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21 Jan '02

Dear Linda:

Fred would have preferred me to Email my viewgraphs but they were in a number of different formats, so I decided to mail you copies instead.

Dave Aspnes

SIMPLIFIED BOND HYPERPOLARIZABILITY MODEL OF SECOND-HARMONIC GENERATION: APPLICATION TO SI-DIELECTRIC INTERFACES

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MOTIVATION:

- Better understand the atomic and electronic structure of Si-dielectric interfaces
- Better understand the origins of linear and nonlinear optical responses of interfaces
- Better control of interface properties
- Improve accuracy of thin-film metrology and optical characterization of interfaces

LINEAR AND NONLINEAR OPTICS:

Interaction energy:

$$H' = q\,\phi_o - \vec{\mathbf{p}}\cdot\vec{\mathbf{E}} - \vec{\mathbf{m}}\cdot\vec{\mathbf{B}} - \sum Q_{ij}\,\frac{\partial E_i}{\partial x_j} - \cdots$$

At high fields:

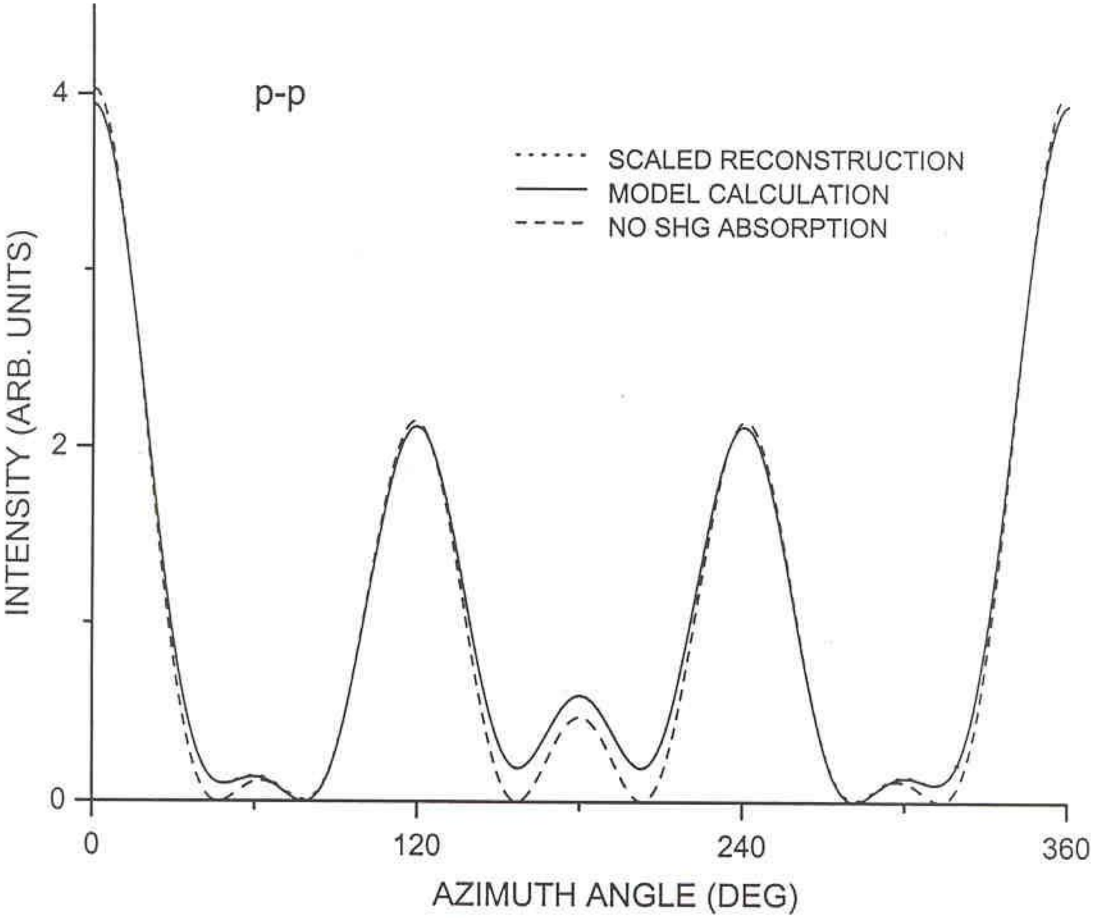
$$P_i = \chi_i^{(1)}\,E_j + \chi_{ijk}^{(2)}\,E_j E_k + \chi_{ijkl}\,E_j E_k E_l + \cdots$$

SHG:

