Chapter 2

Phenomenological theory of SHG from Si surfaces

2.1 Introduction

The incident beam at frequency ω creates a polarization at the harmonic frequency 2ω, which radiates second-harmonic (SH) light. Nonlinear susceptibility tensors connect the fundamental field and the generated SH field. The tensor elements that are allowed by both symmetry of the medium and geometry of the beams are treated as sources of SH polarization. Using a phenomenological theory, we predict the symmetry properties of rotational-anisotropy SHG (RA-SHG) in reflection from either principal or vicinal Si(001) surfaces. We consider bulk and surface SH contributions and SHG from the electric-field-induced SHG (EFISH) contribution if present. We show that under certain circumstances bulk and surface SH contributions can be separated; moreover, individual tensor elements can be uniquely determined by combining polarization selection and RA-SHG.

2.2 The Model

Consider a laser beam, idealized as single incident plane wave at frequency ω and wave vector $\vec{v}_i$, incident from the ambient with dielectric constant $\varepsilon = 1$ on the medium with $\varepsilon(\omega) \neq 1$ of interest at an angle θ_0, as shown in Fig. 2.1.

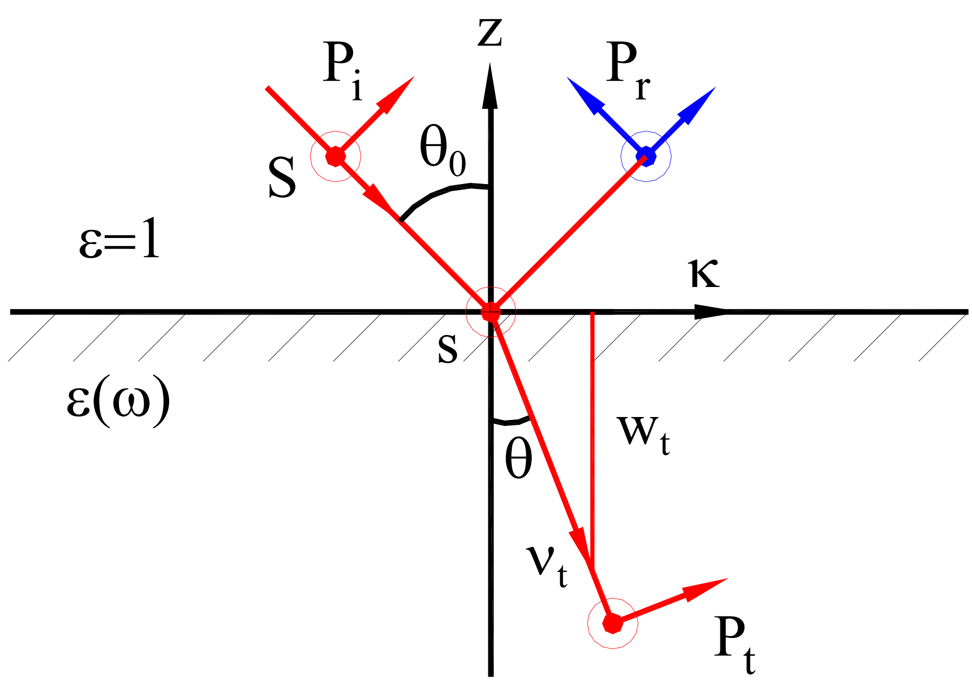

Fig. 2.1. Geometry and unit vectors for the propagating fundamental and SH fields. Note that the diagram assumes that the refractive index of the medium is real.

