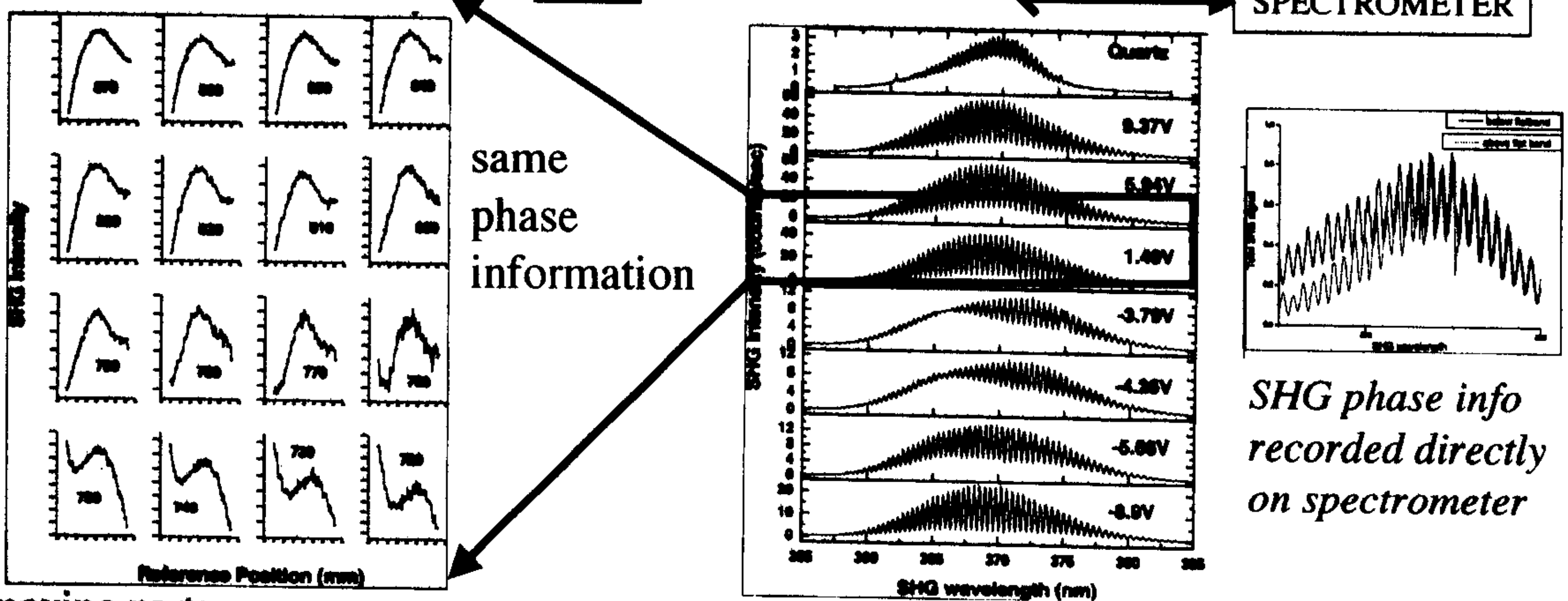
P. T. Wilson, Ph.D. dissertation (2000)

Conventional vs. FDISH spectral phase measurements

SHG from p-type Cr/SiO2/Si MOS structure







SHG phase info recorded directly on spectrometer

2 moving parts:

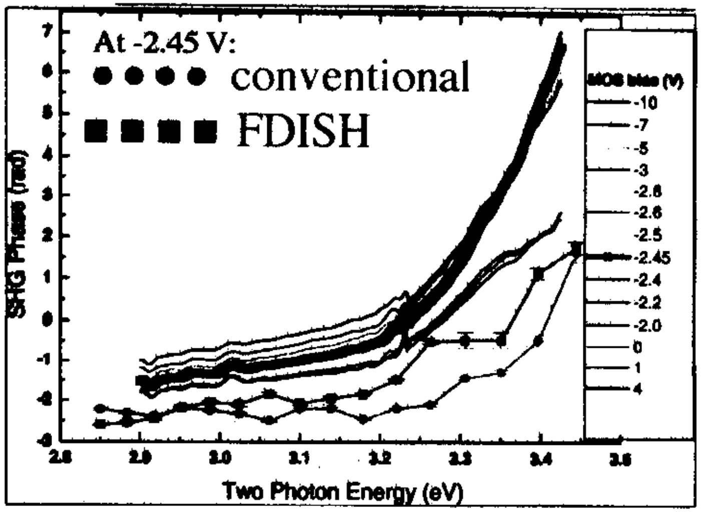
1) Delay scan at each λ
2) Manual tune of λ

} *several hours*

No moving parts ⇒ *several seconds*

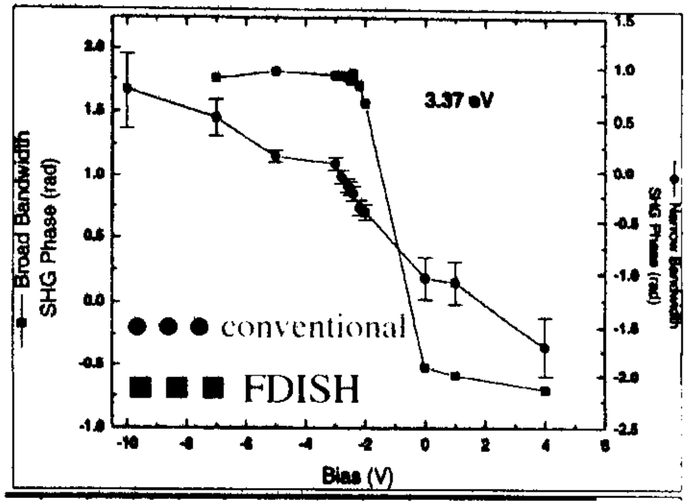
Conventional vs. FDISH spectral phase measurements: *results*

SHG spectral phase



- conventional measurement based on only 1 oscillation cycle.
- FDISH sensitive to ± 1 fs errors in time delay T.

Bias dependence of SHG phase



Sharper bias dependence in FDISH data
$\Rightarrow$ less carrier screening in 10 fs

$$\Delta\phi_{conventional} = \left[\varphi^{\chi}_{sample} + \varphi^{G}_{sample}\right] - \left[\varphi^{\chi}_{reference} + \varphi^{G}_{reference} + \varphi^{reflection}_{standard}\right] + \frac{\omega l}{c}\left[n_{air}(\omega) - n_{air}(\omega/2)\right]$$

$$\Delta\phi_{FDISH} = \left[\varphi^{\chi}_{sample} - \varphi^{G}_{sample} - \varphi^{reflection}_{sample}\right] - \left[\varphi^{\chi}_{standard} + \varphi^{G}_{standard} - \varphi^{reflection}_{standard}\right]$$

CONCLUSIONS

- **SHG spectroscopy directly probes charge transfer accompanying**
  - *- buckling of surface dimers*
  - *- H passivation*
  - *- Ge chemisorption*
  - *- 2nd layer B incorporation*

  at Si(001).

- **The SHG signatures for each surface-adsorbate system are UNIQUE**
- **The SHG signatures have been microscopically modelled by**
  - *- SETB*
  - *- first principles calculations*

- *New surface spectroscopic method that exploits 10 fs lasers: FDISH*
- *EFISH microscope images dc fields with submicron resolution.*
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D. Lim et al., Phys. Rev. Lett. ***84,*** *3406 (2000).*

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TEXAS

CIO - Léon

CSU NORTHRIDGE

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