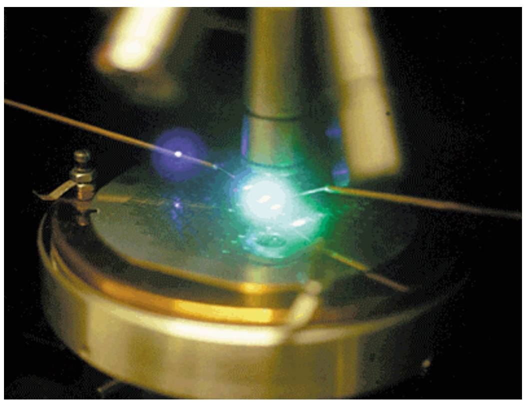
EPI-OPTICS 11
Erice, Sicily
July 20, 2010

Nonlinear Spectroscopy of Si Nanocrystals & Step-Edges

Mike Downer
University of Texas at Austin

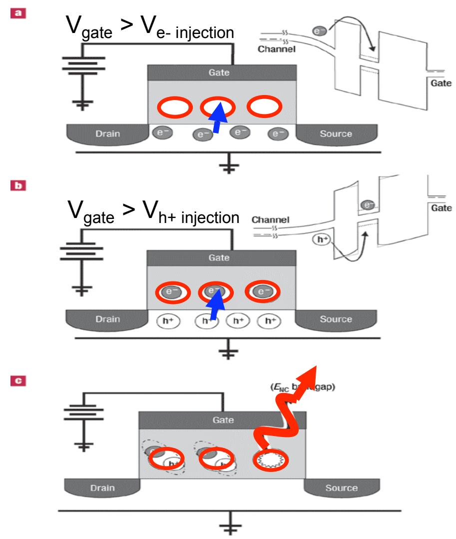
Si nanostructures have properties & applications different from those of bulk Si

"Si lasers start to take shape"



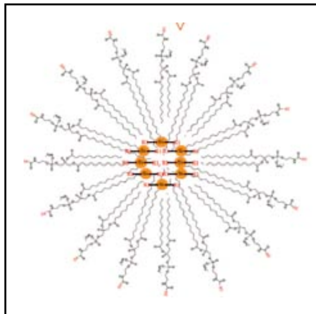
Observation of optical gain in Si nanocrystals embedded in SiO_2
Pavesi *et al.*, *Nature* **408**, 440 (2000)

Field-effect LED

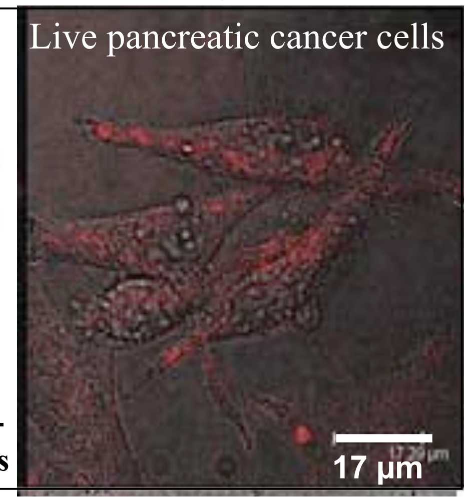


Walters *et al*, *Nature Mat.* **4**,143 (2005).

In vivo bio-sensing



amine-terminated micelle-encapsulated Si NC, a non-toxic alternative to CdSe NCs



Erogbogbo *et al*, *ACS Nano.***2**, 873 (2008)

These interesting properties originate at Si NC/SiO_2 interfaces.
⟹ *SHG has a reputation for being interface-specific*

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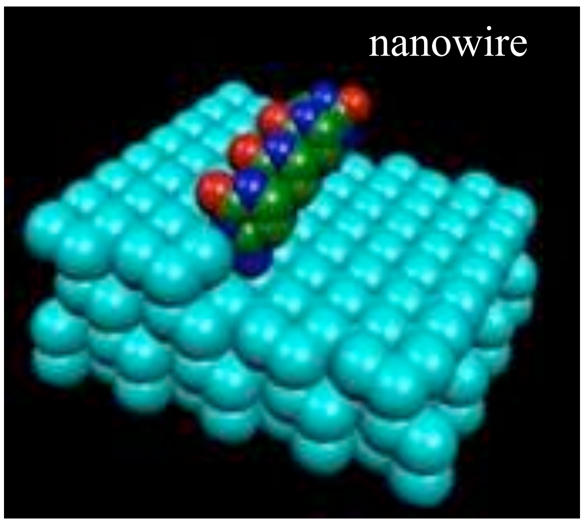
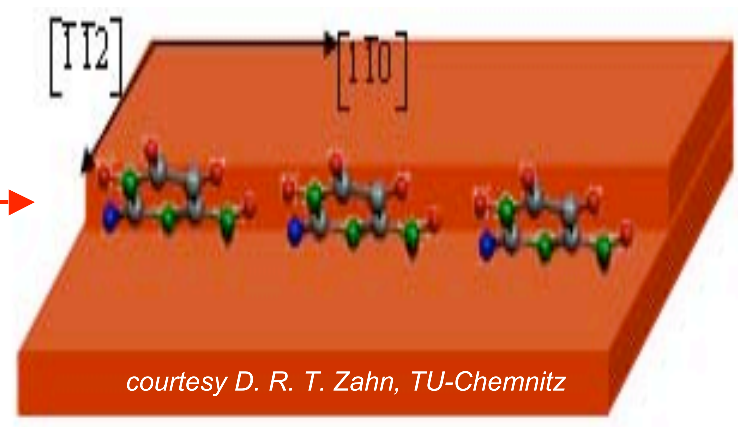


*silicon stepped surfaces provide **templates** for 1D quantum wires,[1] molecular electronics,[2] atomic-scale memory,[3] quantum computers[4] & other nano-electronic structures*

[1]McChesney, *Nanotech.* **13**, 545 (02)
[2]Kasemo, *Surf. Sci.* **500**, 656 (02)
[3]Bennewitz, *Nanotech.* **14**, 499 (02)
[4]Ladd, *Phys. Rev. Lett.* **89**, 017901 (02)



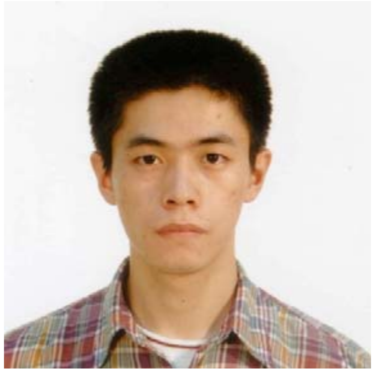
DNA bases adsorbed at vicinal Si
Mauricio *et al.*, *Nanoletters* **3**, 479 (2003)

These interesting properties originate at Si ~~NC/SiO_2 interfaces.~~ → ***step-edges***

⟹ *SHG has a reputation for being interface-specific*

Co-workers

Si NCs



Junwei Wei

Y. Jiang
PhD 2002

Liangfeng Sun
PhD 2006

Pete Figliozzi
PhD 2007

Adrian Wirth (MS 2007)

Si step-edges

Robert Ehlert

Jinhee Kwon
PhD 2006

Yongqiang An
PhD UC-Boulder
2004

Theory

Bernardo Mendoza
CIO, León, México

W. Luis Mochan
U. Nacional Autónoma
Cuernavaca, México

Financial Support:

- Robert Welch Foundation
- U.S. National Science Foundation

Their elusive nano-interfaces make Si NCs interesting & challenging

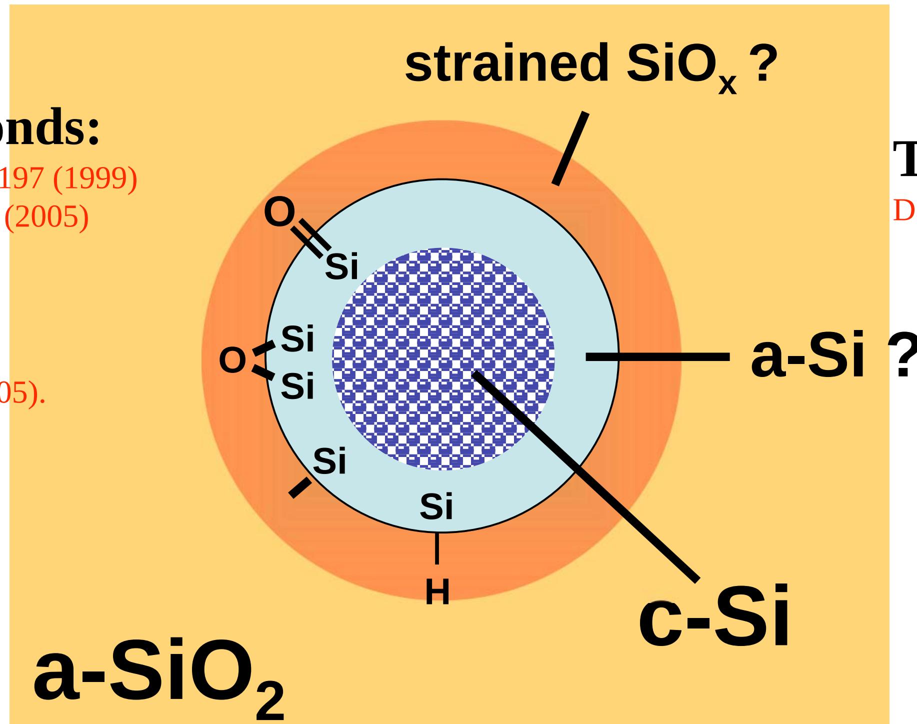
diameter	# atoms	# surface atoms	surface atom fraction
2 nm	209	98	0.47
5 nm	3272	616	0.19

(PL)

Radiative double bonds:
Wolkin *et al*., Phys. Rev. Lett. **82**, 197 (1999)
Luppi & Ossicini, Phys. Rev. B **71** (2005)

Bridge bonds:
Sa'ar et al., Nano Lett. **5**, 2443 (2005).

Dangling bonds



(XPS, Raman)

Transition layer(s):
Daldosso *et al*., Phys. Rev. B **68**, (2003)

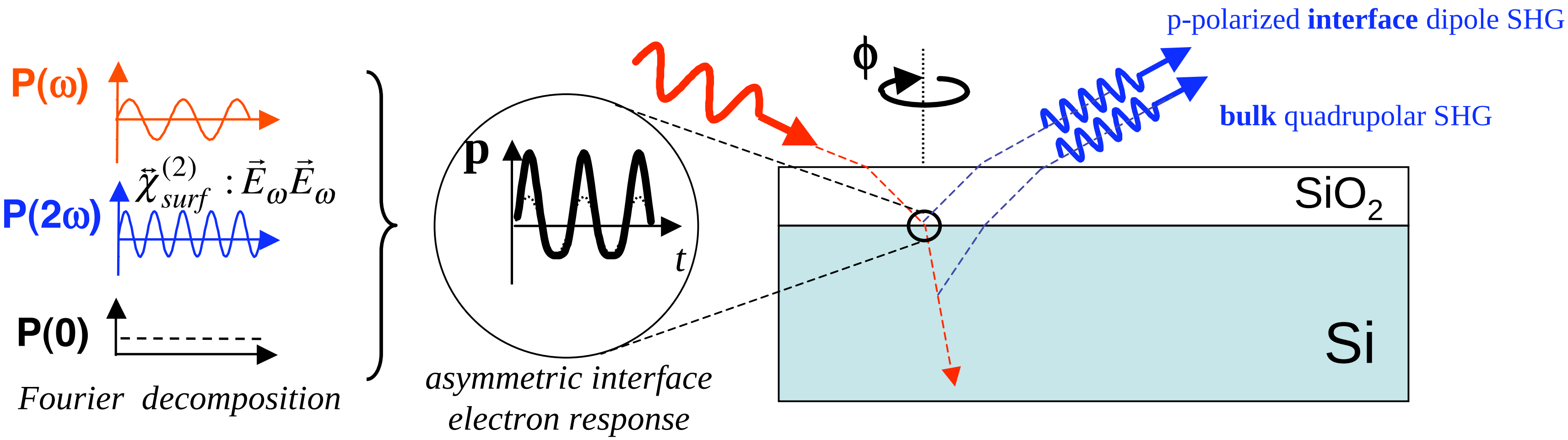
(SHG)

(SE)

- **Buried nano-interfaces inaccessible to many surface science probes and challenging to described theoretically (e.g. by DFT, Monte Carlo)**
- **Here we use multiple complementary spectroscopies**

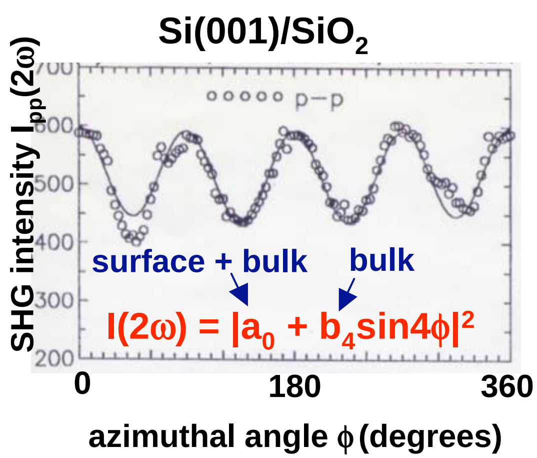
Surface & bulk contributions to SHG from planar surfaces are never separated with full rigor...

J. E. Sipe *et al.*, Phys. Rev. B **35**, 1129 (1987)



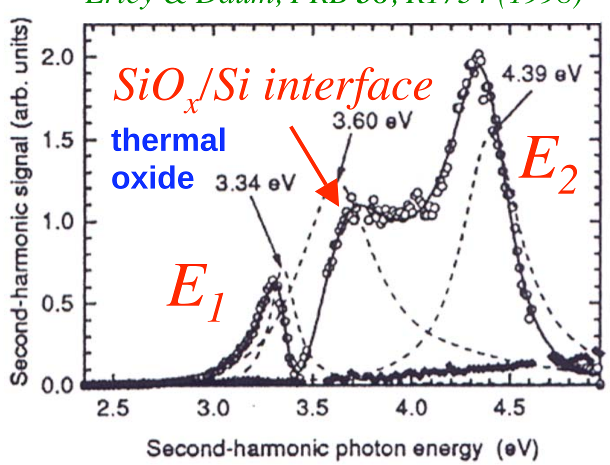
... but empirical separation is usually possible based on:

1. azimuthal anisotropy

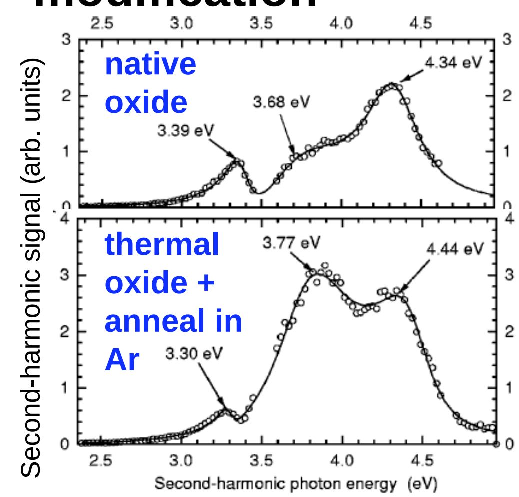


2. spectrum

Erley & Daum, PRB ***58****, R1734 (1998)*



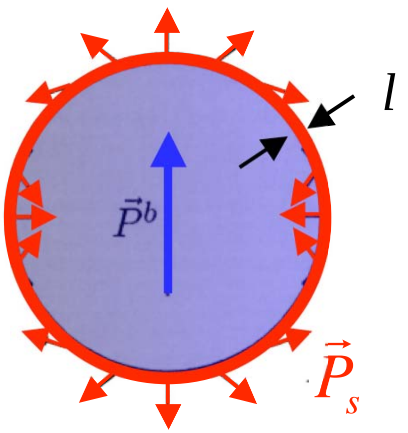
3. sensitivity to interface modification



Similarly, nano-interface & bulk contributions to SHG from Si NCs are intertwined, and must be distinguished empirically

Mochan *et al.*, Phys. Rev. B **68**, 085318 (03)

single nanoparticle:



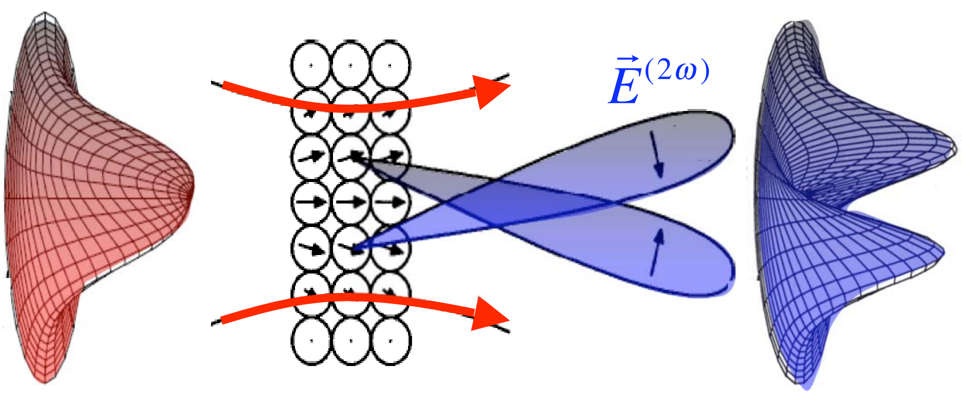
From symmetry alone,

$$\vec{P}^b(\vec{r}) = \gamma\nabla E^2 + \delta'\vec{E}\cdot\nabla\vec{E}$$

$$\vec{P}^s(\vec{r}) = \chi^s_{ijk}(a,b,f)F_jF_k,$$

assuming $l << r_{NC} << \lambda$

uniform nano-composite:



TEM$_{00}$ mode

TE$_{01}$ mode

$$\vec{P}^{NL} = \Delta'\vec{E}\cdot\nabla\vec{E}$$

$$\Delta' \equiv n_{NC}[\gamma_e(\delta',\gamma,a,b,f) - \gamma_m(\delta',\gamma,a,b,f) - \gamma_q(a,b,f)/6]$$

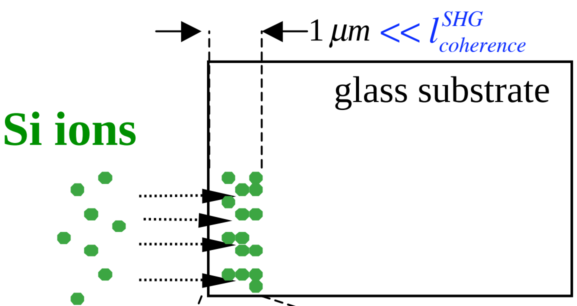
One group of samples is prepared by Si ion implantation into SiO_2

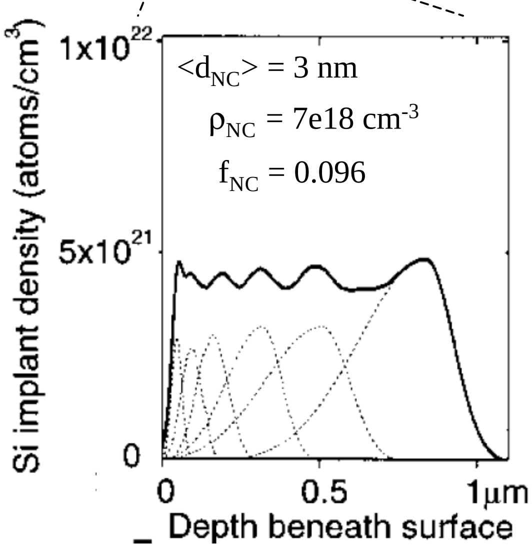
C. W. White *et al.*, NIM B **141**, 228 (1998) - ORNL