We study the SH field $\vec{E}^{(2\omega)}$ in reflection geometry. The incident field $\vec{E}_i(\vec{r},t)$, the reflected field $\vec{E}_r(r,t)$, and the transmitted field $\vec{E}_t(\vec{r},t)$ are written in the general form

$$\vec{E}_n(r,t) = \vec{E}_n e^{i\vec{v}_n\cdot\vec{r} - i\omega t} + c.c., \quad (2.1)$$

where the subscript n can be replaced by i, r, or t to represent the incident, the reflected, or the transmitted field, respectively. Each of the amplitudes of the electric fields can be expressed as a superposition of its p- and s-polarized components as

$$\vec{E}_n = E_{np}\hat{p}_n + E_{ns}\hat{s}. \quad (2.2)$$

We take the normal to the surface to be the $\hat{z}$ direction and the wave-vector component perpendicular to $\hat{z}$ as $\vec{\kappa} = \hat{\kappa}|v_i|\sin\theta_0$. In terms of these, the wave vectors for these three fields are

$$\vec{v}_n = \vec{\kappa} - w_n\hat{z}. \quad (2.3)$$

For all three fields, the components of the wave vector normal (w_n) and parallel (κ) to the medium surface are related by

$$w_i = (\tilde{\omega}^2 - \kappa^2)^{1/2} = -w_r, \quad (2.4a)$$

$$w_t = (\tilde{\omega}^2\varepsilon(\omega) - \kappa^2)^{1/2}, \quad (2.4b)$$

where $\tilde{\omega} = \omega / c$ and $\varepsilon(\omega)$ is the dielectric constant of the medium. In Eq. (2.4), we choose the root with $\mathrm{Im}(\omega) \geq 0$, and if $\mathrm{Im}(\omega) = 0$, we take $\mathrm{Re}(\omega) \geq 0$.

The reflected and transmitted fields are obtained from the incident field as

$$\vec{E}_r = (\hat{s}r_s\hat{s} + \hat{p}_r r_p\hat{p}_i)\cdot\vec{E}_i, \quad (2.5a)$$

$$\vec{E}_t = (\hat{s}t_s\hat{s} + \hat{p}_t t_p\hat{p}_i)\cdot\vec{E}_i, \quad (2.5b)$$

where r_s and r_p (t_s and t_p) are the usual Fresnel coefficients of reflection (transmission) from the ambient into the medium for *s*- and *p*-polarized light, respectively,

$$
\begin{aligned}
r_s &= \frac{w_i - w_t}{w_i + w_t}, \qquad r_p = \frac{w_i\varepsilon(\omega) - w_t}{w_i\varepsilon(\omega) + w_t}; \\
t_s &= \frac{2w_i}{w_i + w_t}, \qquad t_p = \frac{2nw_i}{w_i\varepsilon(\omega) + w_t},
\end{aligned}
\tag{2.6}
$$

while $\hat{p}_t$ is the direction of polarization of *p*-polarized light in the medium given by

$$
\hat{p}_t = \frac{\kappa\hat{z} + w_t\hat{\kappa}}{n\tilde{\omega}} = f_s\hat{z} + f_c\hat{\kappa}\,. \tag{2.7}
$$

where $n = \sqrt{\varepsilon(\omega)}$ is the complex refractive index of the medium, and f_s and f_c are the Fresnel factors. Note that if *n* is real, f_s and f_c are simply the sine and cosine of the angle of beam propagation in the medium, respectively.

We introduce the analogous equations to Eqs. (2.4)-(2.7) for the SH fields, viz.,

$$
\begin{aligned}
&\tilde{\Omega} = \frac{2\omega}{c}, K = 2\kappa, N = \sqrt{\varepsilon(2\omega)}, \\
&W_t = [\tilde{\Omega}^2\varepsilon(2\omega) - K^2]^{1/2}, W_i = [\tilde{\Omega}^2 - K^2]^{1/2}, \\
&\hat{P}_t = \frac{K\hat{z} + W_t\hat{\kappa}}{N\tilde{\Omega}} = F_s\hat{z} + F_c\hat{\kappa}, \\
&\hat{P} = F_s\hat{z} - F_c\hat{\kappa}, \\
&T_s = \frac{2W_t}{W_i + W_t}, T_p = \frac{2NW_t}{W_i\varepsilon(2\omega) + W_t}.
\end{aligned}
\tag{2.8}
$$

Again, if *N* is real, F_s and F_c are the sine and cosine of the angle of SH beam propagation in the medium. $\hat{P}_t$ and $\hat{P}$ are the directions of polarization of *p*-polarized SH light in the medium and vacuum, respectively. T_s and T_p are the

Fresnel transmission coefficients from the medium into the ambient for *s*- and *p*-polarized SH light, respectively.