Spectra still difficult to obtain, therefore SHG typically studied as anisotropies (dependences of $I^{(2)}(\phi)$ as a function of sample azimuth ϕ)

Classical methods of analysis:

1. As symmetry-allowed components of $\chi^{(2)}$
   [No microscopic insight]
2. As Fourier coefficients of $I^{(2)}(\phi)$
   [No microscopic insight]
3. By first-principles band structure calculations
   [Arcane, physical insight not easy to obtain]



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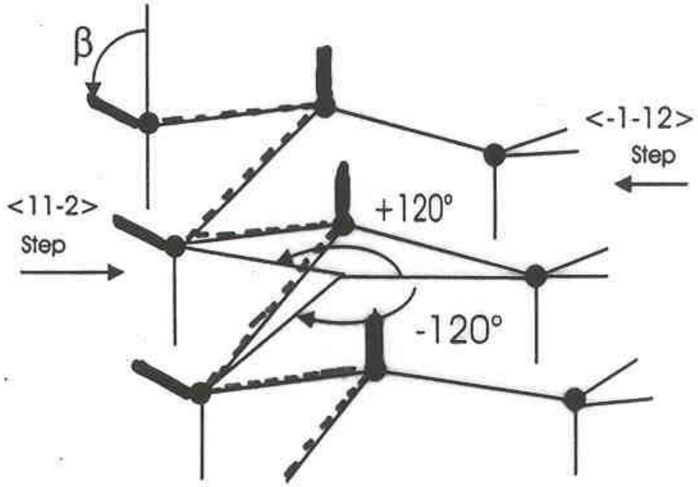

Figure 4.7: Geometry of interface bonds for vicinal (111) Si.

Bond vectors:

$$\hat{b}_1 = \frac{1}{\sqrt{3}}(\hat{x} + \hat{y} + \hat{z})$$

$$\hat{b}_2 = \frac{1}{\sqrt{3}}(\hat{x} - \hat{y} - \hat{z})$$

$$\hat{b}_3 = \frac{1}{\sqrt{3}}(-\hat{x} + \hat{y} - \hat{z})$$

$$\hat{b}_4 = \frac{1}{\sqrt{3}}(-\hat{x} - \hat{y} + \hat{z})$$

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Simple model of electric-dipole second-harmonic generation from interfaces

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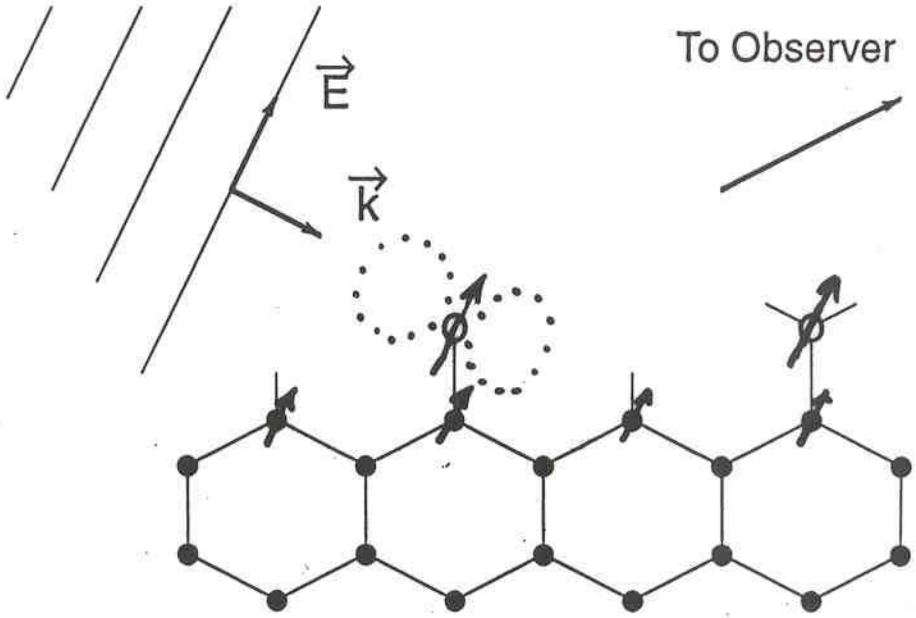
$$
\begin{aligned}
X(\omega_1,\omega_2)=\sum_s f(s)\sum_n[1-f(n)]\sum_r[1-f(r)]\Bigg[&\frac{[V_E(\omega_3)]_{sn}[V_A(\omega_2)]_{nr}[V_A(\omega_1)]_{rs}}{(\omega_{rs}-\omega_1-i0)(\omega_{ns}-\omega_1-\omega_2-i0)}+\frac{[V_A(\omega_2)]_{sn}[V_E(\omega_3)]_{nr}[V_A(\omega_1)]_{rs}}{(\omega_{rs}-\omega_1-i0)(\omega_3-\omega_1+\omega_{ns}-i0)}\\
&+\frac{[V_A(\omega_2)]_{sn}[V_A(\omega_1)]_{nr}[V_E(\omega_3)]_{rs}}{(\omega_3+\omega_{rs}-i0)(\omega_3-\omega_1+\omega_{ns}-i0)}\Bigg]\\
-\sum_s f(s)\sum_n[1-f(n)]\sum_m f(m)\Bigg[&\frac{[V_E(\omega_3)]_{mn}[V_A(\omega_2)]_{sm}[V_A(\omega_1)]_{ns}}{(\omega_{ns}-\omega_1-i0)(\omega_{nm}-\omega_1-\omega_2-i0)}\\
&+\frac{[V_A(\omega_2)]_{mn}[V_E(\omega_3)]_{sm}[V_A(\omega_1)]_{ns}}{(\omega_{ns}-\omega_1-i0)(\omega_3-\omega_1-\omega_{mn}-i0)}+\frac{[V_A(\omega_2)]_{mn}[V_A(\omega_1)]_{sm}[V_E(\omega_3)]_{ns}}{(\omega_3+\omega_{ns}-i0)(\omega_3-\omega_1-\omega_{mn}-i0)}\Bigg]\,.
\end{aligned}
\tag{3}
$$