① • Multi-energy implant (35-500 keV) yields uniform NC density (simplifies optical analysis)

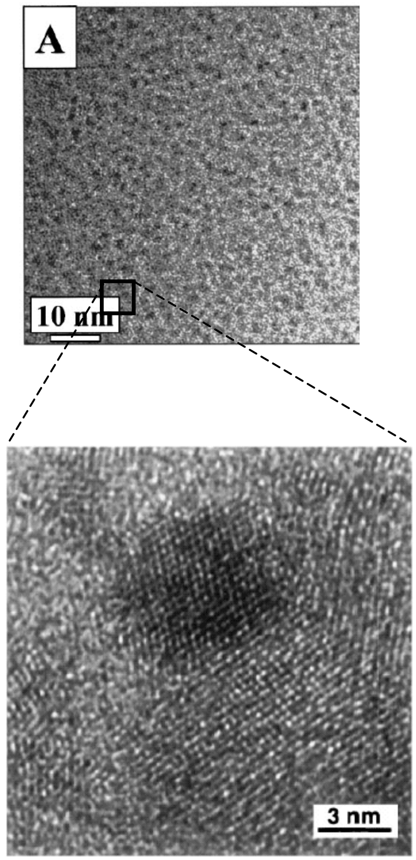
② • Samples annealed @ 1100 C / 1 hr in Ar **or** Ar + H_2 to precipitate NC formation

$\langle d_{NC} \rangle$ = 3, 5, 8 nm ± 50%



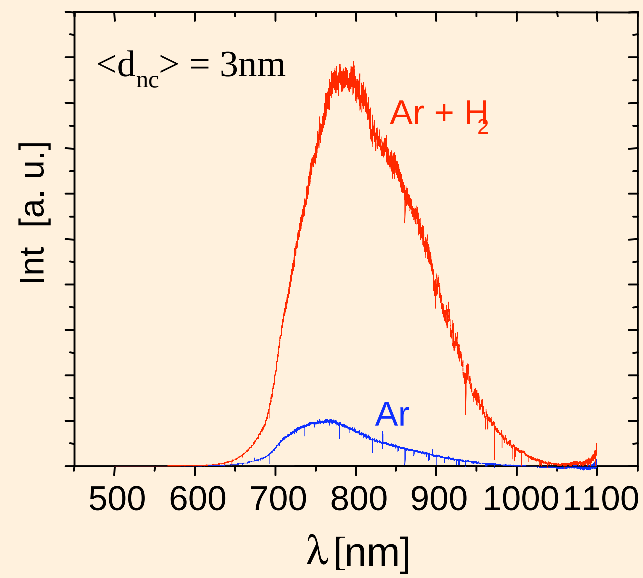


TEM Images



single 5 nm NC

Photoluminescence
excitation @ 486 nm



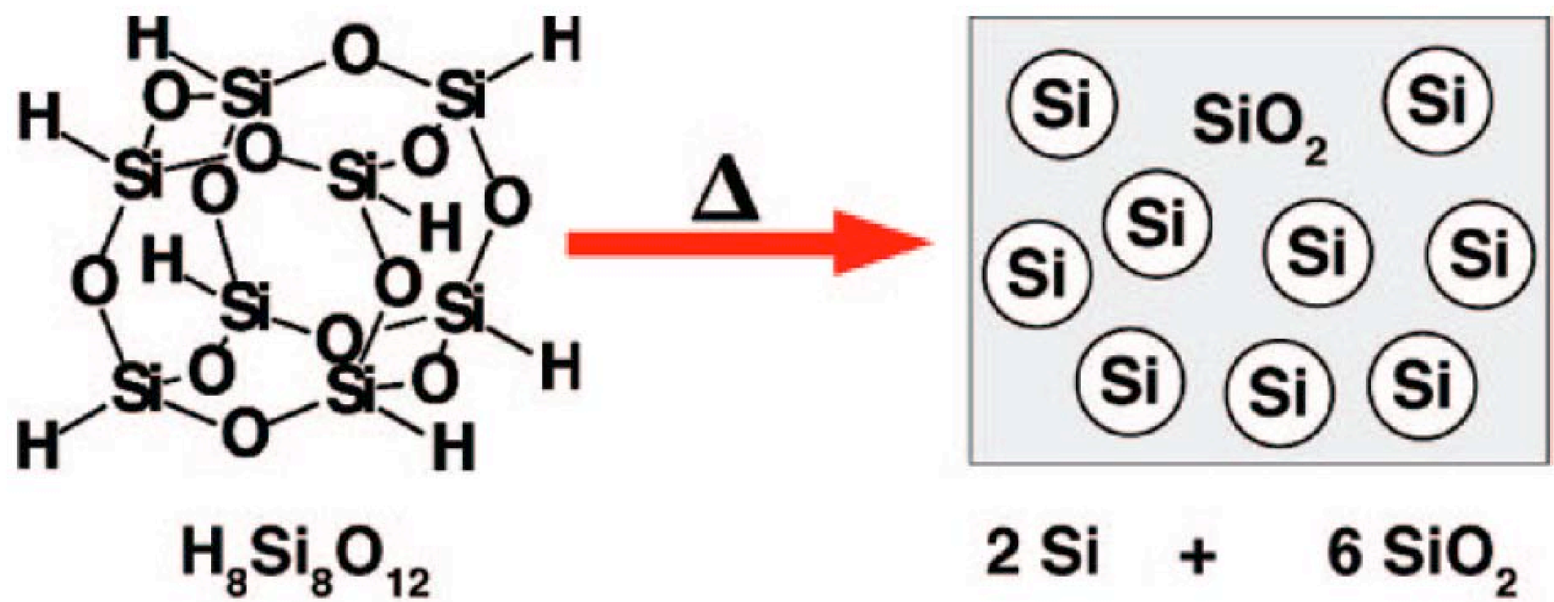
PL spectrum is unchanged throughout the excitation range 250 < λ < 500 nm

López *et al.*, Appl. Phys. Lett. **9**, 1637 (2002)

X-ray diffraction confirms crystallinity after annealing

We also fabricate Si NC samples on a benchtop by thermolysis of hydrogen silsesquioxane (HSQ)

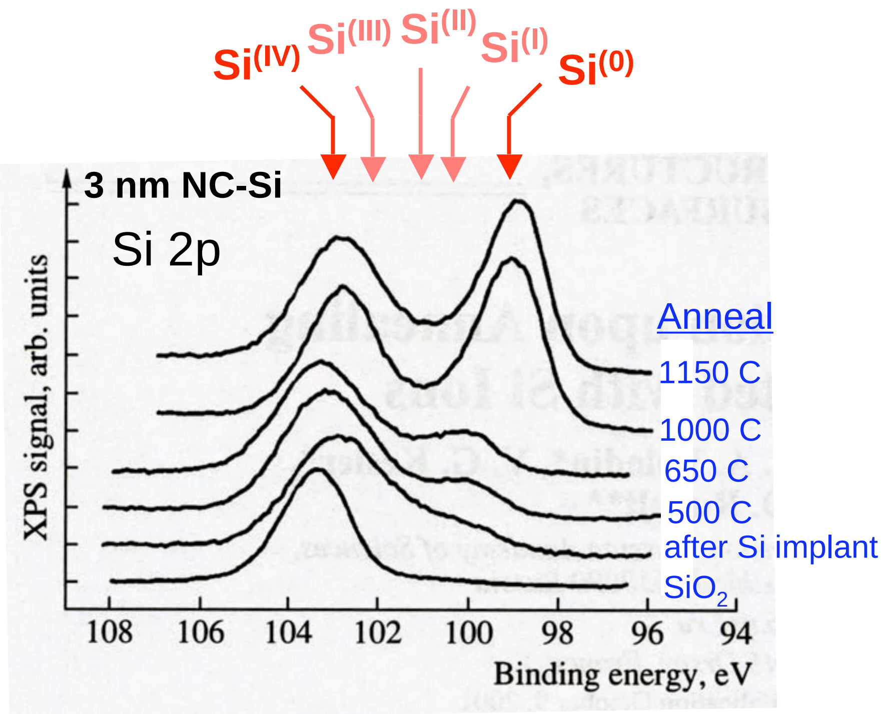
• C. M. Hessel *et al.*, Chem. Mater. **18**, 6139 (2006); J. Phys. Chem. C **111**, 6956 (2007)



XPS and Raman scatter document conversion of multiply-coordinated a-Si clusters into 4-fold-coordinated c-Si NCs

Similar measurements by previous investigators:
- Kachurin *et al.*, *Semiconductors* **36**, 647 (2002)
- ____________ , *Fiz. Tekh. Poluprov*. **36**, 685 (2002)
- Hessel, J. Chem. Phys. **112**, 14247 (2008)

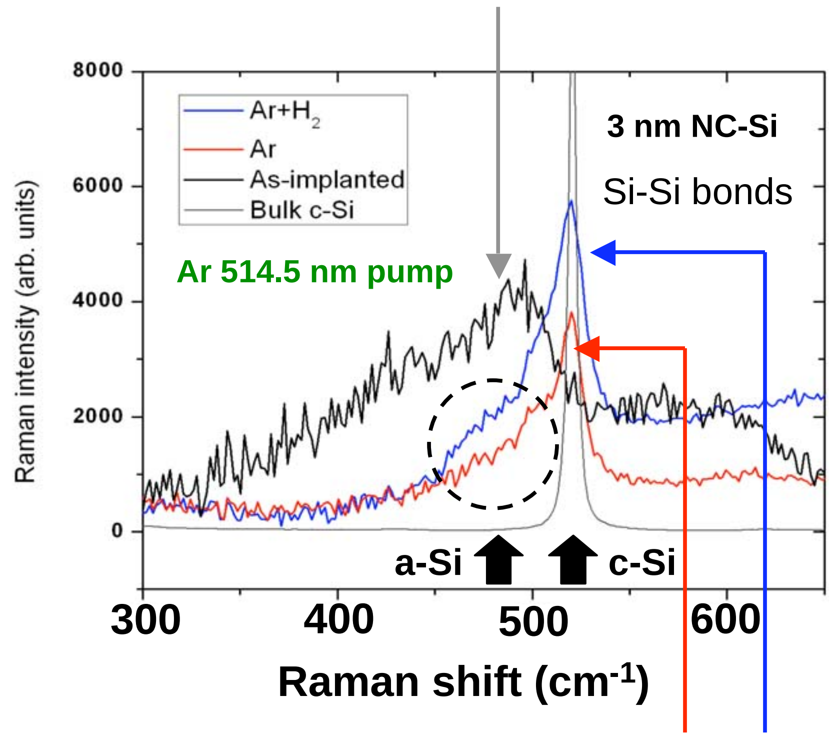
XPS



After annealing at > 1000 C, negligible sub-oxide is detectable by XPS.

Raman backscatter

As-implanted layer is dominated by clusters of a-Si (480 cm^{-1})



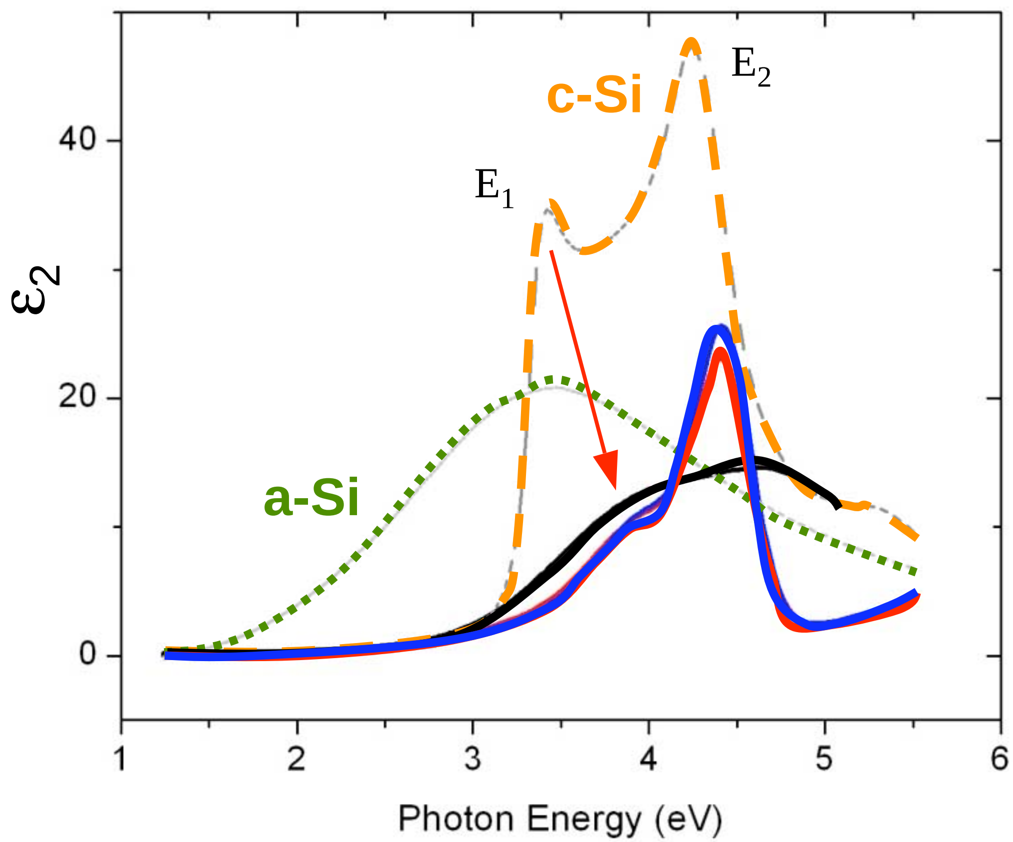
Annealed layer is dominated by c-Si (520 cm^{-1}) ...

... but low energy tail suggests residual a-Si content

Spectroscopic ellipsometry (SE) shows modified c-Si E_1 and E_2 critical points after annealing

[1] En Naciri *et al*. J. Chem. Phys. **129**, 184701 (2008)
[2] Cen *et al*., Appl. Phys. Lett. **93**, 023122 (2008)
[3] Seino, Bechstedt, Kroll, Nanotech. **20**, 135702 (2009)

} previous related SE results



as-implanted:

- no $E_{1,2}$ critical point features
- consistent with small a-Si clusters

after 1100 C anneal in Ar:

- $E_{1,2}$ peaks appear
- E_1 suppressed, blue-shifted
- consistent with:
  - previous SE measurements [1,2]
  - *ab initio* calculations of optical properties of Si NCs in SiO_2 [3]

after 1100 C anneal in Ar + H_2:

- negligible further change

- **SE appears selectively sensitive to c-Si core of Si NCs**
- **Measured $\varepsilon_{1,2}$ determine Fresnel factors used in SHG analysis**

PL excitation spectrum demonstrates that linear absorption occurs primarily in bulk c-Si cores, consistent with SE

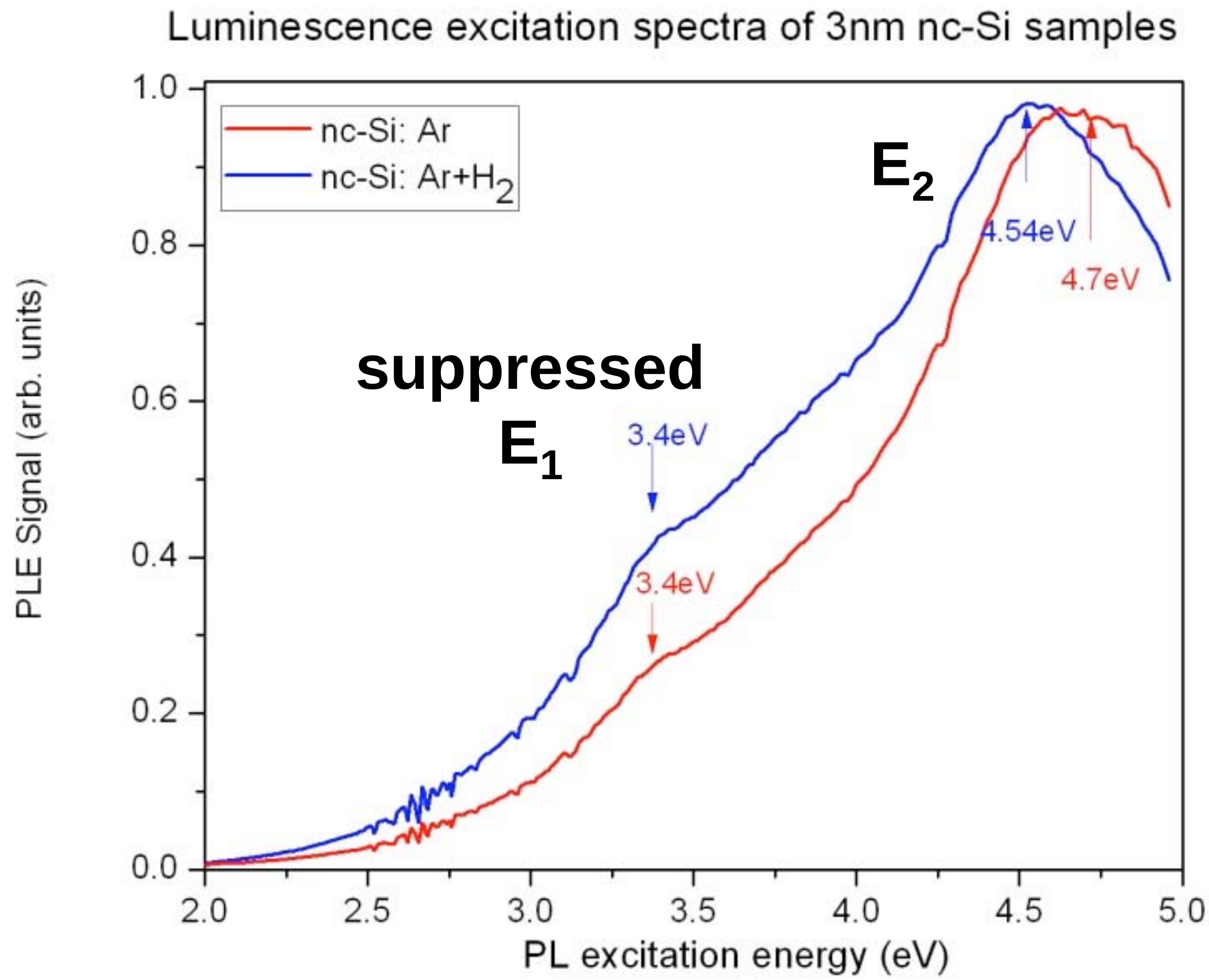


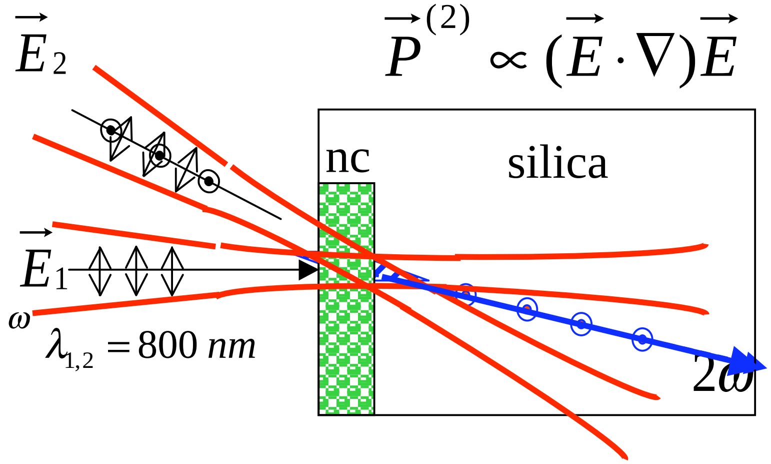
Photo-excited carriers cross-relax to interface states for PL