The amplitude of the generated SH field in vacuum can be expressed as a superposition of *p*- and *s*-polarized components as

$$\vec{E}^{(2\omega)} = E_p^{(2\omega)}\hat{P} + E_s^{(2\omega)}\hat{s}\ . \qquad (2.9)$$

If the dielectric constant of the medium and the wave-vector of the incident beam are known, all of the Fresnel factors and coefficients should be readily calculated using these equations.

2.3 Rotational-anisotropy SHG

2.3.1 Bulk and surface SH contributions

For a centrosymmetric medium, SHG due to the electric dipole response is forbidden in the bulk because of inversion symmetry, but is allowed at the surface because of broken symmetry. At the surface, in addition to the dipole response, a discontinuity in the normal component of the electric field can produce SHG due to the non-local response as well. Both effects have been discussed in details before [26] and combined through the definition of an effective dipole response characterized by a surface susceptibility tensor $\chi_{ijk}^{(2)}$. In the bulk, although SHG due to the dipole response is zero, higher-order terms of polarization, such as the electric quadrupole response [12, 45] give a contribution to SHG, which could be quite significant in comparison with the surface SH contribution. In the presence of an external dc electric field in the medium and at the surface, SHG can have a contribution arising from dc electric-field-induced SH (EFISH) effect. The EFISH effect should be split into a bulk and a surface contribution, because the symmetry at the surface is different from that in the bulk.

For a centrosymmetric medium, second-order nonlinear polarization $\vec{P}^{(2\omega)}$ at the SH frequency 2ω is given by

$$\vec{P}^{(2\omega)} = \vec{P}^{SD,(2\omega)} + \vec{P}^{BQ,(2\omega)} + \vec{P}^{BE,(2\omega)} + \vec{P}^{SE,(2\omega)} . \qquad (2.10)$$

These four terms correspond to the surface dipole, bulk quadrupole, bulk EFISH, and surface EFISH polarizations, respectively.

The bulk quadrupole response can be written in terms of an effective polarization [24, 27], as

$$P_i^{BQ,(2\omega)}(\vec{r}) = \Gamma_{ijkl}^{(2)} E_j(\vec{r}) \nabla_k E_l(\vec{r}) , \qquad (2.11)$$

where the gradient is determined with respect to the field coordinates and the summation convention is used. $E_i(\vec{r})$ is the fundamental field inside the medium as a function of position $\vec{r}$. $\Gamma_{ijkl}^{(2)}$ is a 4th rank susceptibility tensor that connects the fundamental field and the SH field.

For a crystal with bulk cubic symmetry, such as Si, when the crystal axes are taken to be the standard cubic axes, all distinct elements for the tensor $\Gamma_{ijkl}^{(2)}$ are given by [46]

$$\Gamma_{ijkl}^{(2)} = a_0 \delta_{ijkl} + a_1(\delta_{ij}\delta_{kl} + \delta_{il}\delta_{jk}) + a_2 \delta_{ik}\delta_{jl} , \qquad (2.12a)$$

where a_i are non-zero phenomenological constants. In summation of indices, $\delta_{ij}\delta_{kl}$ implies $i, j \neq k, l$. If such a restriction is eliminated, the tensor is written as

$$\Gamma^{(2)}_{ijkl} = (a_0 - 2a_1 - a_2)\delta_{ijkl} + a_1\delta_{ij}\delta_{kl} + a_1\delta_{il}\delta_{jk} + a_2\delta_{ik}\delta_{jl} . \quad (2.12b)$$

Here, the relation $a_0 \neq 2a_1 + a_2$ holds for cubic symmetric media.