OBSERVATION:

Because SHG from Si-dielectric interfaces originates from within several monolayers of the interface...

...why not use a bond model?

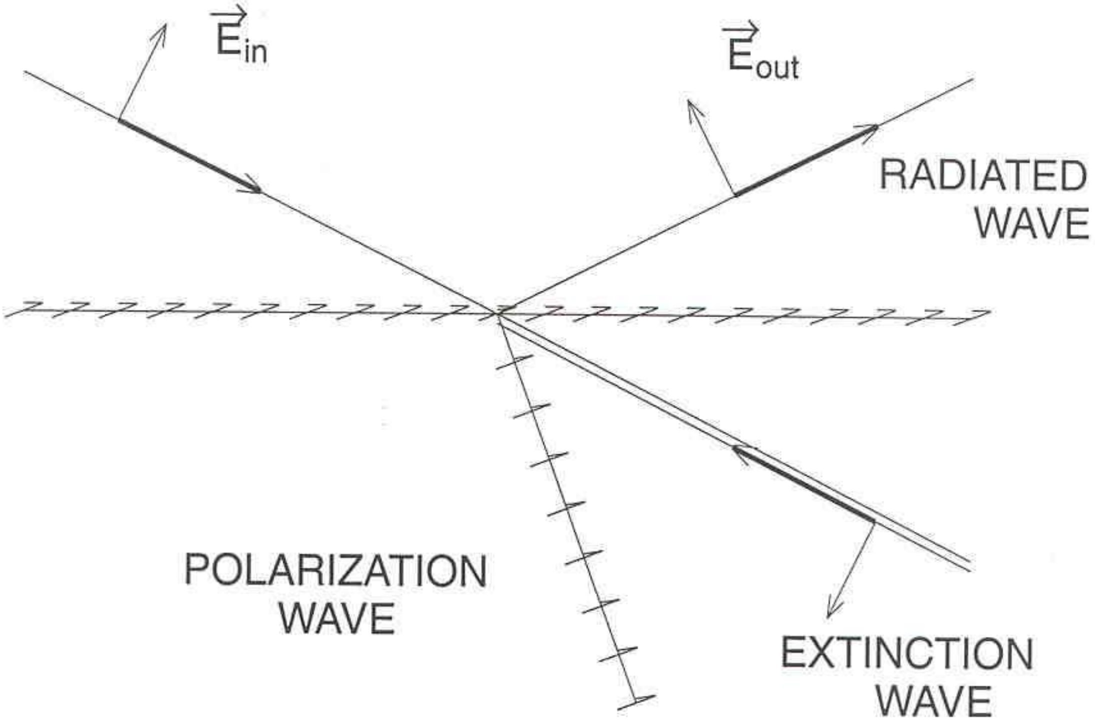
INTERACTION OF LIGHT WITH MATERIALS:



Radiation Zone:

$$\vec{E} = \frac{k^2}{r} e^{ikr - i\omega t} \sum_n [\vec{p}_n - \hat{k}(\hat{k}\cdot\vec{p}_n)] e^{i(\vec{k}_i - \vec{k}_f)\cdot\vec{R}_n}$$