Conventional single-beam SHG is weak

Cross-Polarized **2**-beam SHG (XP2-SHG) enhances signal 100×

Single beam SHG

$$\vec{P}^{(2)} \propto (\vec{E}\cdot\nabla)\vec{E}$$

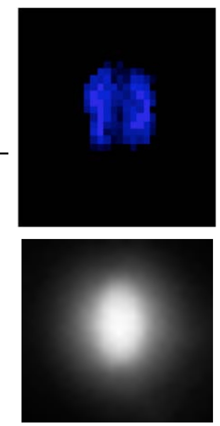


XP2-SHG

SH signal

$\propto \frac{1}{w_0^2}$

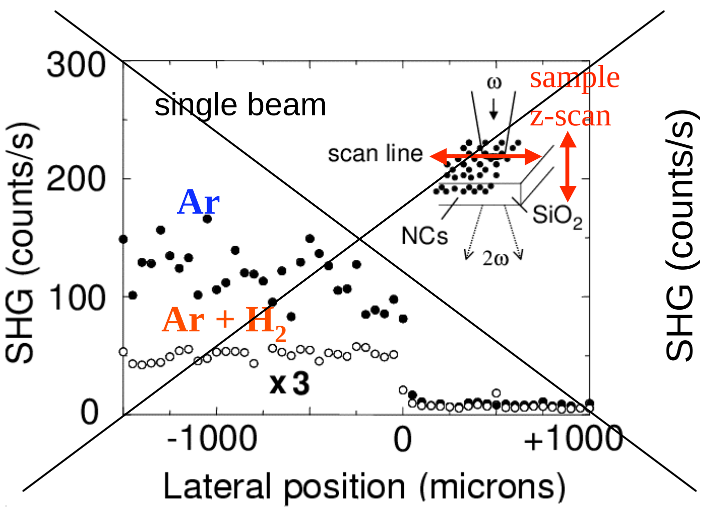
$\propto \frac{1}{\lambda^2}$

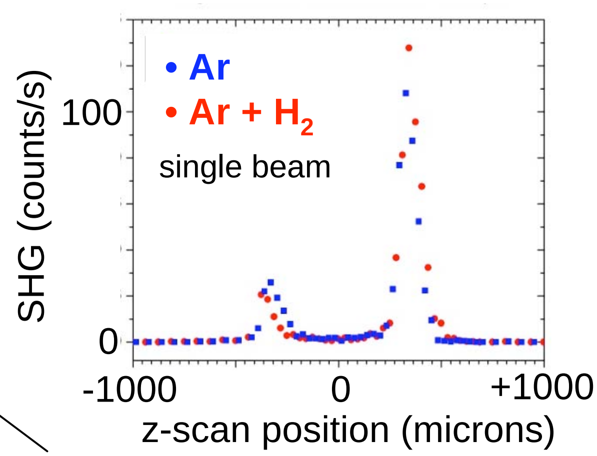


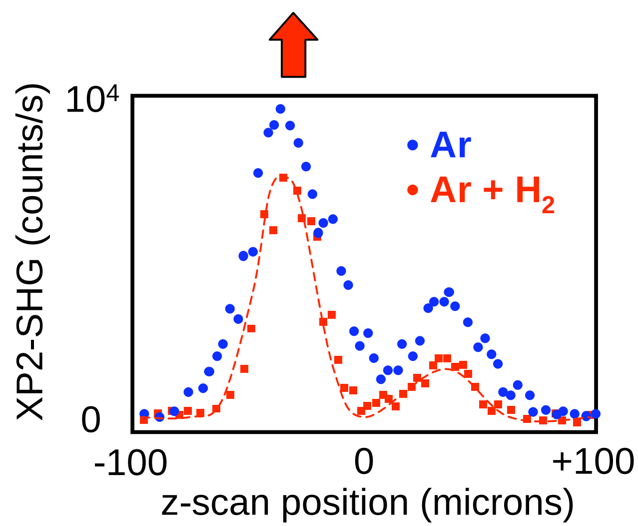
Three parameters needed to describe XP2-SHG response

$$\vec{P}_g^{(2)} \approx \underbrace{(\delta - \beta - 2\gamma)}_{\Gamma_g}(\vec{E}\cdot\nabla)\vec{E} + \dots$$

$$\vec{P}_{nc}^{(2)} \approx \underbrace{n_b\left(\gamma^e - \gamma^m - \gamma^q/6\right)}_{\Gamma_{NC} = |\Gamma_{NC}|e^{i\phi}}(\vec{E}\cdot\nabla)\vec{E} + \dots$$







Jiang et al., Appl. Phys. Lett., **78**, 766 (2001)

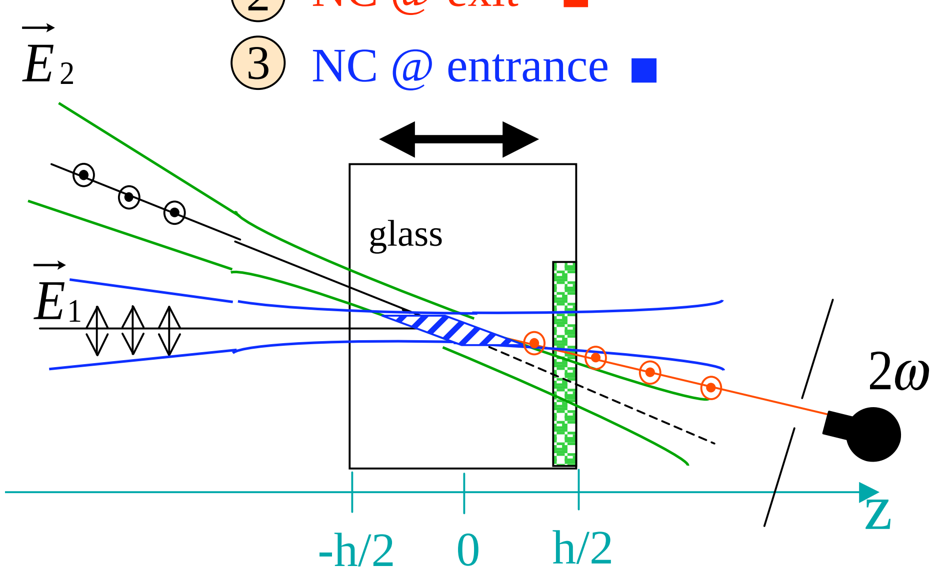
L Sun *et al*, Opt. Lett, **30**, 2287 (2005)
Figliozzi *et al*, Phy. Rev. Lett. **94**, 047401 (2005)

Three independent z-scan measurements determine Γ_g, $|\Gamma_{NC}|$ and ϕ

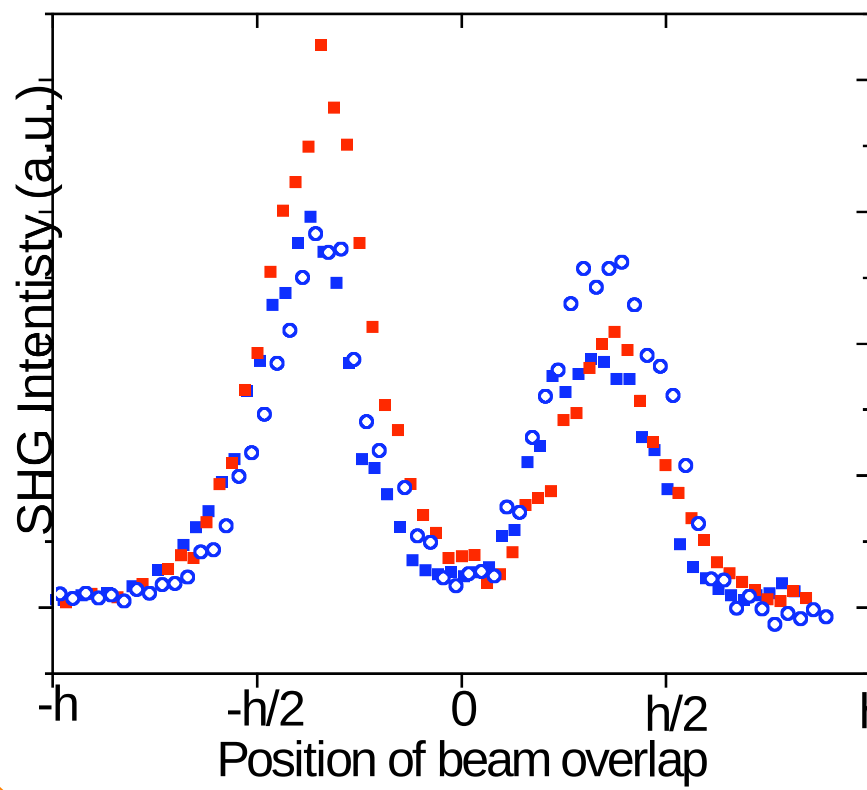
- SHG signal growth in the glass is affected by phase mismatch
- The peaks result from relaxation of phase mismatch when boundaries of the sample fall within the 2-beam overlap region
- An analogous enhancement underlies 3rd harmonic microscopy with focused beams
  Barad, Appl. Phys. Lett. 70, 922 (1997)
- Peak heights are asymmetric because of linear absorption of SH light by NCs and interference of SHG signals generated by NCs and silica

<u>Measurements (scans):</u>

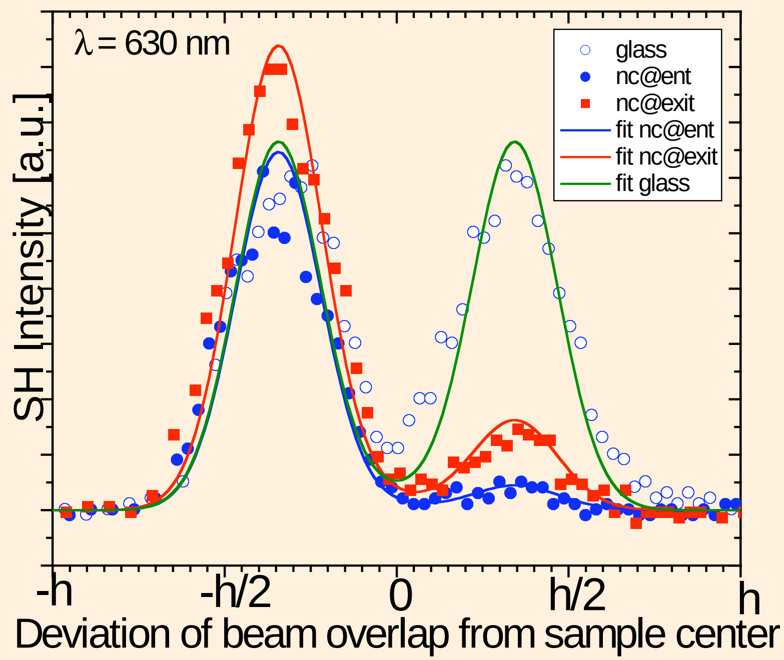
1. substrate ○
2. NC @ exit ■
3. NC @ entrance ■



L. Sun et al., Optics Lett. **30**, 2287 (2005)

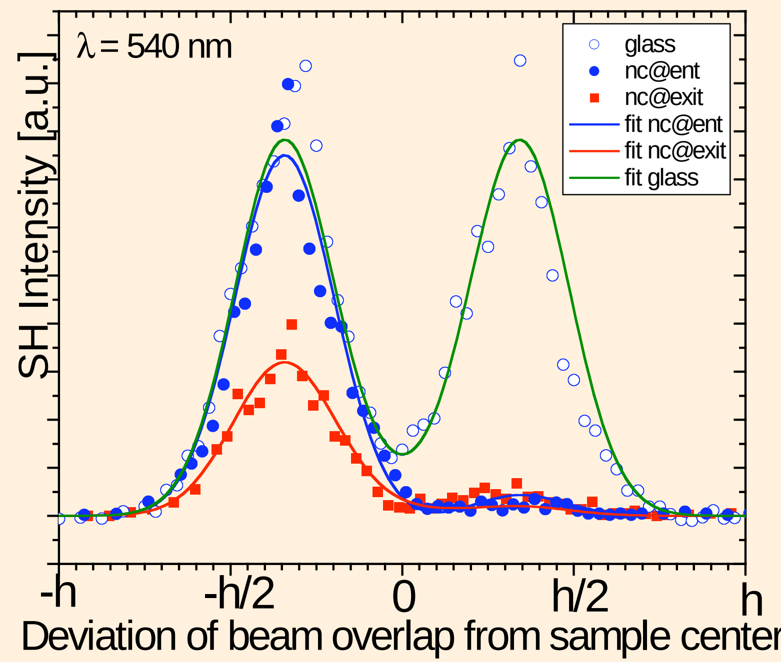


Examples at 2 wavelengths illustrate extraction of fitting parameters $|\Gamma_{nc}|/\Gamma_g$ and ϕ



$$\frac{|\Gamma_{nc}|}{\Gamma_g} = 1.743 \pm 0.064$$

$$\phi = (0.241 \pm 0.020)\pi$$

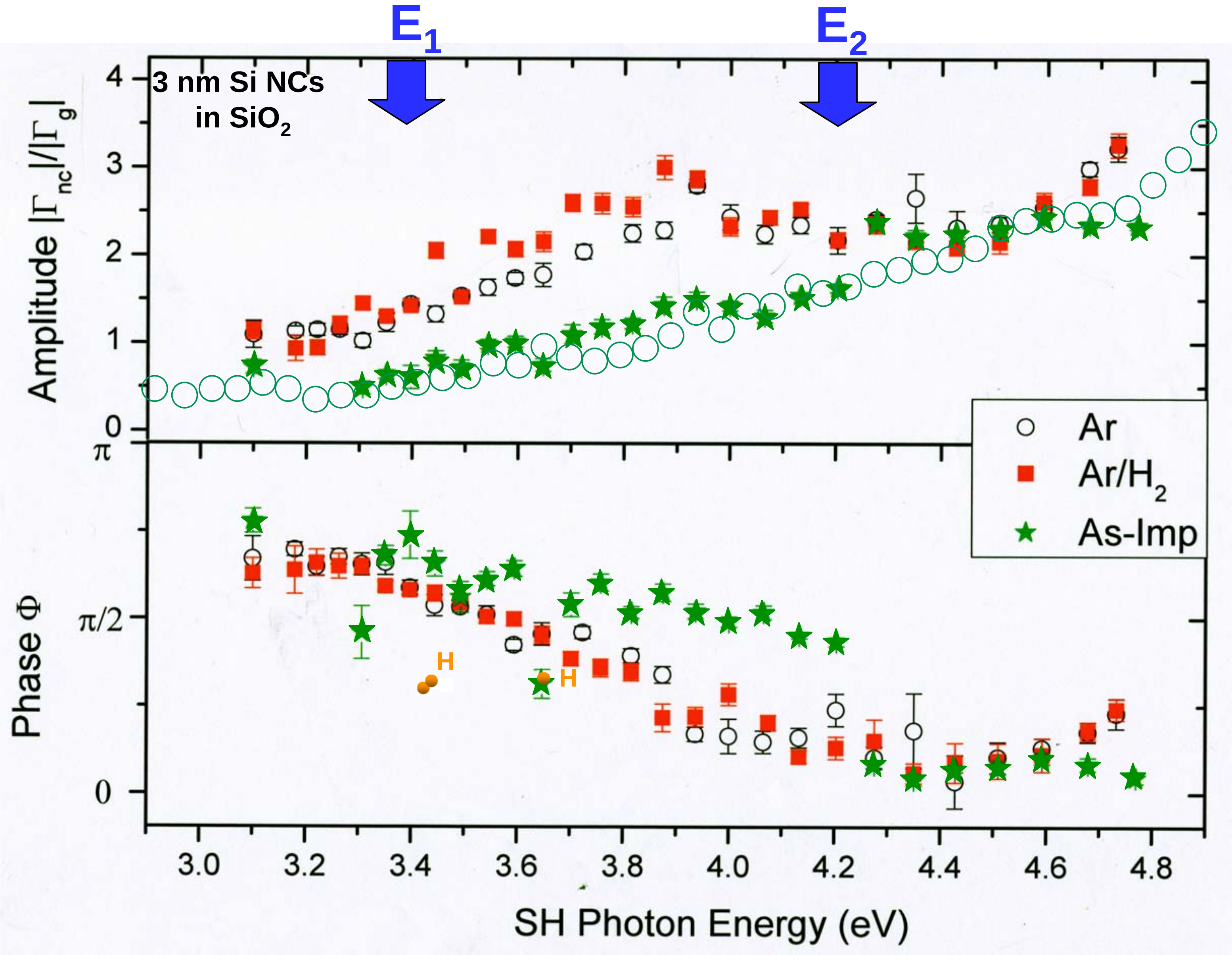


$$\frac{|\Gamma_{nc}|}{\Gamma_g} = 1.5217 \pm 0.060$$

$$\phi = (0.159 \pm 0.040)\pi$$

SE determined Fresnel factors used in this analysis

SHG spectra lack $E_{1,2}$ critical point resonances



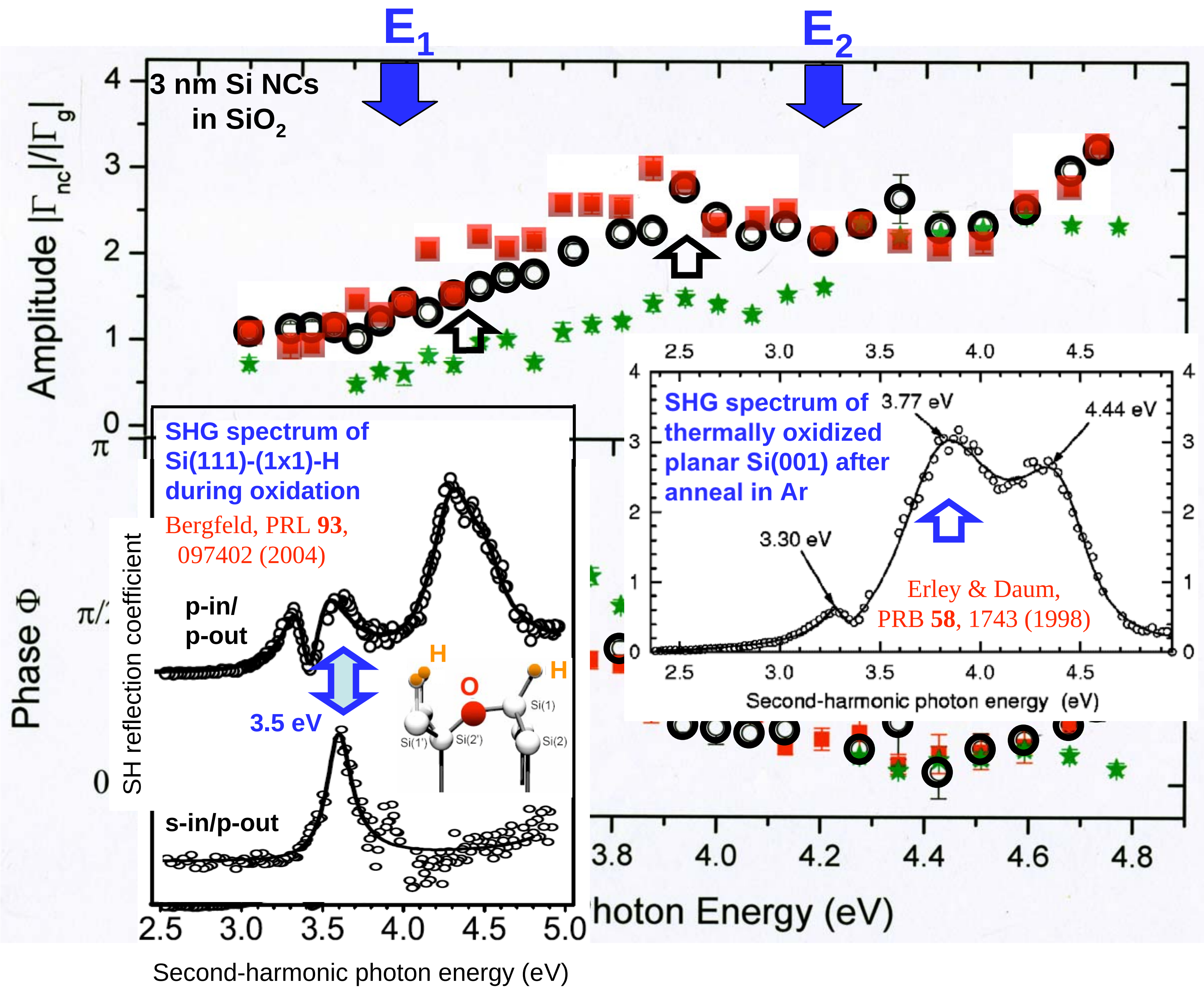
• Kramers-Kronig consistency between $|\Gamma_{NC}|/|\Gamma_g|$ and Φ