We consider the transformation characteristics of $\Gamma^{(2)}_{ijkl}$ under the symmetry operation of rotating the crystal about its surface normal. The last three terms are all isotropic, because each term keeps it own form under an arbitrary rotation with the transformation matrix R, i.e.,

$$\delta_{ij}\delta_{kl} = R_{io}R_{jp}R_{kq}R_{lr}\delta_{op}\delta_{qr} . \quad (2.13)$$

The first term of Eq. (2.12b) is anisotropic because such an arbitrary rotation operation does not exist in general.

By using Eq. (2.12b), Eq. (2.11) can then be written in the form

$$P_i^{BQ,(2\omega)} = \zeta E_i \nabla_i E_i + a_1 E_i[\nabla \cdot \vec{E}] + a_1[\vec{E} \cdot \nabla]E_i + \gamma \nabla_i(\vec{E} \cdot \vec{E}) , \quad (2.14)$$

where $E_i = E_i(\vec{r})$ for simplicity and

$$\zeta = a_0 - 2a_1 - a_2 , \qquad \text{and } \gamma = \frac{1}{2}a_2 . \quad (2.15)$$

Notice that Eq. (2.14) is similar to the previous usual form [27], but the second-order nonlinear polarization of magnetic dipole origin is not included here. However, adding of the magnetic dipole effect is equivalent to adjusting of the phenomenological constants.

For excitation of a homogeneous medium by a single transverse plane wave, the middle two terms of Eq. (2.14) are zero, thus, we recover the polarization to the previous results [27]. The bulk susceptibility tensor is split into an isotropic piece, $\Gamma^{(2),i}_{ijkl} = 2\gamma\delta_{ik}\delta_{jl}$, and an anisotropic piece, $\Gamma^{(2),a}_{ijkl} = \zeta\delta_{ijkl}$.

The isotropic nonlinear polarization is given by

$$\vec{P}^{(2\omega),i} = \gamma\nabla(\vec{E}\cdot\vec{E}) = 2i\gamma(\vec{\kappa} - w\hat{z})(E_s^2 + E_p^2)e^{2i(\vec{\kappa}\cdot\vec{R} - wz)}, \qquad (2.16)$$

where $\vec{R} = (x, y)$, $\vec{r} = \vec{R} + z\hat{z}$, and $w = w_t$.

The SH fields arising from the bulk isotropic source are identical for all crystal faces and independent of the surface orientation. Following Sipe [27], the generated isotropic fields at 2ω outside of the medium for general linear polarized light and for either *s*- or *p*-polarized harmonic light are

$$E_s^{BQ,(2\omega),i} = 0, \qquad (2.17)$$

$$E_p^{BQ,(2\omega),i} = A_0 T_p F_s \gamma(E_s^2 + E_p^2). \qquad (2.18)$$

Here $A_0 = 2\pi i\widetilde{\Omega} / NF_c$ is a constant.

2.3.2 RA-SHG from vicinal Si faces

We first study a vicinal surface, which is disoriented by a small angle α from the Si(001) face but still has a mirror plane of symmetry normal to the surface plane, as shown in Fig. 2.2. The offset direction is from the [001] axis toward [110]. For cubic centrosymmetric crystals, Lüpke presented two ways of miscutting to form a surface with symmetry of one mirror plane in the vicinal face [47]: the misorientation from [001] toward [011] and the misorientation from [001] toward [110]. It is important to note that for crystals with diamond structure, which preserve cubic centrosymmetry, the first way of miscut does not produce a vicinal surface with one mirror plane of symmetry.