EWALD-OSEEN EXTINCTION THEOREM



$$\vec{\mathbf{F}} = m\vec{\mathbf{a}}$$

GENERAL FORCE-MODEL RESULT:

$$\text{Linear: } \mathbf{p}^{(1)} = \frac{q\,\mathbf{E}\,e^{-i\omega t}}{k/m - \omega^2 - i\Gamma\omega} = \alpha^{(1)}\cdot\mathbf{E}$$

$$\text{2nd–order: } \mathbf{p}^{(2)} = \frac{q\,\kappa_2\,\Delta\mathbf{x}_1^2}{k/m - 4\omega^2 - 2i\Gamma\omega} = \alpha^{(2)}\cdot\cdot\,\mathbf{E}\,\mathbf{E}$$

where $\alpha^{(1)}$ and $\alpha^{(2)}$ are the polarizability and hyperpolarizability, respectively.

SIMPLIFIED BOND HYPERPOLARIZABILITY MODEL

(1) Charge is localized in bonds j with directions $\hat{\mathbf{b}}_j$

(2) Charge driven by external field results in dipoles $\mathbf{p}_j$

(3) Dipoles radiate according to standard dipole-radiation relation

(4) The only relevant motion for SHG is that along the bond axis, equivalent to assuming cylindrical symmetry

(5) The bond directions $\hat{\mathbf{b}}_j$ are those of the bulk material.

GENERAL SBHM FAR-FIELD EXPRESSIONS:

Linear:

$$\mathbf{E}^{(1)} \sim [\,\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}\,]\cdot[\,\sum_{j} \alpha_j^{(1)}\, \hat{\mathbf{b}}_j \hat{\mathbf{b}}_j\,]\cdot\mathbf{E}_{inc}$$

SHG:

$$\mathbf{E}^{(2)} \sim [\,\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}\,]\cdot[\,\sum_{j} \alpha_j^{(2)}\, \hat{\mathbf{b}}_j \hat{\mathbf{b}}_j \hat{\mathbf{b}}_j\,]\cdot\cdot\mathbf{E}_{inc}\mathbf{E}_{inc}$$

These are simple enough to solve analytically for low-index surfaces.

for the p-p case:

$$\vec{\mathbf{E}}_{\mathrm{ff}} = [\,\hat{\mathbf{x}}\cos\beta + \hat{\mathbf{z}}\sin\beta\,]\,[\,\alpha_u \sin^2\alpha \sin\beta + \alpha_d\,(\cos^3\theta \sin^2\alpha \sin\beta + \frac{3}{4}\sin\theta \sin 2\theta\,(\cos^2\alpha \sin\beta - \sin 2\alpha \cos\beta\,) + \frac{3}{4}\sin^3\theta \cos^2\alpha \cos\beta \cos 3\phi\,)\,]\,; \tag{8a}$$

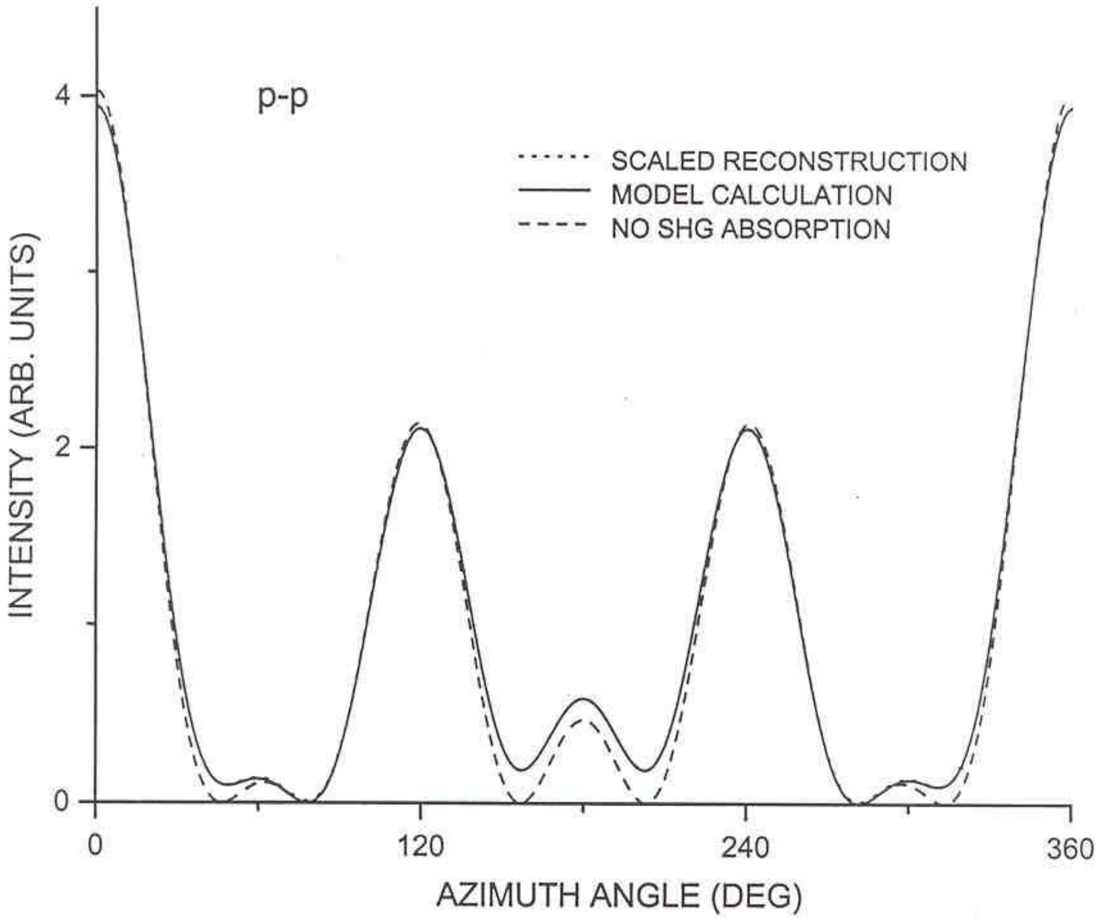
for the p-s case:

$$\vec{\mathbf{E}}_{\mathrm{ff}} = \hat{\mathbf{y}}\,\frac{3}{4}\,\alpha_d \sin^3\theta \cos^2\alpha \sin 3\phi\,; \tag{8b}$$

CRITICAL TESTS:

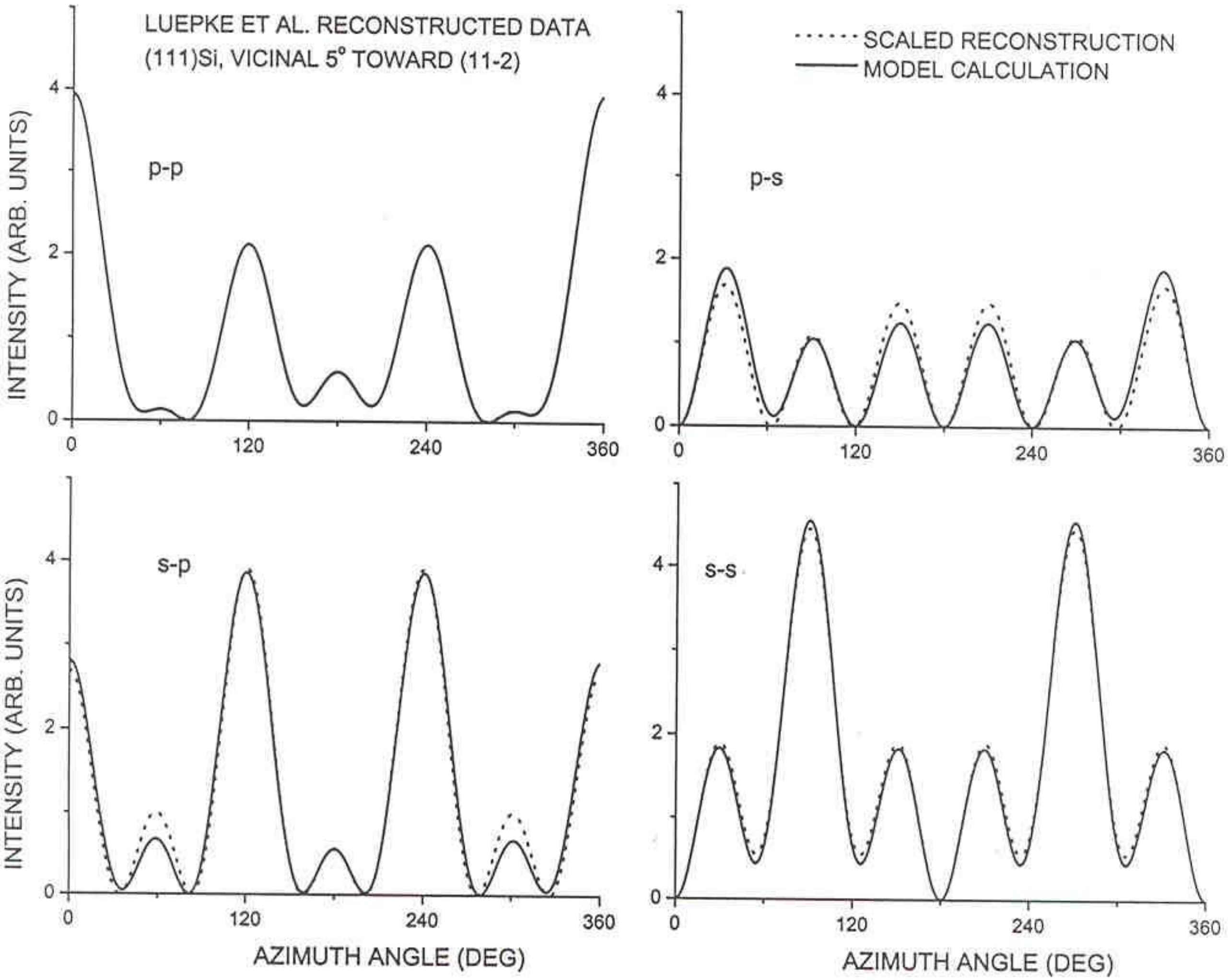
Use Lüpke et al. oxidized 5° vicinal (111)Si data:

- All four configurations pp, ps, sp, ss are available
- Amplitudes normalized to 3ϕ field (6ϕ intensity) component, automatically taking Fresnel factors into account


p-p
SCALED RECONSTRUCTION
MODEL CALCULATION
NO SHG ABSORPTION
INTENSITY (ARB. UNITS)
4
2
0
0
120
240
360
AZIMUTH ANGLE (DEG)

HYPERPOLARIZABILITIES FOR p-p, (111) Si/SiO_2:

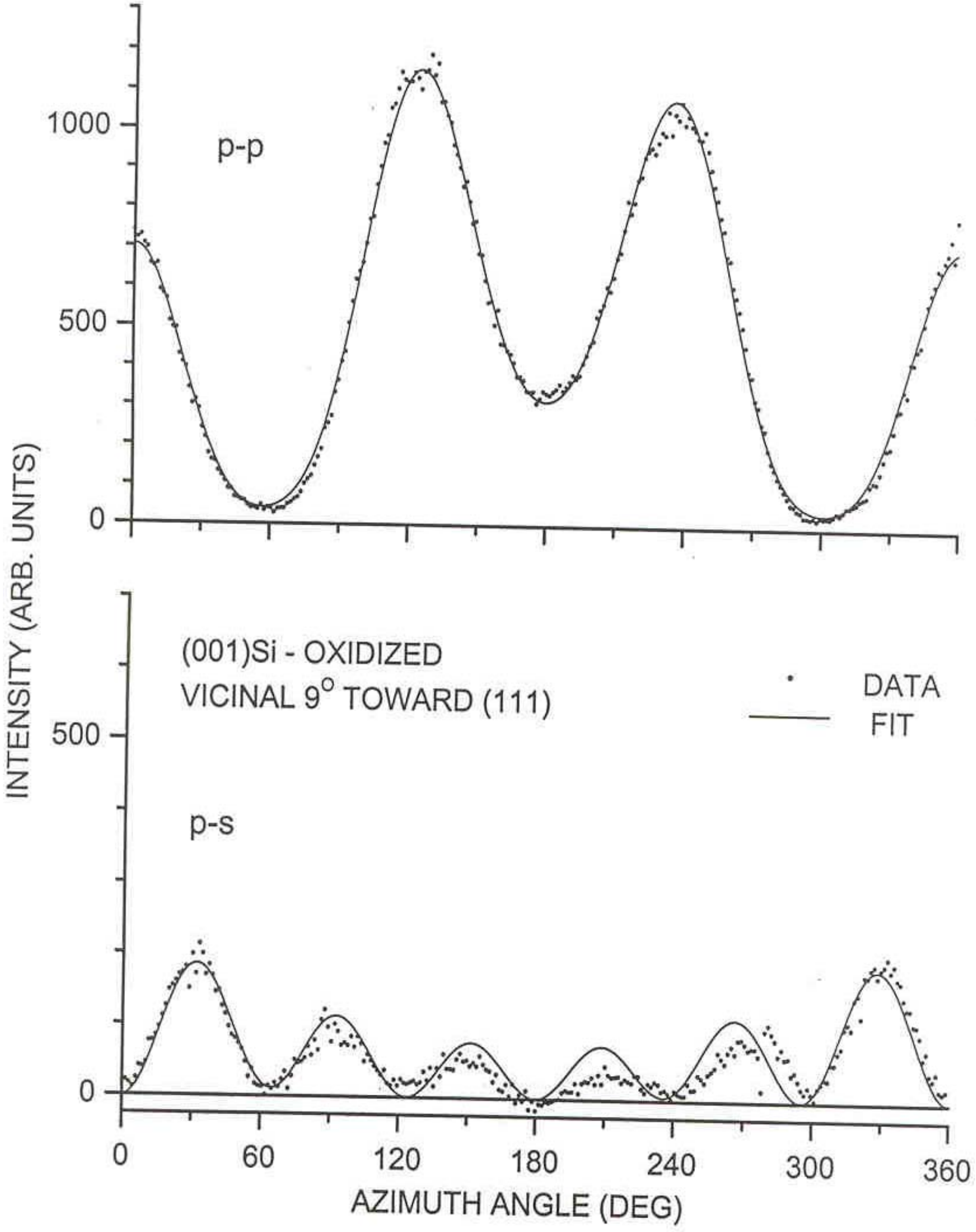
Bond:	Re	Im
Up:	1.78	0.15
Step:	2.76	1.42
Back 1:	2.19	–0.01
Back 2:	2.19	–0.01