★ as-implanted: like a-Si

○ SHG spectrum of a-Si:

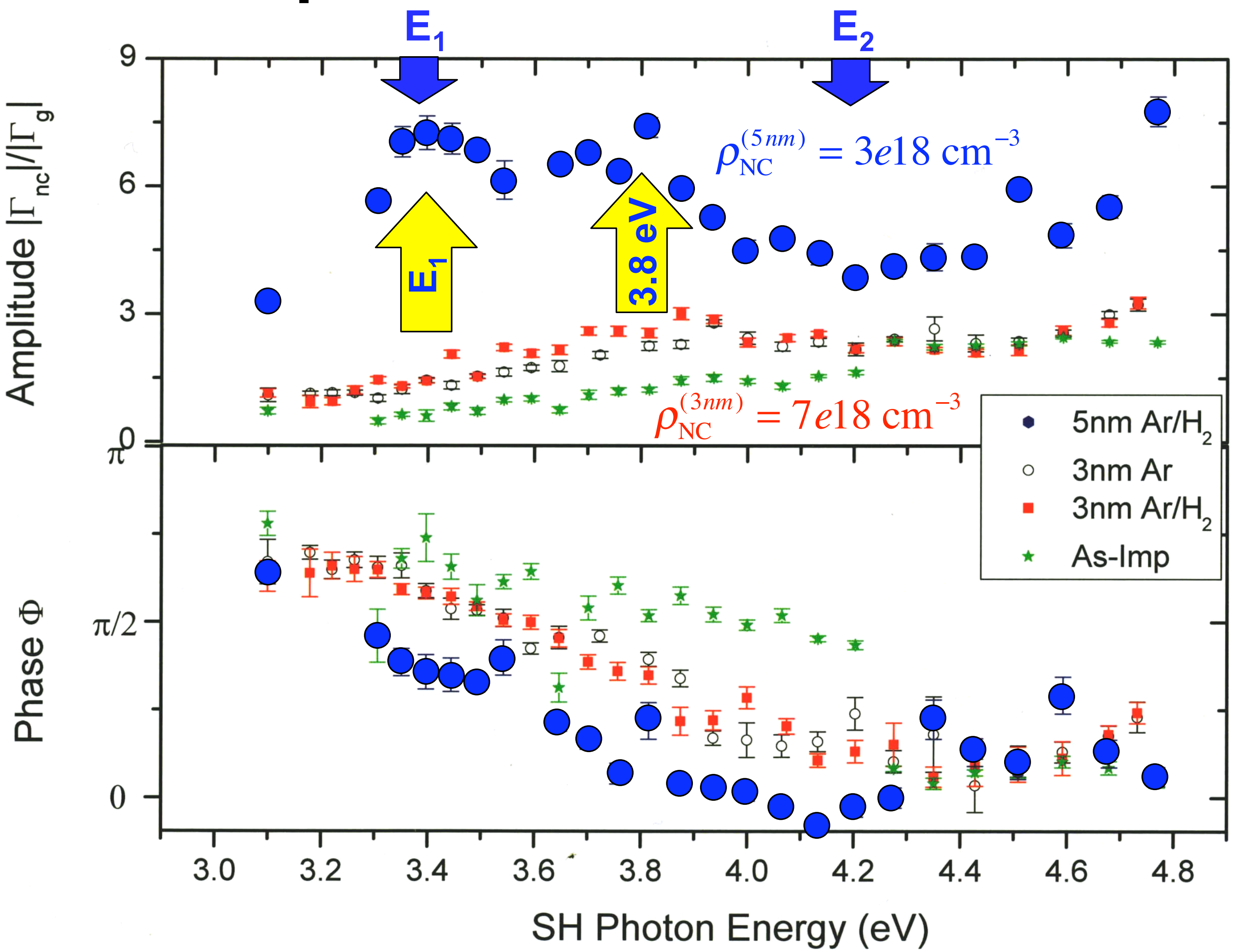
Erley & Daum, Phys. Rev. B **58**, R1734 (1998)

SHG spectra lack $E_{1,2}$ critical point resonances



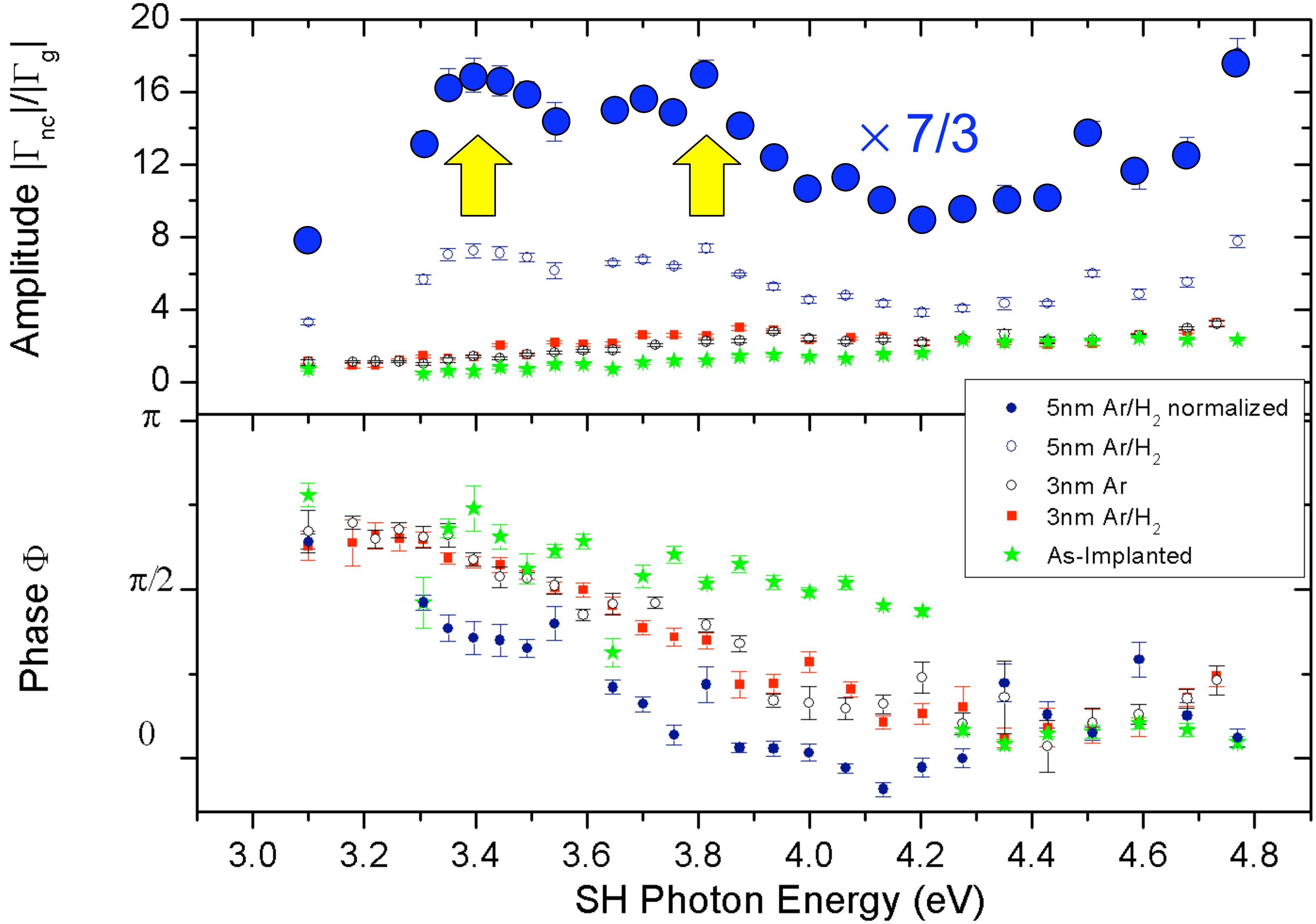
- **annealed in Ar:** enhanced Γ_{NC} near known SiO_x resonances
- **annealed in Ar/H_2:** minimal H-effect consistent with previous SHG

E_1 (3.4 eV) and 3.8 eV resonances appear in SHG spectra of 5 nm diameter Si NCs



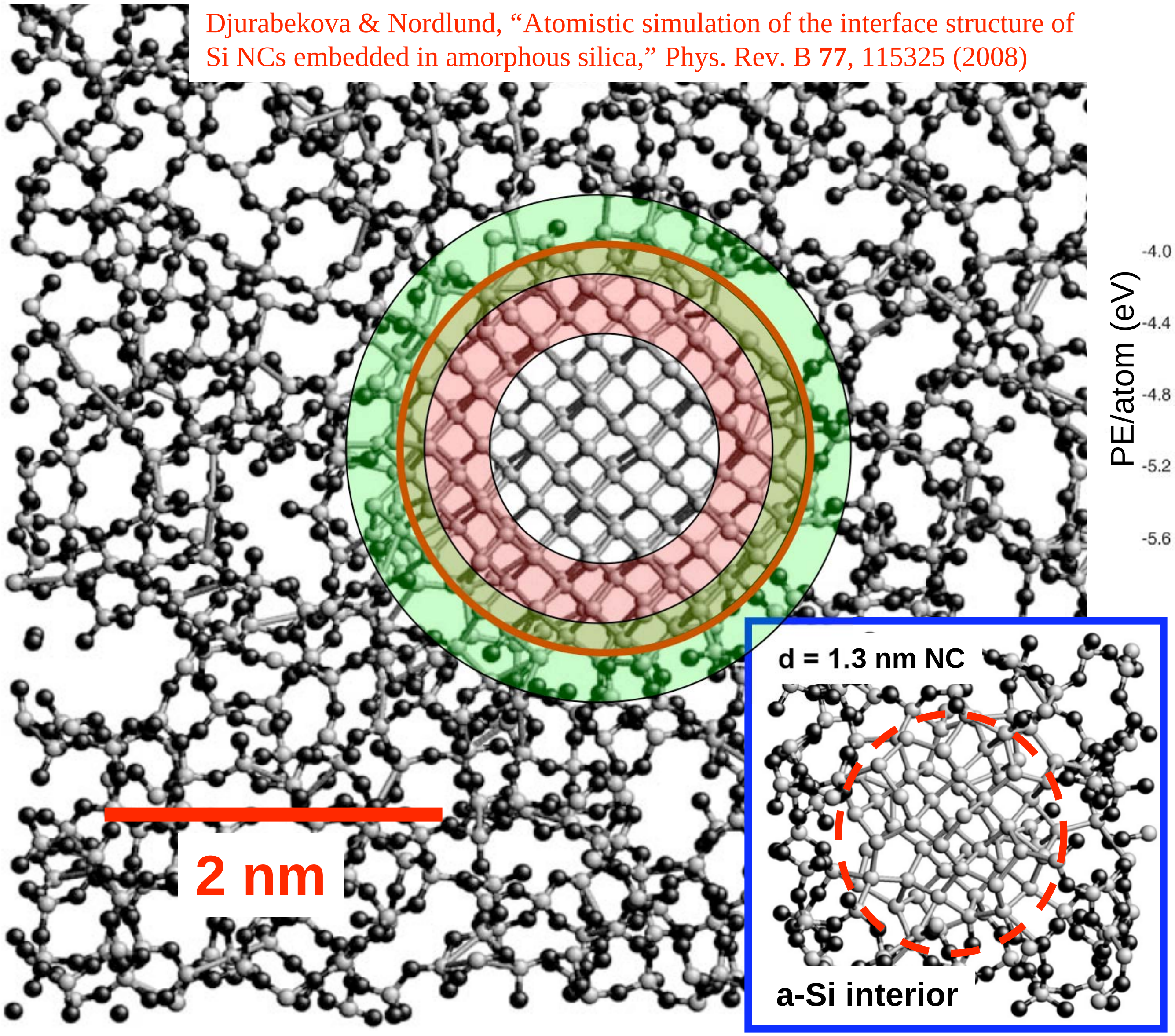
SHG per NC is >10× stronger from 5 nm NCS than from 3 nm NCs

Ideal single particle SHG scaling: $(5/3)^6 = 21$ *[Dadap, PRL (1999)]*



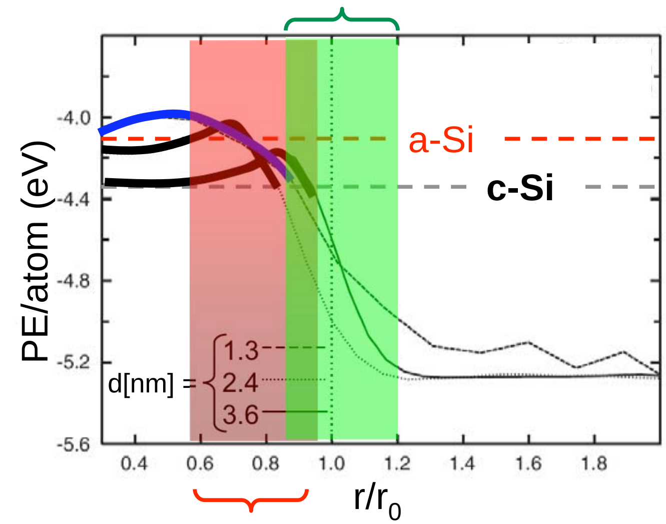
Spectroscopic XP2-SHG is sensitive to nc-Si/SiO_2 interfacial features* not observed by other spectroscopies that appear in recent MD simulations

Djurabekova & Nordlund, "Atomistic simulation of the interface structure of Si NCs embedded in amorphous silica," Phys. Rev. B **77**, 115325 (2008)



~ 10% undercoordinated bonds, Si=O bonds also present

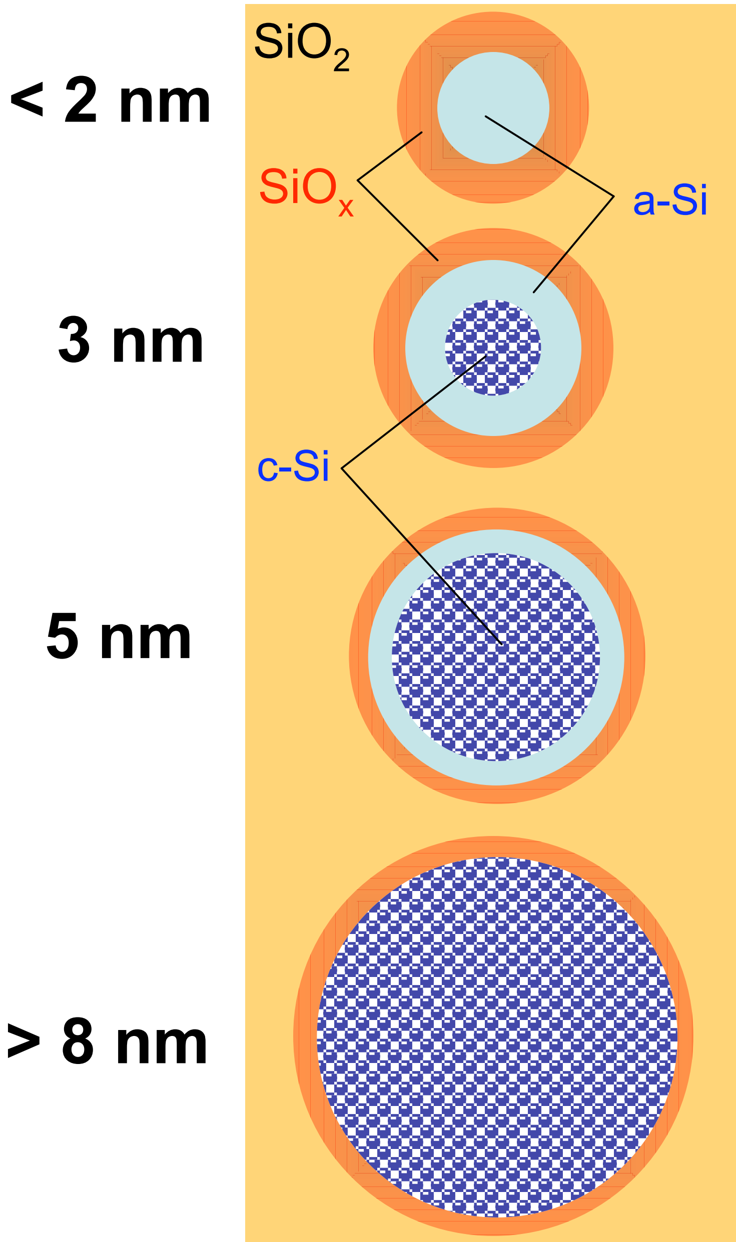
~ 10% suboxide*

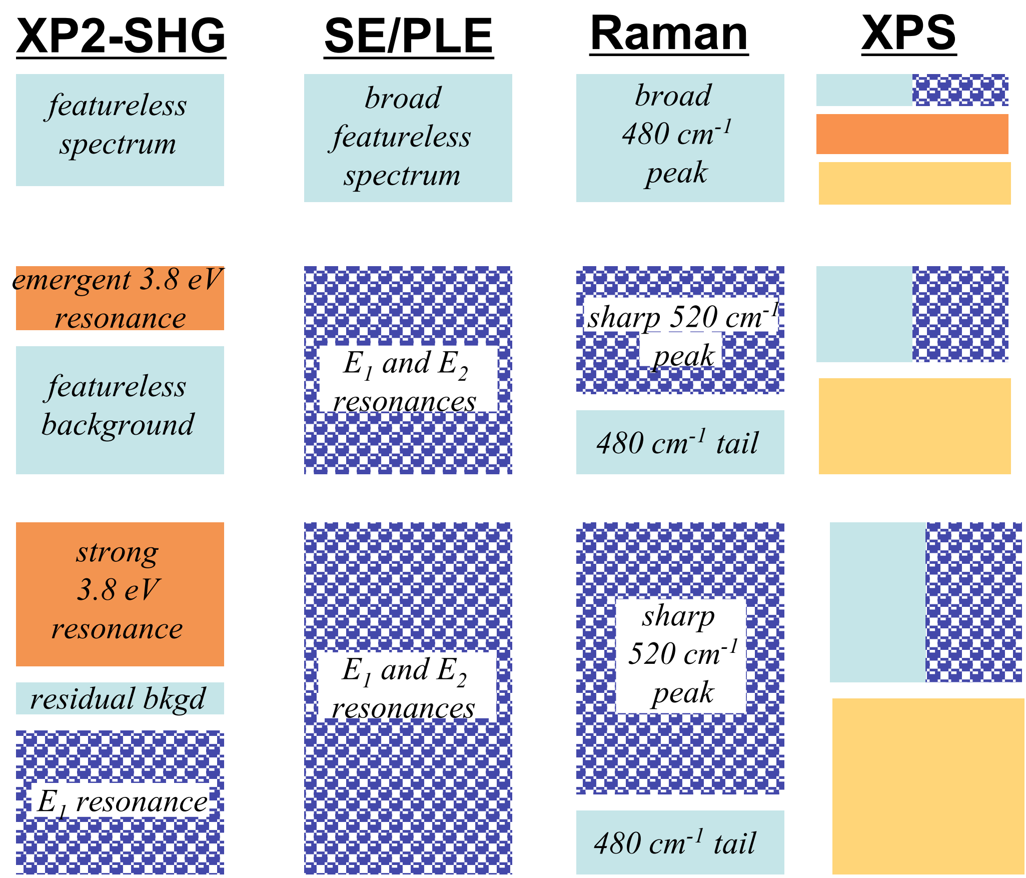


*elevated PE/atom ⇒ a-Si shell

S-SHG validates & guides simulations of the nc-Si/SiO_2 interface

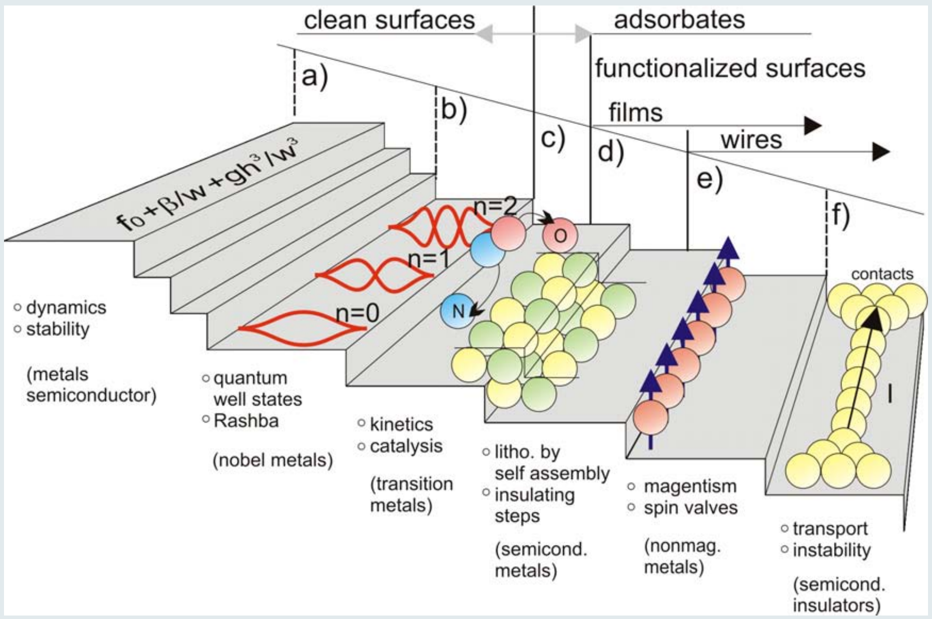
Conclusions about Si embedded nanocrystals





- interface region stabilizes and thins with increasing d_{NC}

Stepped (vicinal) Si surfaces are attractive templates for nanofabrication



- investigation of step-enhanced chemical reactions
- atomic wires suitable for transport
- "lithography" by self assembly of nanostructures
- …

Non-invasive in-situ sensors that provide atomic-scale information over the dimensions of a wafer are needed

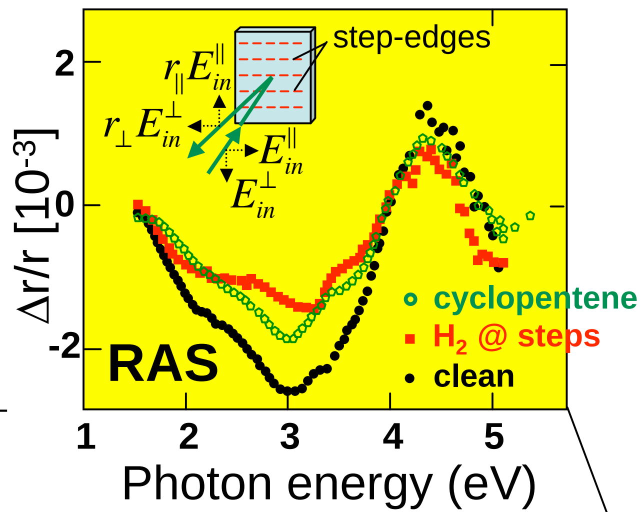
Optical metrology bridges the nano-scale & wafer-scale

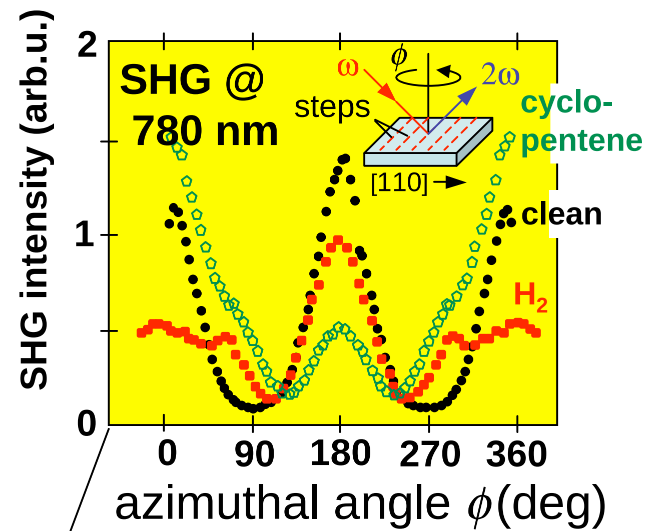
Aspnes & Studna, PRL **54**, 1956 (1985)

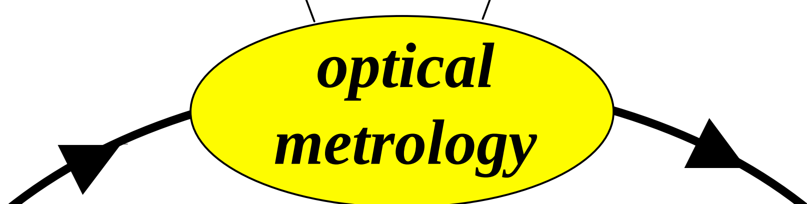
Reflectance
Anisotropy
Spectroscopy

$$r_\perp \neq r_\parallel$$

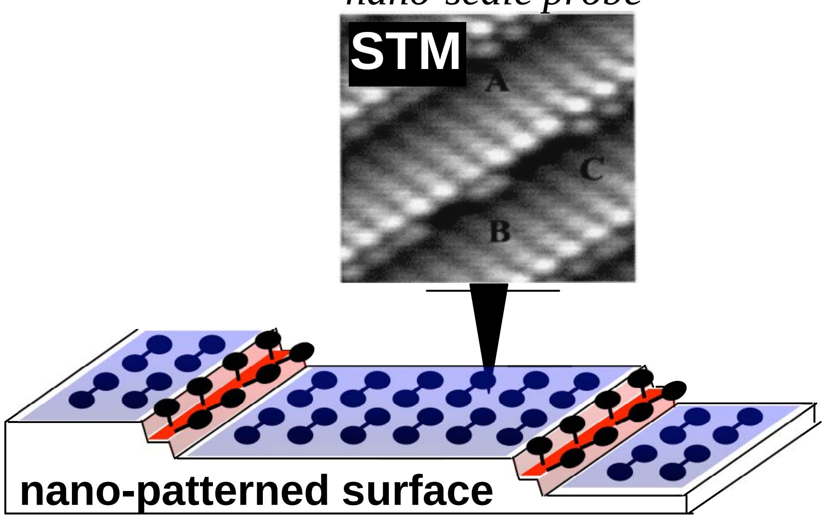
$$\frac{\Delta\tilde{r}}{\tilde{r}} = 2\,\frac{\tilde{r}_\perp - \tilde{r}_\parallel}{\tilde{r}_\perp + \tilde{r}_\parallel}$$





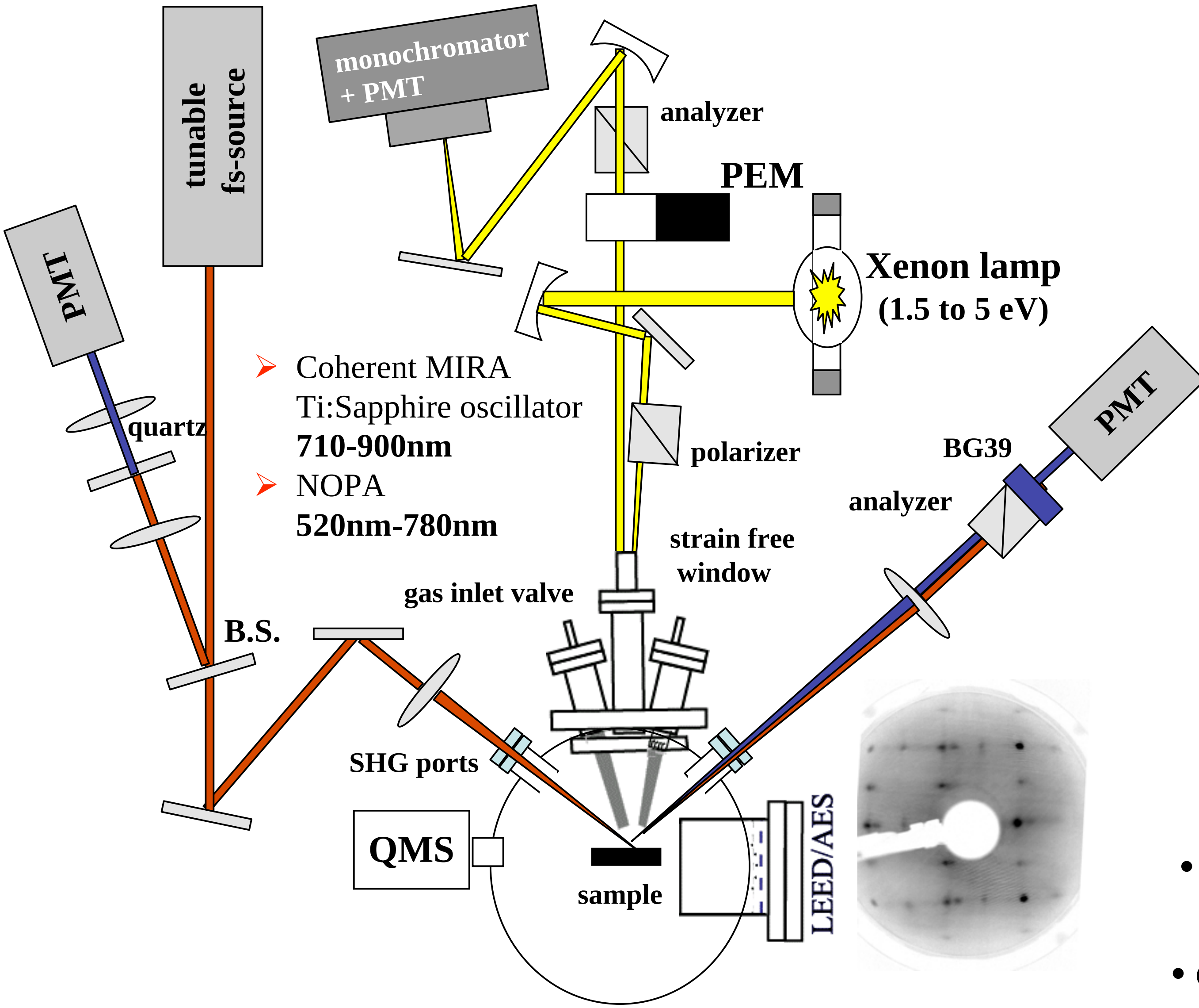


nano-scale probe

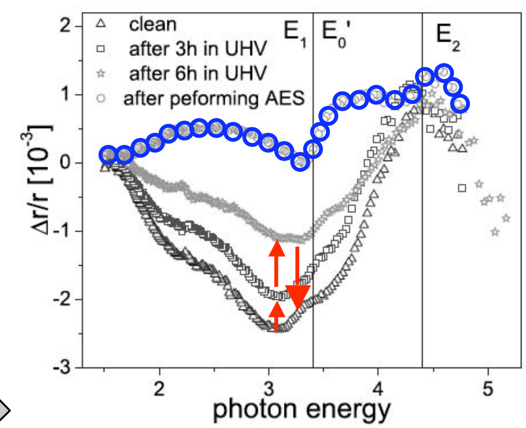


wafer-scale nanomanufacturing

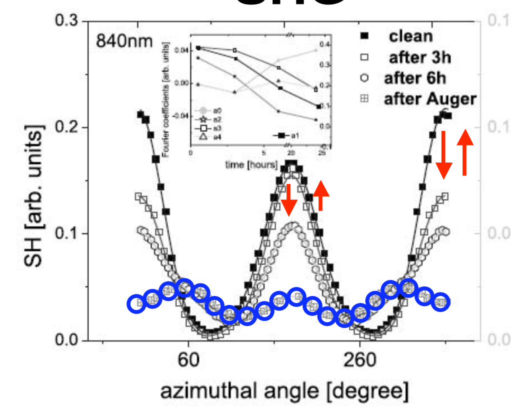
We combine SHG & RAS probes of stepped Si(001) surfaces in UHV



RAS



SHG



- **RAS & SHG track contamination non-invasively**
- **completely reversible**

We have studied 3 very different surface chemical reactions on Si(001):6°

1) H_2

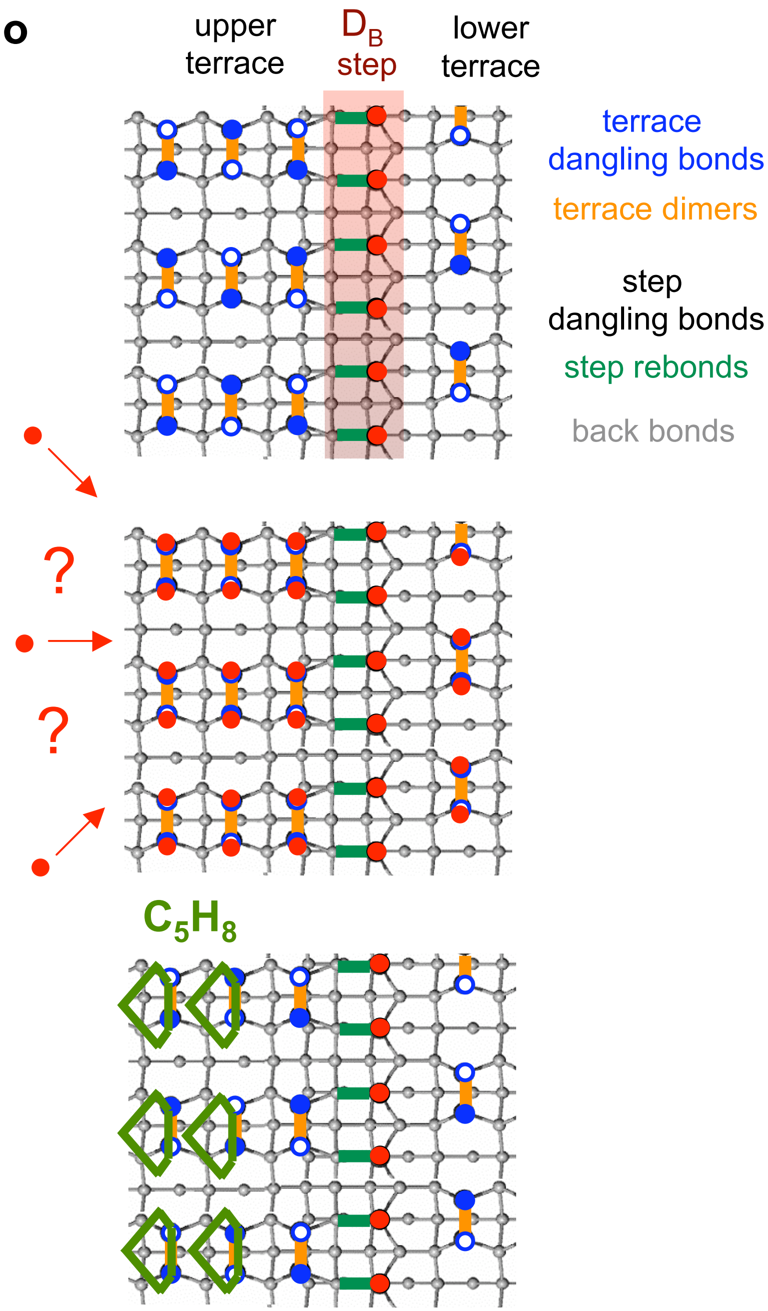
- ~ 1000 L H_2 @ 150 C
- bonds selectively to step-edge db's
- Dürr *et al.*, Phys. Rev. B **63**, 121315 (2001)

2) H_2 + atomic H

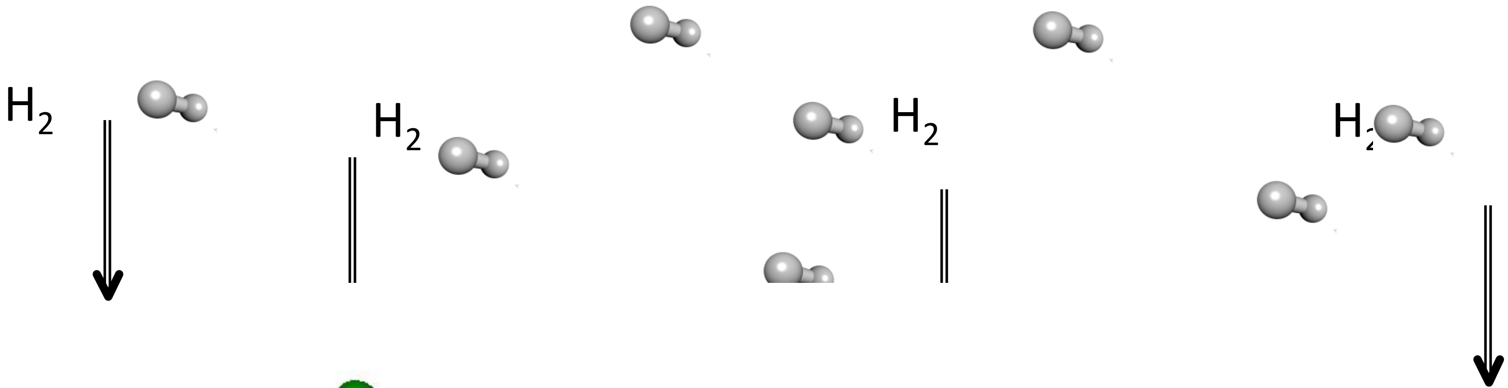
- ~ 10^6 L H_2 (saturation dose)
- passivates step AND terrace db's, leaving steps and dimers intact
- atomic H can react with step rebonds and/or terrace dimers. Which happens first?