LUEPKE ET AL. RECONSTRUCTED DATA
(111)Si, VICINAL 5° TOWARD (11-2)
SCALED RECONSTRUCTION
MODEL CALCULATION
p-p
p-s
s-p
s-s
INTENSITY (ARB. UNITS)
AZIMUTH ANGLE (DEG)
0
2
4
0
120
240
360

SCALING FACTORS FOR p-s, s-p, s-s:

	Exp.	Theor.	θ
p-p	1.00 (ref.)	1	...
p-s	1.40	$1/\cos^2\theta$	32.5°
s-p	1.93	$1/\cos^4\theta$	32.0°
s-s	2.26	$1/\cos^6\theta$	29.2°

Snell's Law at air-SiO_2 interface: 29.0°



p-p
1000
500
0
(001)Si - OXIDIZED
VICINAL 9° TOWARD (111)
DATA
FIT
INTENSITY (ARB. UNITS)
500
p-s
0
0
60
120
180
240
300
360
AZIMUTH ANGLE (DEG)

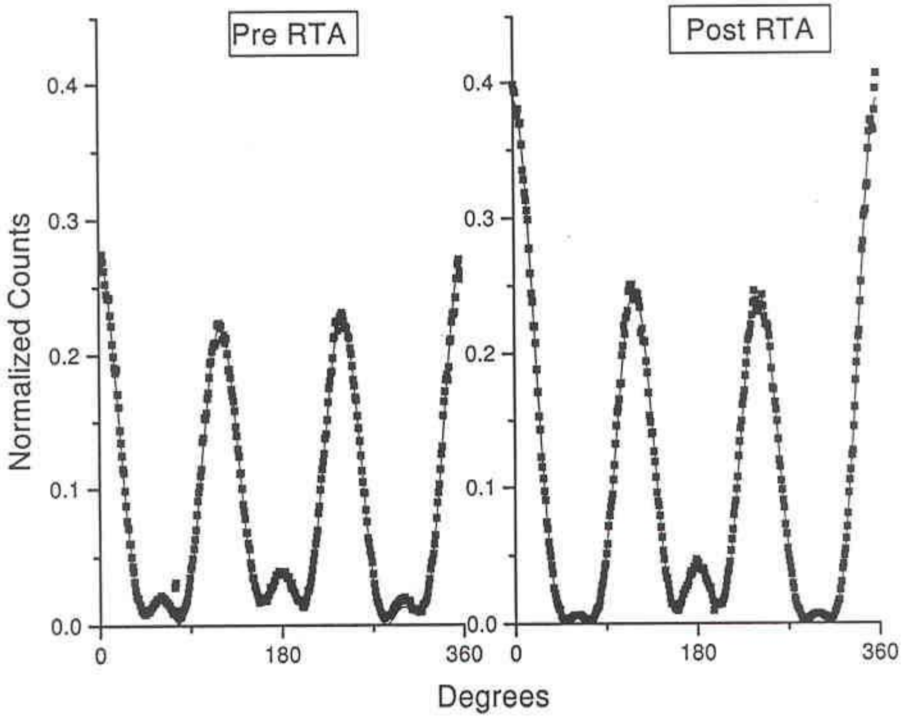
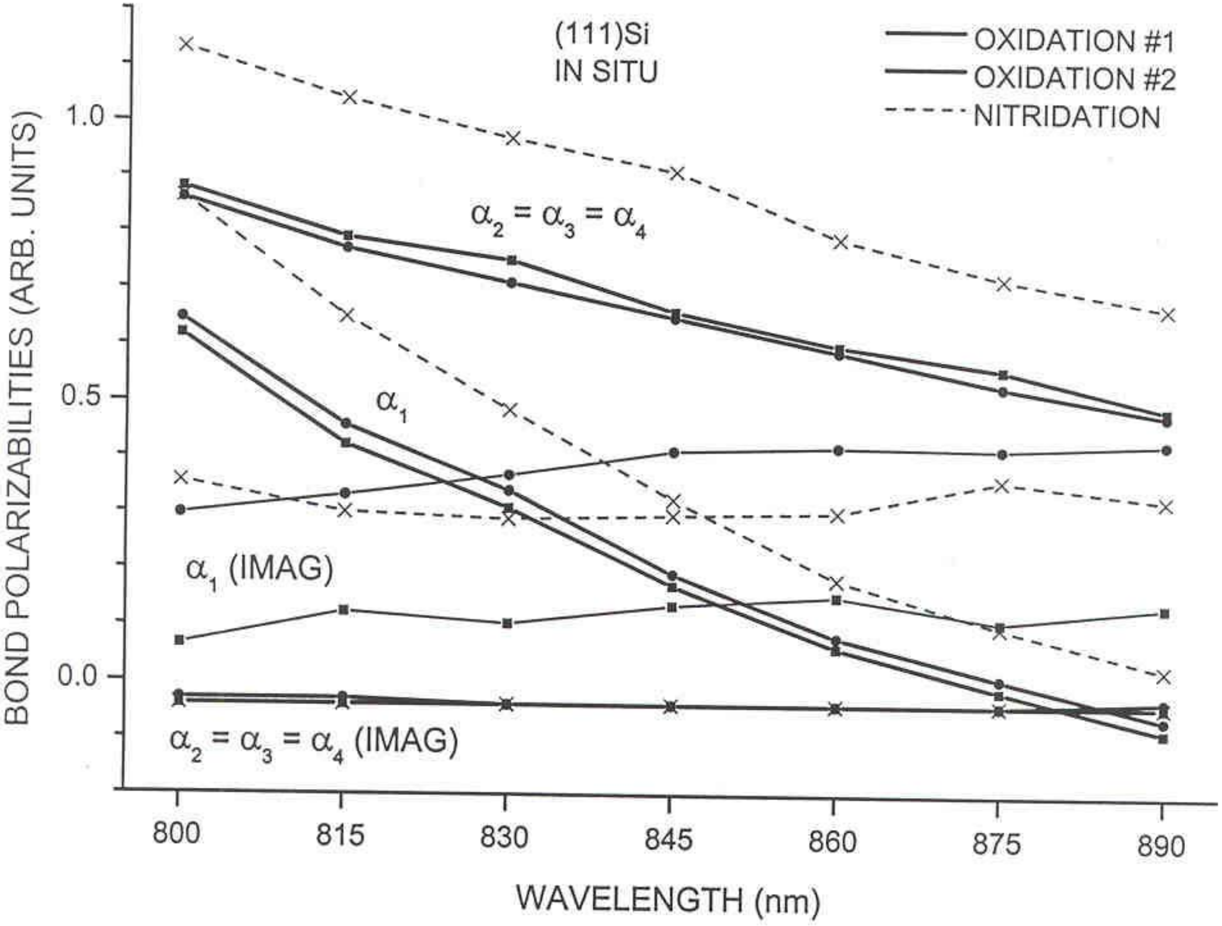


Figure 3.6: Example ex-situ SHG anisotropies and phenomenological fits at 830nm for vicinal (111) Si cut 5° toward $\langle 11\bar{2} \rangle$ with oxidation and oxide cap before and after RTA.


(111)Si
IN SITU
OXIDATION #1
OXIDATION #2
NITRIDATION
$\alpha_2 = \alpha_3 = \alpha_4$
α_1
α_1 (IMAG)
$\alpha_2 = \alpha_3 = \alpha_4$ (IMAG)
BOND POLARIZABILITIES (ARB. UNITS)
1.0
0.5
0.0
800
815
830
845
860
875
890
WAVELENGTH (nm)

CONCLUSIONS:

(1) The SBHM enormously simplifies the analysis of SHG data relative to previous methods

(2) It also provides insights at the microscopic level (complex hyperpolarizabilities of specific bonds) as well as SHG mechanisms (effective angles of incidence, origin of SHG signals)

(3) We obtain consistent descriptions of pp, ps, sp, and ss data where available

(4) We conclude that in many if not most cases SHG is actually simpler than linear optics

(5) Next step: spectral responses...

(6) ...followed, we believe, by renewed interest in the use of SHG as a diagnostic probe.