3) H_2 + C_5H_8 (cyclopentene)

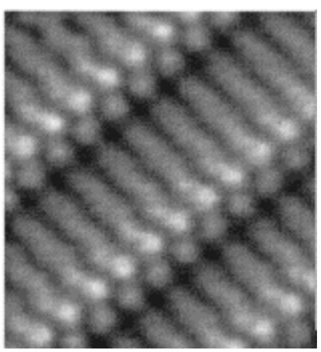
- C_5H_8 bonds by 2+2 cycloaddition to terrace dimers, forming crystalline organic monolayer
- step-adsorbed H may help modify & control C_5H_8 adsorption

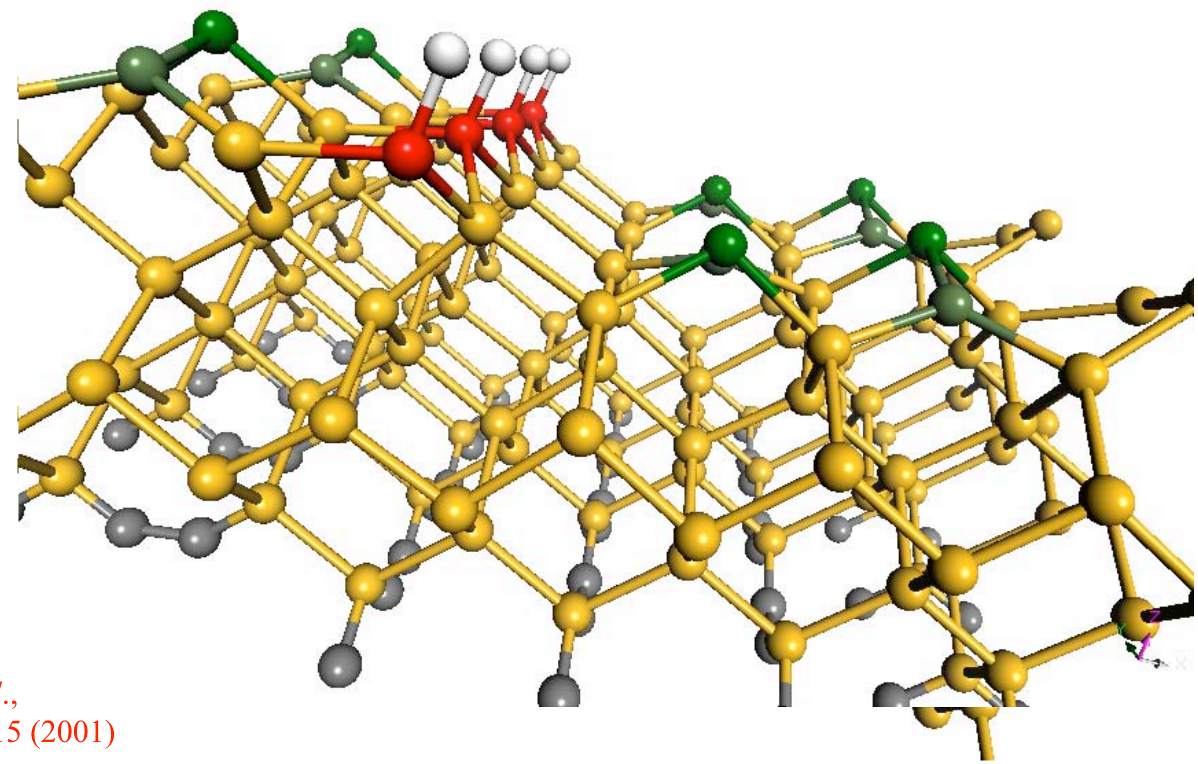


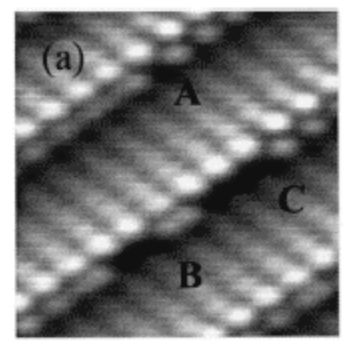
SHG/RAS Case Study #1: Dissociative adsorption of H_2 at D_B steps of Si(001):6°



clean Si(001):6°



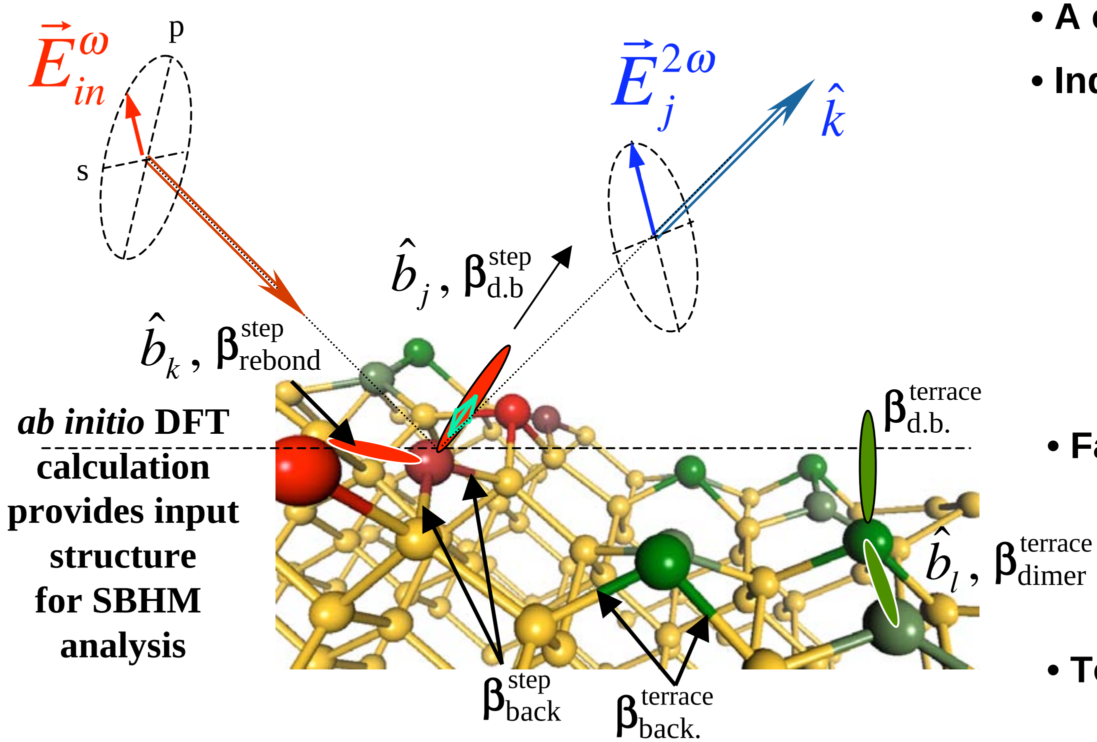


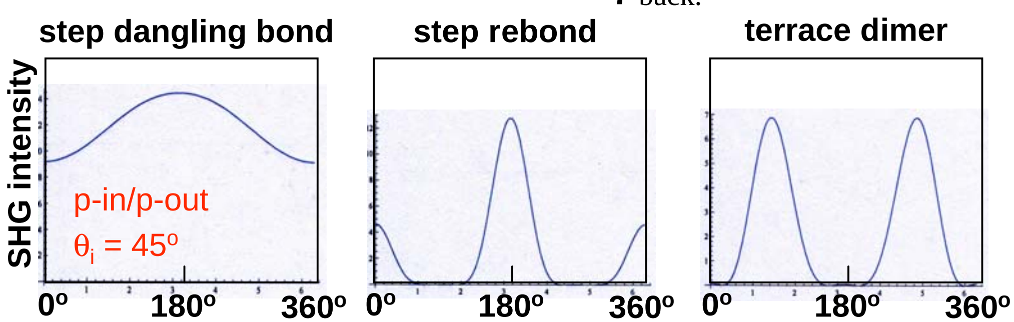


M. Durr, U. Höfer *et al*.,
Phys. Rev B. **63**, 121315 (2001)

In the absence of first principles theory, Simplified Bond Hyperpolarizability Model (SBHM) provides SHG - RAS interpretation at the molecular bond level

Powell *et al.*, Phys. Rev. B **65**, 205320 (2002)





- **A chemical bond is the basic polarizable unit**
- **Induced axial SH polarization of bond j:**

$$\vec{p}_j^{\,(2\omega)} = \beta_j^{\parallel}\ \hat{b}_j(\hat{b}_j \cdot \vec{E}_{in}^{\omega})^2$$

$$\hat{b}_j = \textit{bond unit vector}$$
$$\beta_j^{\parallel} = \textit{axial hyperpolarizability}$$

- **Far-field SH radiation of bond *j* :**

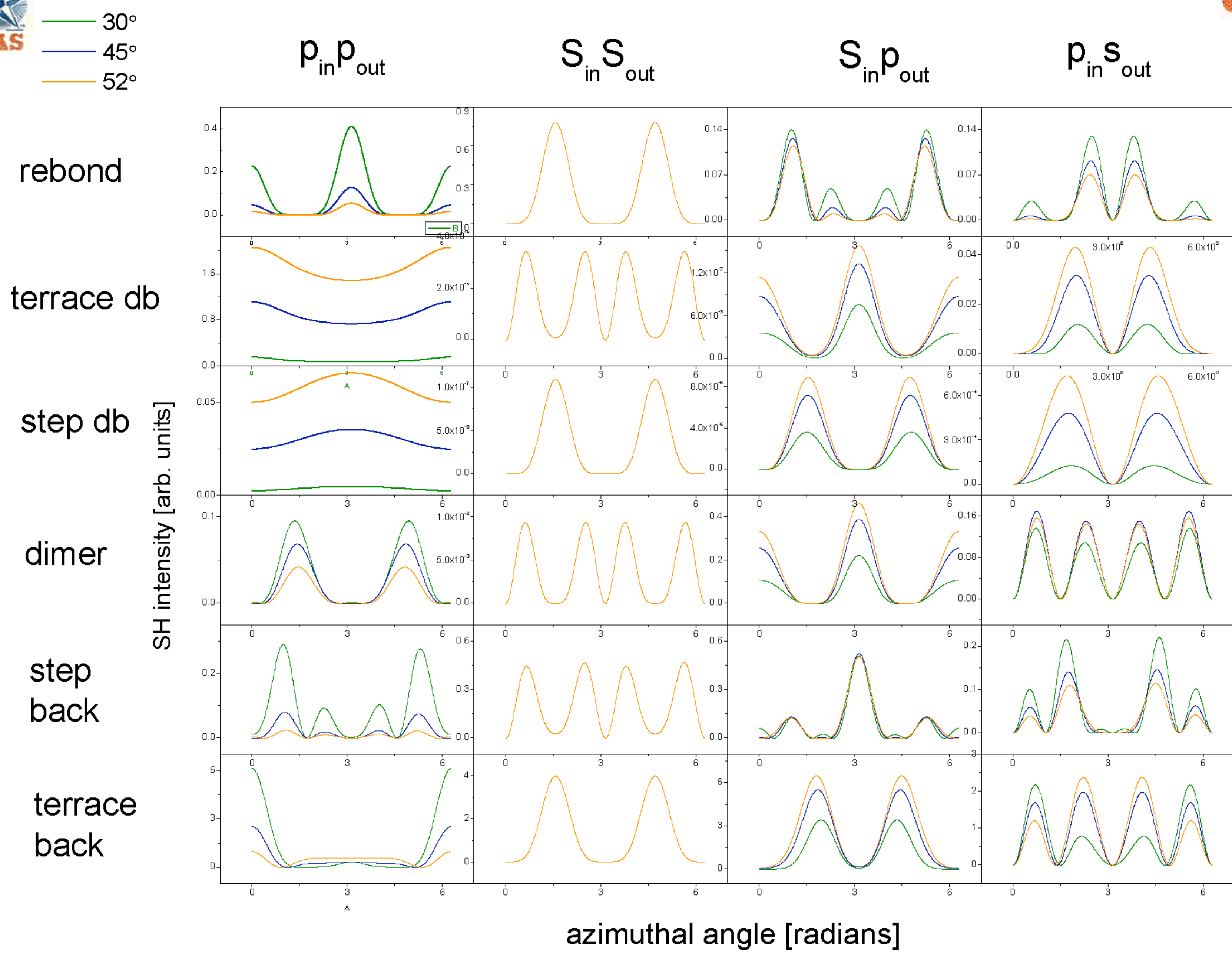
$$\vec{E}_j^{2\omega} = \frac{e^{ikr}}{r^2}(\overleftrightarrow{I} - \hat{k}\hat{k}) \cdot \vec{p}_j^{\,(2\omega)}$$

- **Total far-field SH radiation:**

$$\vec{E}_j^{2\omega} = \frac{e^{ikr}}{r^2}(\overleftrightarrow{I} - \hat{k}\hat{k}) \cdot \sum_j \vec{p}_j^{\,(2\omega)}$$

- **Simplifications:**
  - transverse hyperpolarizabilities neglected
  - local field corrections folded into β's
  - boundary conditions not treated rigorously

SHG “dictionary” for Si(001): 6°

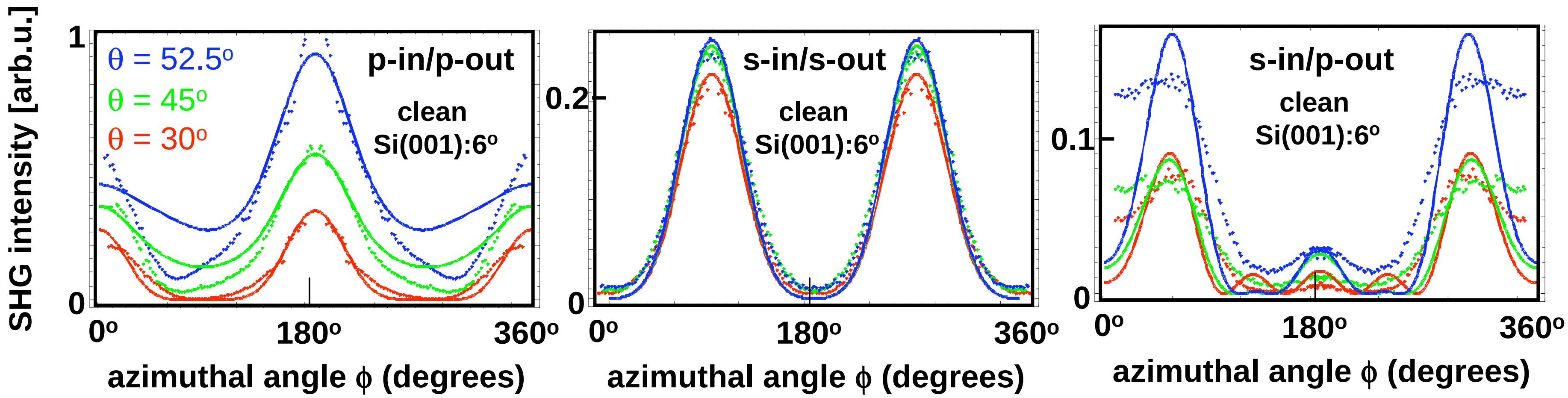


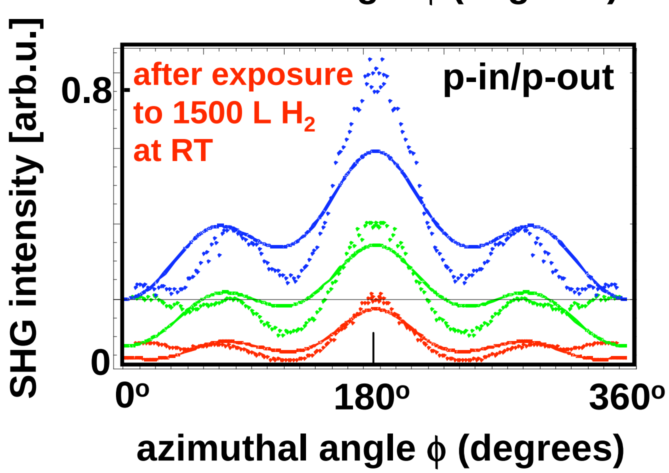
Multi-parameter fitting (like Wall St. investing) requires "government regulation" based on...

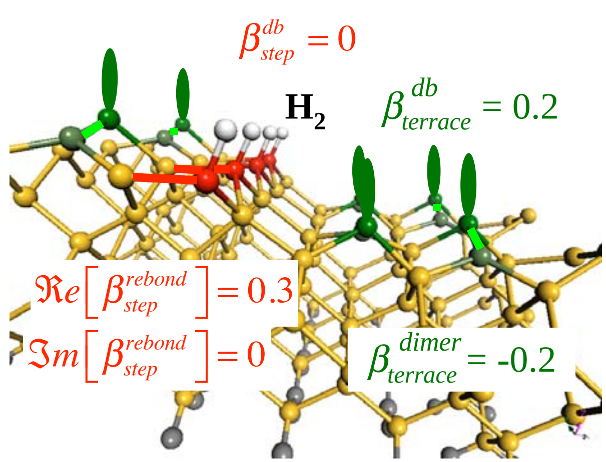
... Bond physics & chemistry **... Kramers-Kronig consistency**

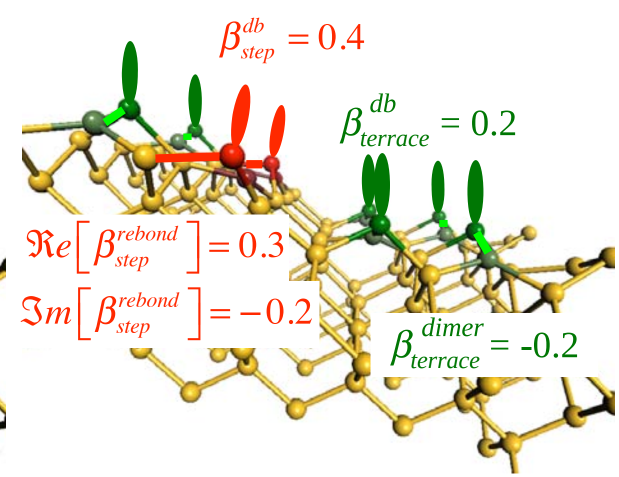
Bonds that are parallel to **E**$^{\omega}$, charge-rich and non-centrosymmetric contribute most strongly

.. Consistency for Multiple Angles (θ) and Polarizations (MAP)







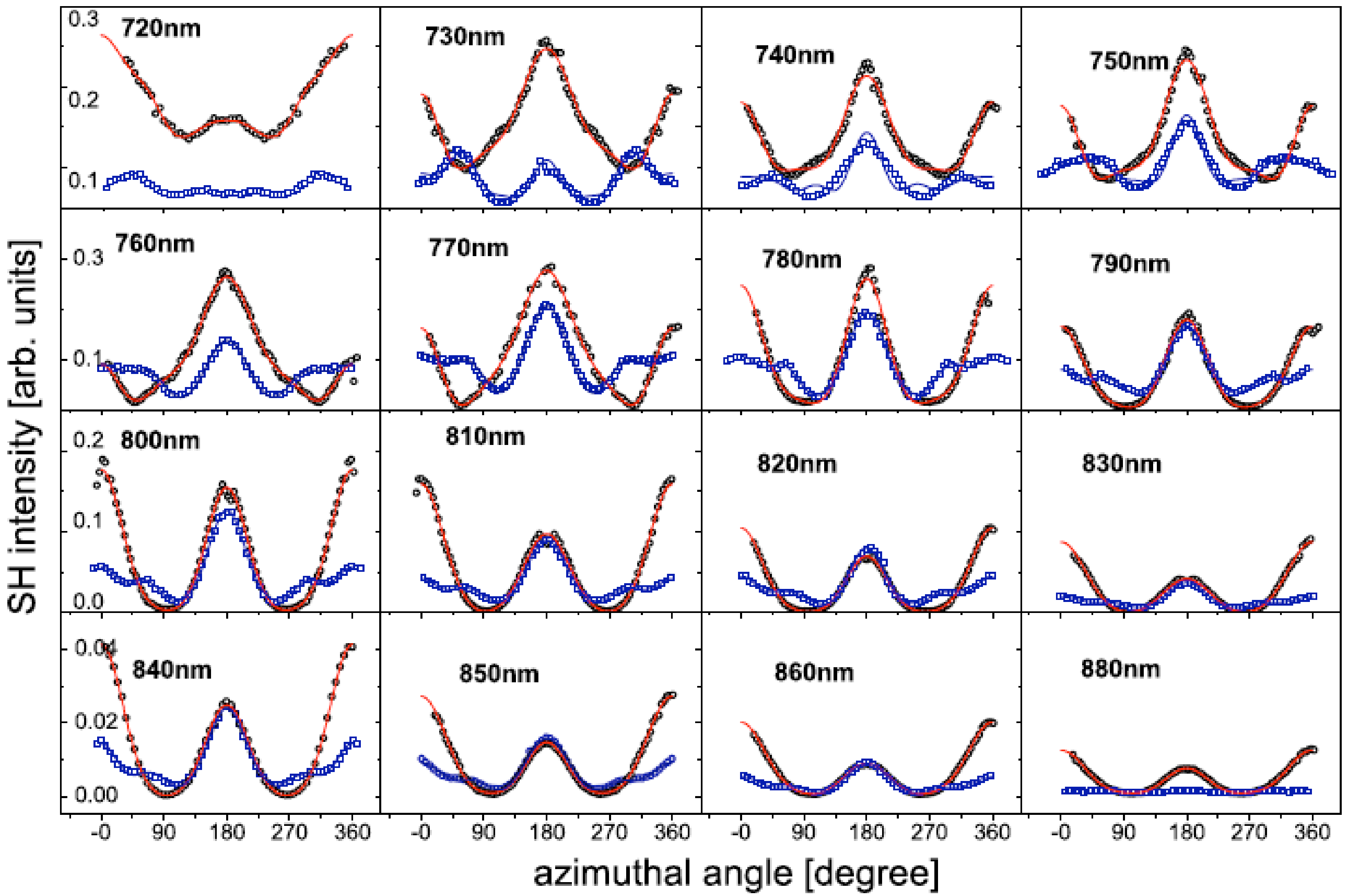


Full SBHM fits SHG data with high fidelity

clean Si(001): 6º

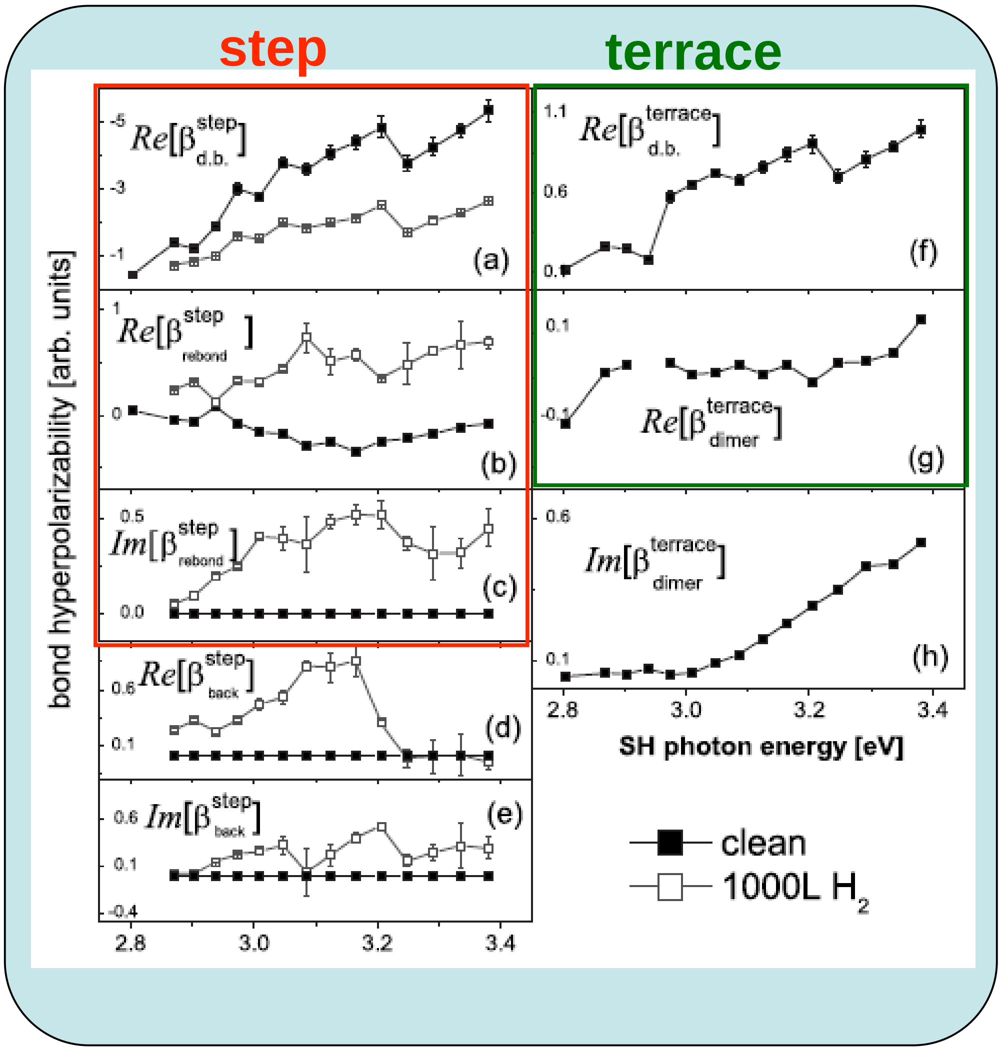
Si(001): 6º with H-terminated steps

$\theta = 42^o$
p-in/p-out



Strict regulation: derive RAS response from SHG data

Fitted bond hyperpolarizability spectra $\beta_j^{\|}$

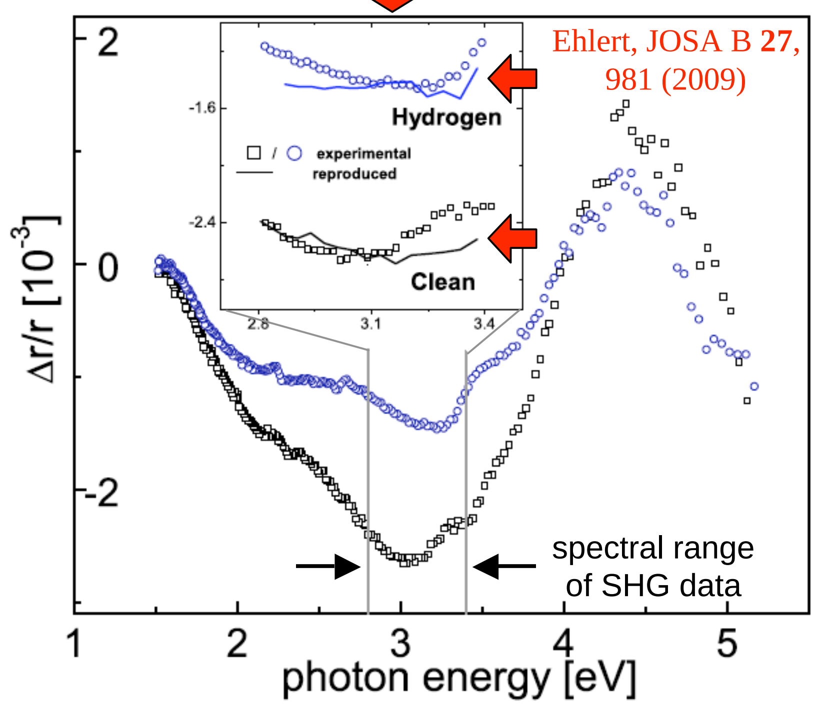


linear bond polarizabilities

*Miller's theorem: $\beta_j^{\|} = \Delta\alpha^{\|}_{j,2\omega}\alpha^{\|}_{j,\omega}\alpha^{\|}_{j,\omega}$

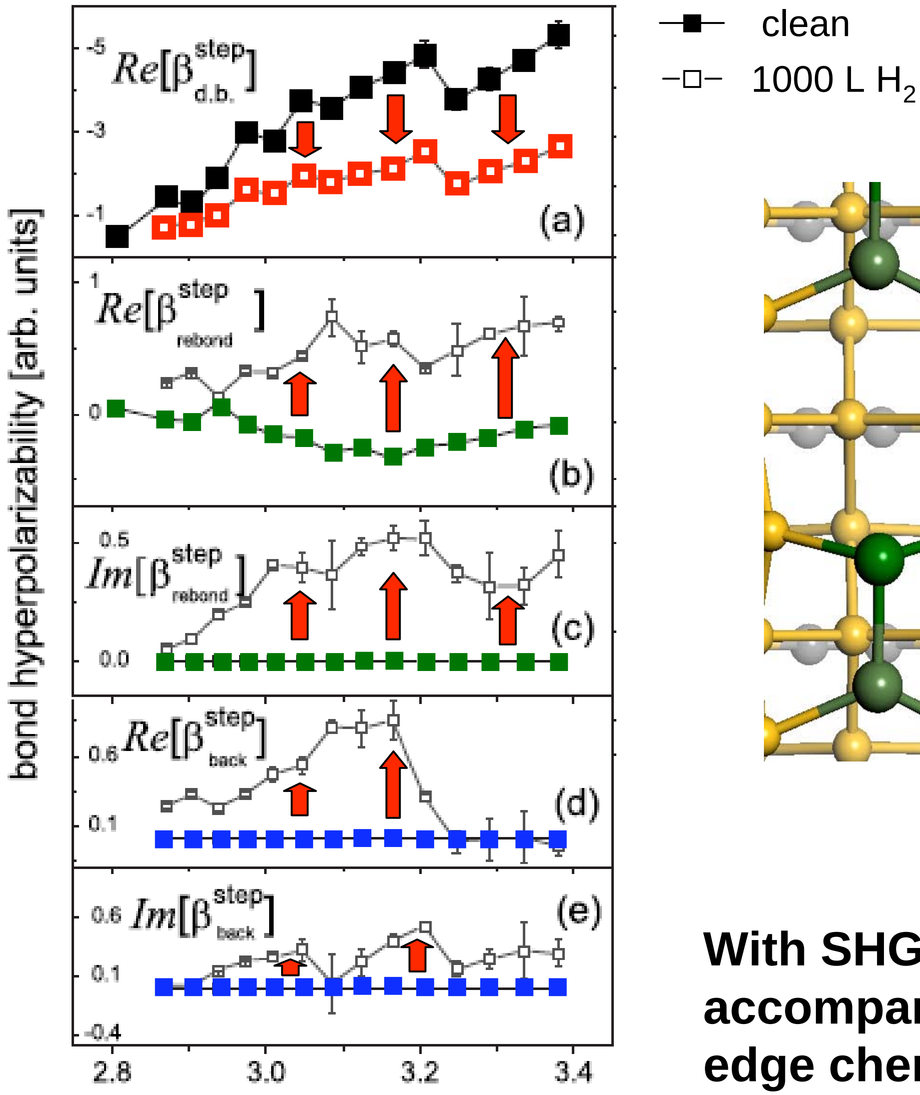
$$\vec{E}^{2\omega}_{linear} \propto (\hat{I} - \hat{k}\hat{k}) \cdot \sum_j \alpha^{\|}_{j,2\omega}\hat{b}_j\hat{b}_j \cdot \vec{E}^{2\omega}_{in}$$

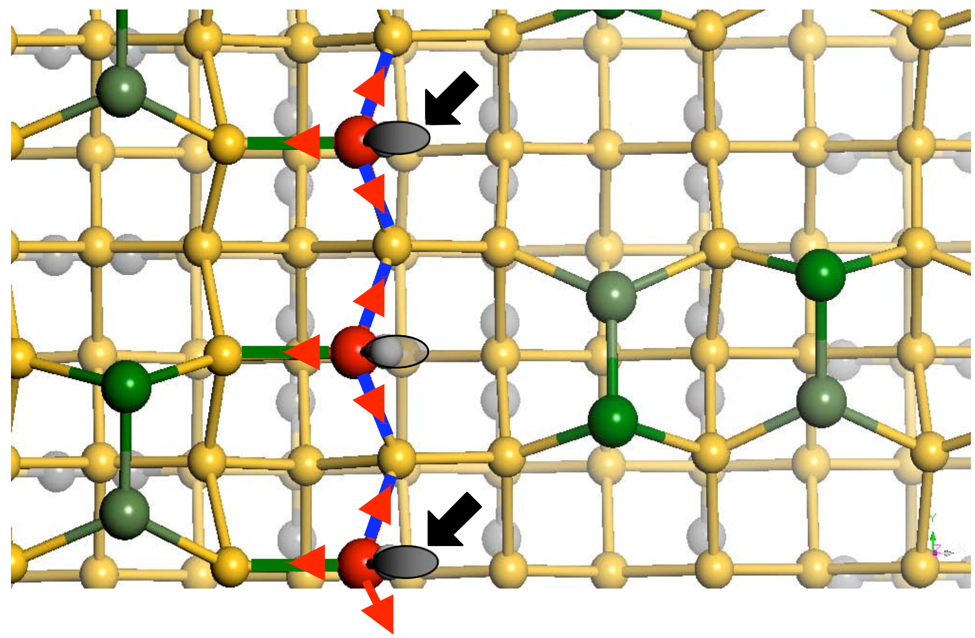
$$\frac{\tilde{r}_{\bar{1}10} - \tilde{r}_{110}}{\tilde{r}}$$



*R. C. Miller, Appl. Phys. Lett. **5**, 17 (1964)

Hyperpolarizability spectra show charge transfer from step dangling bond to 3 underlying bonds when H_2 dissociatively adsorbs at step-edges

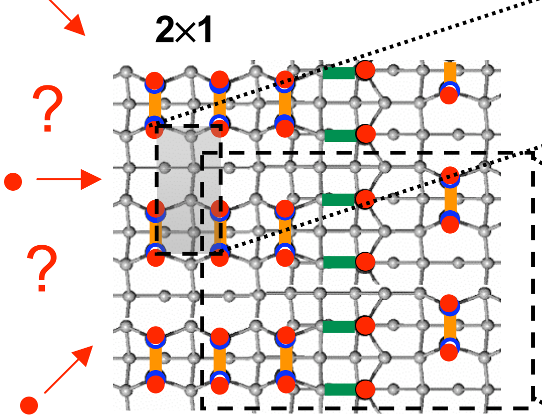


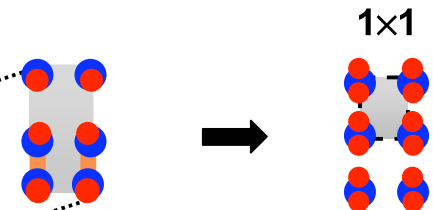


With SHG-RAS-SBHM, we watch charge transfer accompanying the formation of specific step-edge chemical bonds.

SHG/RAS/SBHM Case Study #2: Reaction of atomic H with H_2-saturated Si(001):6° surface

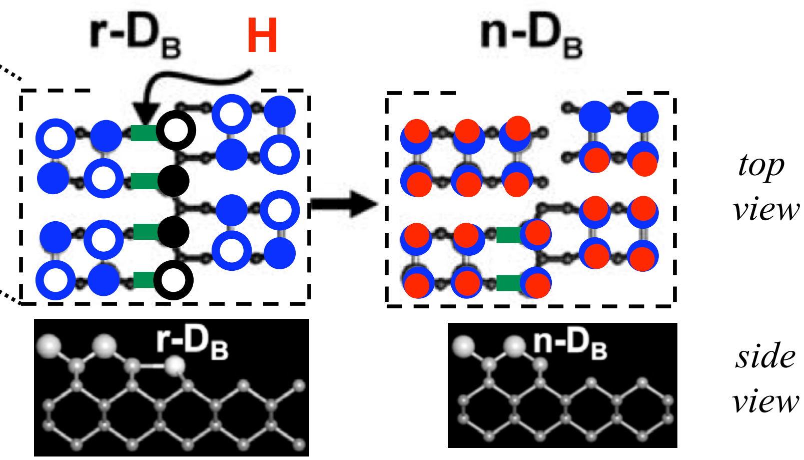
1000 L H_2 × 1000





• 2×1 monohydride terraces convert to 1×1 dihydride, breaking dimers

Borenzstein *et al*., Phys. Rev. Lett.**95**, 117402 (2005)



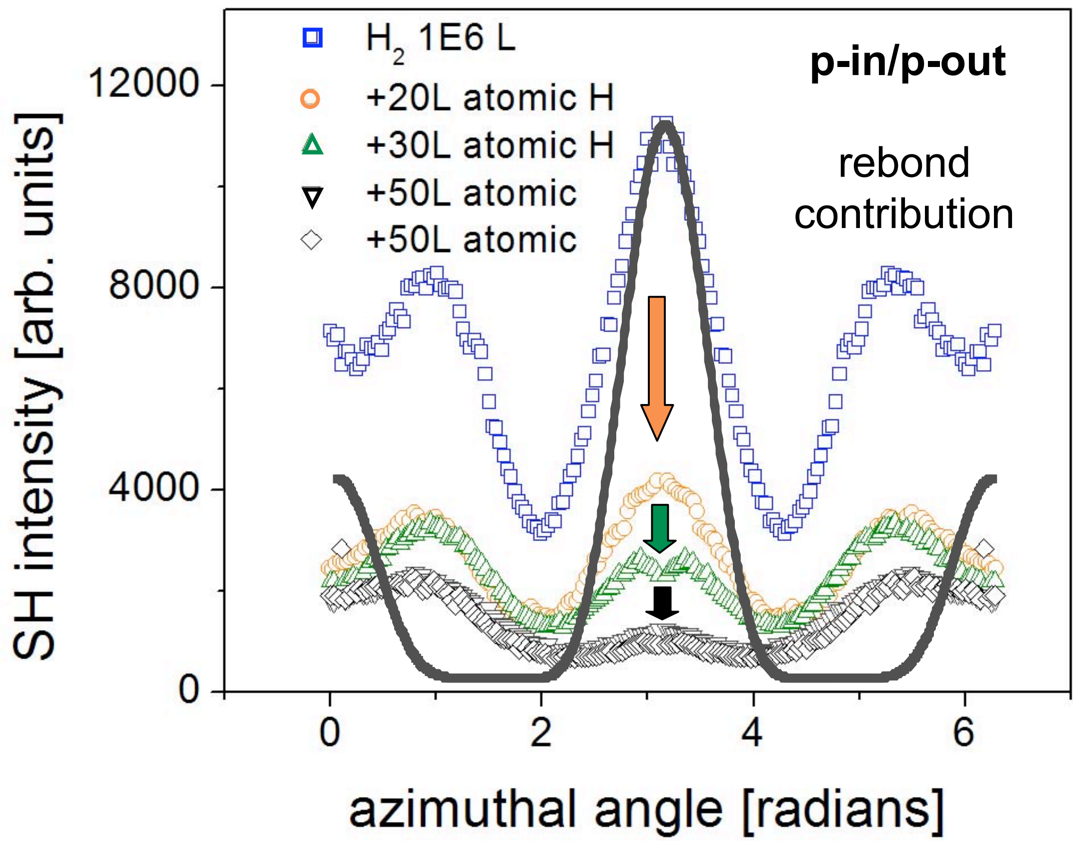
• symmetrized dimers
• 2×1-reconstructed terraces
• re-bonded (r) D_B steps intact

Pehlke & Kratzer, Phys. Rev. B **59**, 2790 (1999)

• atomic H catalyzes conversion of r-D_B to non-rebonded D_B, S_B and S_A steps

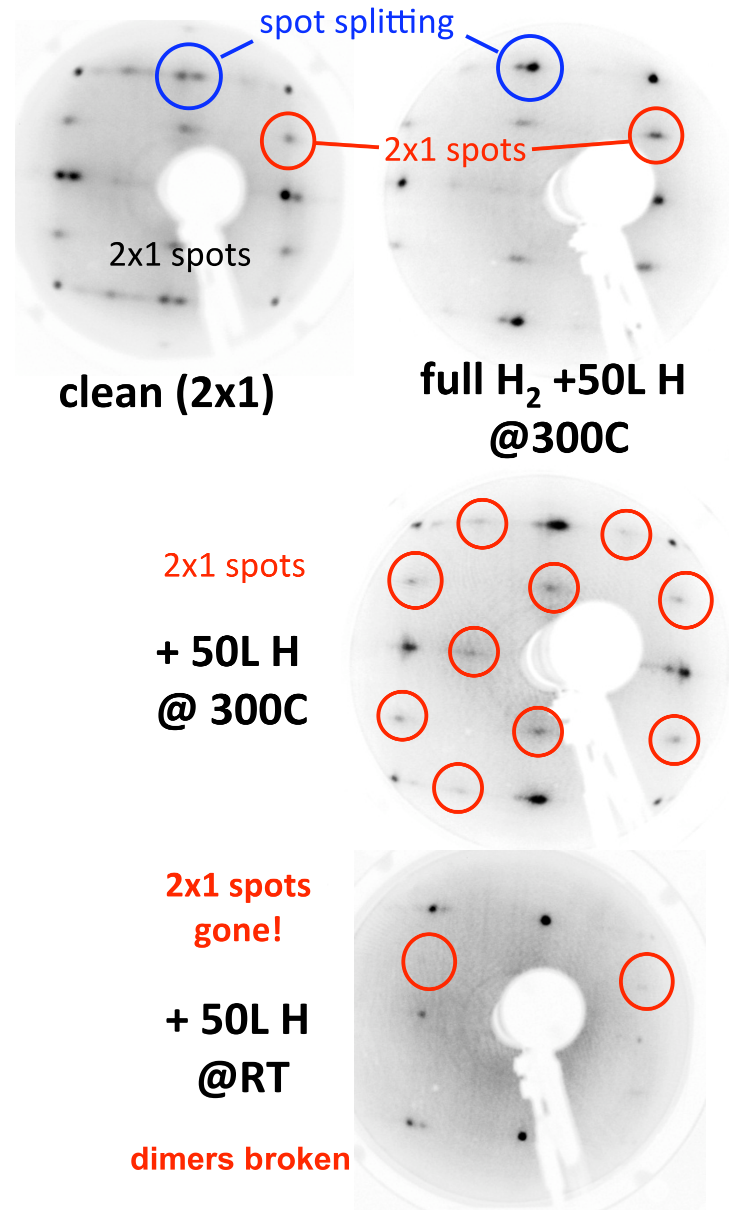
Laracuente & Whitman, Surf. Sci.**545**, 70 (2003)

SHG: Rebonds break immediately

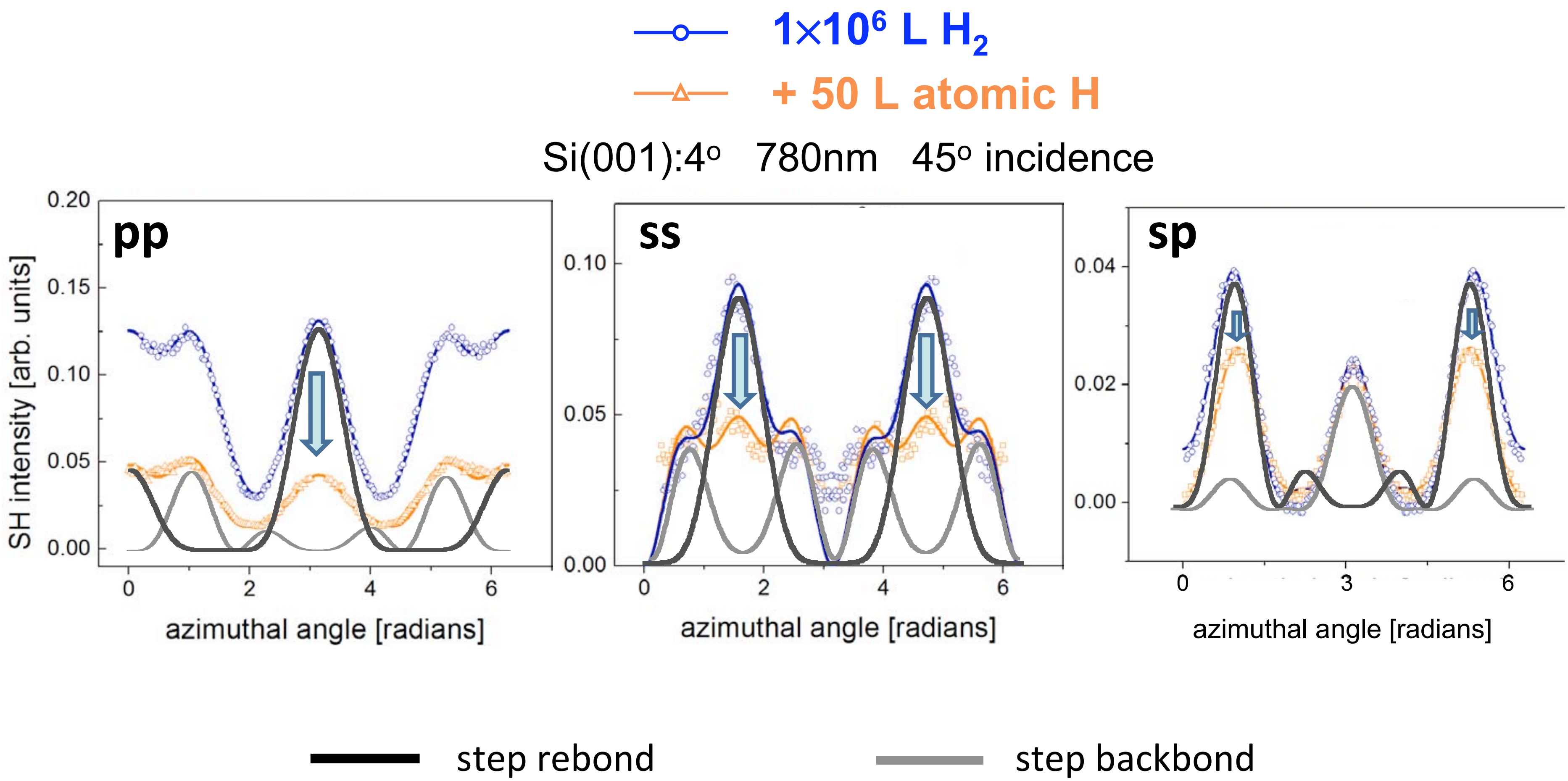


No remaining SHG signature of rebond after ~ 100 L atomic H

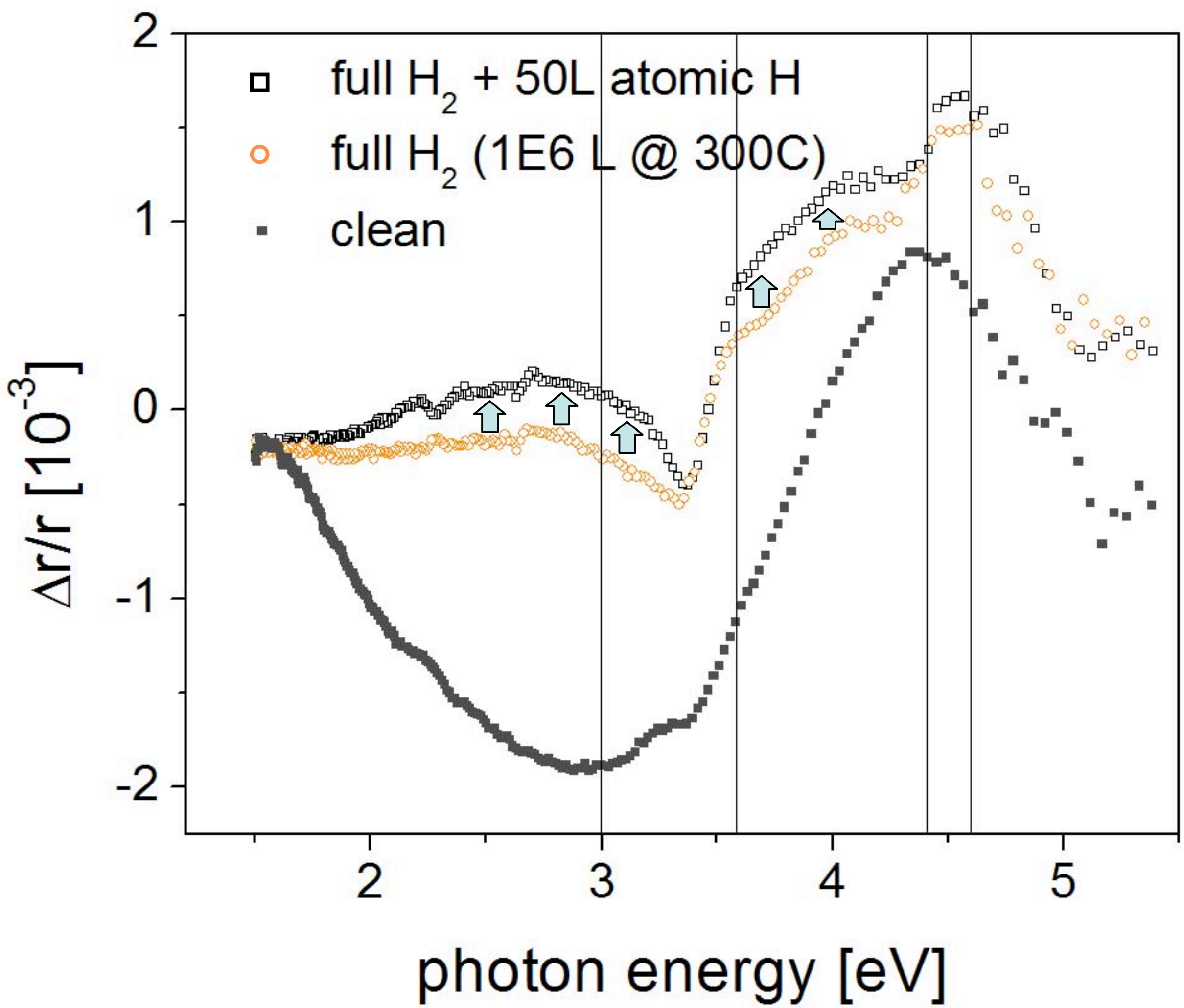
LEED: Dimers break later



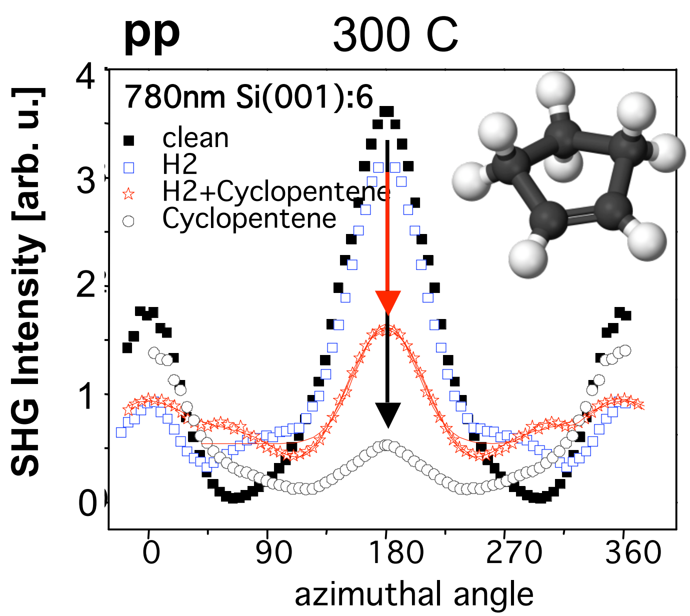
SHG-MAP shows shows decreasing rebond, in-creasing backbond, expression during H exposure



RAS is a “spectator” as the rebond breaks



RAS-SHG-SBHM Case Study #3: monitor and control of nanofabrication of organic monolayers on Si(001)

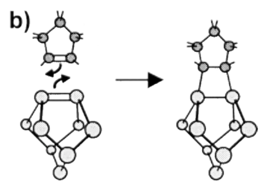


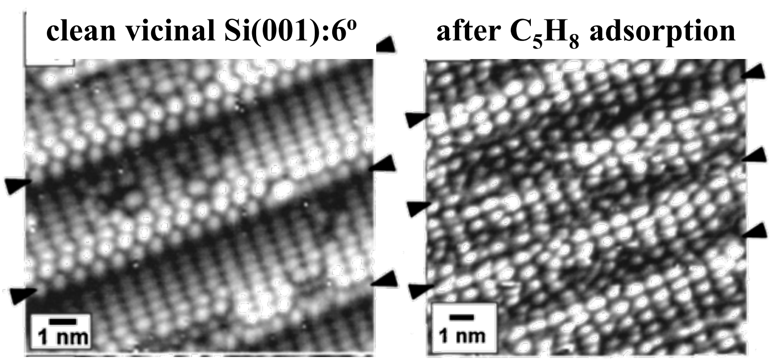
SHG, on the other hand, shows ...

... C_5H_8 reacts immediately & strongly with <u>step rebonds</u> of the clean Si(001):6° surface

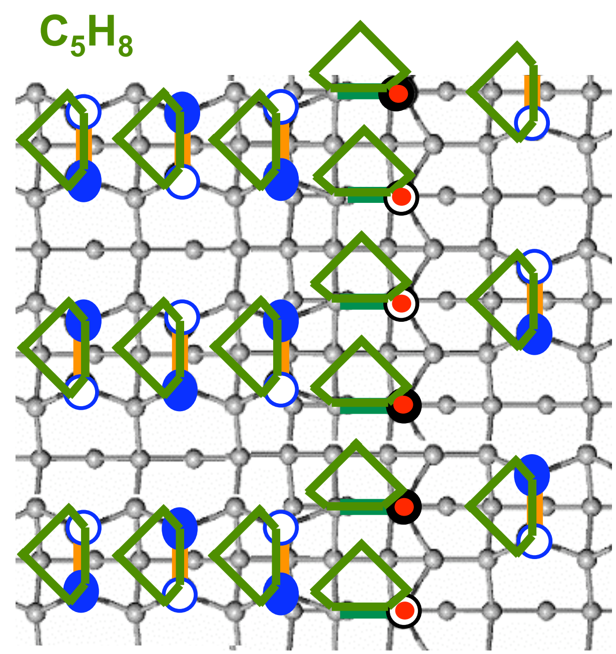
... H_2 pre-adsorption at step db's partially protects steps from reacting with C_5H_8

STM shows C_5H_8 bonds to Si=Si terrace dimers to form an ordered monolayer.



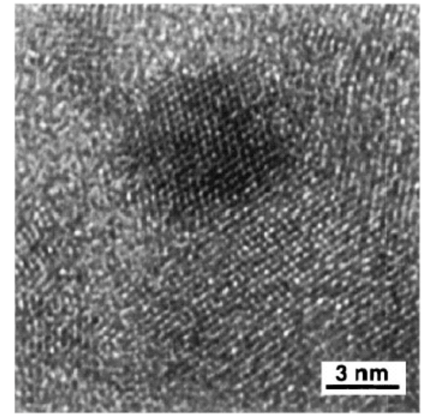


Hamers *et al*. (2000). Acc. Chem. Res. **33**(9): 617-624
Lu *et al*., Phys. Rev. B **68**, 115327 (2003)



Summary:
Noninvasive optical spectroscopy of nano-interfaces

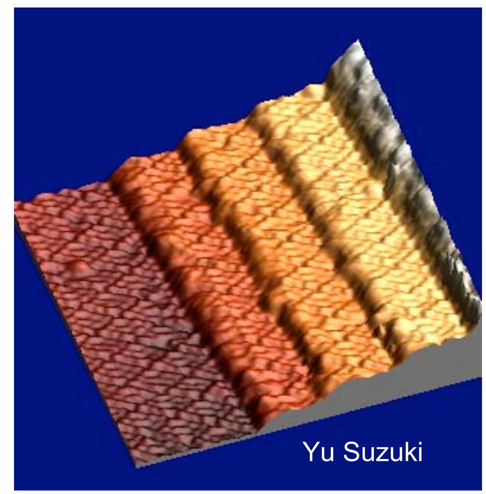
I. 0-D: Si NCs embedded in SiO_2



- importance: Si LEDs, bio-sensors
- method: **XP2-SHG + SE, Raman, XPS, PL**
- results: new SHG evidence for a-Si and SiO_x nano-interfacial transition regions

Figliozzi *et al*., Phys. Rev. Lett. 94, 047401 (2005); Wei *et al*., in preparation

II. 1-D: step-edges of vicinal Si



- importance: templates for molecular electronics, quantum wires & computers
- method: **SHG & RAS & SBHM**
- results: visualization of formation of step Si-H bond and of breaking of step rebond;
  - control & optical monitoring of cyclopentene nano-lithography by self-assembly

Kwon *et al*., Phys. Rev. B **73**, 195330 (2006).
Ehlert *et al*., J. Opt. Soc. Am. B **27**, 981 (2009) & more in the oven.

END