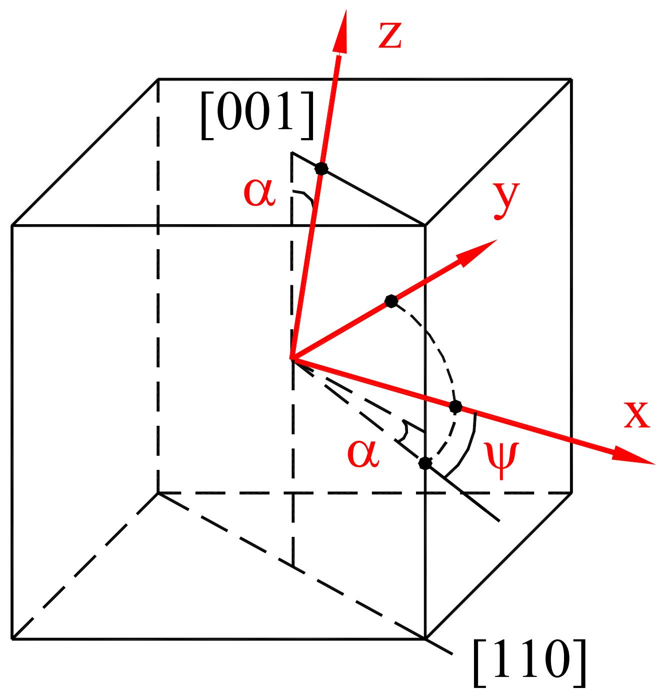

Fig. 2.2. Diagram of the beam frame and the vicinal surface with respect to the cubic crystal axes.

The angles α =0, $\arccos(1/\sqrt{3})$, and $\pi/2$ yield the low-index (001), (111), and (110) crystal faces, respectively; therefore the results of RA-SHG from such a general face is applicable to low-index crystal faces by adjusting the vicinal angle.

To study the transformation properties of anisotropic susceptibility tensors, we establish three coordinate systems. The coordinates ($\hat{x}_0, \hat{y}_0, \hat{z}_0$) are chosen as the natural crystallographic coordinate system corresponding to the [100], [010], and [001] directions, respectively. The coordinates ($\hat{x}_1, \hat{y}_1, \hat{z}_1$) are defined to be the crystallographic directions corresponding to the [110], $[\bar{1}10]$, and [001] directions, respectively. The coordinates $(\hat{x}, \hat{y}, \hat{z})$ are defined to be a fixed beam frame with the $\hat{z}$ axis to be the normal of the macroscopic vicinal surface, as shown in Fig. 2.2. By virtue of these definitions, the azimuthal angle ψ is defined to between $\hat{x}$ and the downward miscut direction.

The susceptibility tensor is transformed from the natural crystallographic coordinates to the final beam coordinates following three steps. First, is the rotation of coordinate counterclockwise about the $\hat{z}_0$ axis by an angle $\psi_0 = 45^\circ$ from the coordinates ($\hat{x}_0, \hat{y}_0, \hat{z}_0$) to ($\hat{x}_1, \hat{y}_1, \hat{z}_1$) with the transformation matrix

$$R_z(\psi_0) = \begin{bmatrix} \cos(\psi_0) & \sin(\psi_0) & 0 \\ -\sin(\psi_0) & \cos(\psi_0) & 0 \\ 0 & 0 & 1 \end{bmatrix}. \qquad (2.19)$$

Second, is the rotation counterclockwise about the $\hat{y}_1$ axis by an angle α from ($\hat{x}_1, \hat{y}_1, \hat{z}_1$) to $(\hat{x}, \hat{y}, \hat{z})$ when ψ =0 following the transform matrix

$$R_y(\alpha) = \begin{bmatrix} \cos(\alpha) & 0 & -\sin(\alpha) \\ 0 & 1 & 0 \\ \sin(\alpha) & 0 & \cos(\alpha) \end{bmatrix}. \quad (2.20)$$

Third, is the rotation of coordinate counterclockwise about the $\hat{z}$ axis for an angle ψ from the coordinates $(\hat{x}, \hat{y}, \hat{z})$ when ψ=0 to the coordinates $(\hat{x}, \hat{y}, \hat{z})$ when ψ>0. The transform matrix is $R_z(\psi)$, which has the same matrix form as $R_z(\psi_0)$ but with a different rotation angle. Thus, the final transformation matrix is the ordered product of the three matrixes, written as

$$R = R_z(\psi) R_y(\alpha) R_z(\psi_0). \quad (2.21)$$

The tensor $\Gamma^{(2),a}_{opqr}$ in the crystallographic coordinate is transformed to $\Gamma'^{(2),a}_{ijkl}$ in the beam coordinate according to the tensor transformation rule

$$\Gamma'^{(2),a}_{ijkl} = R_{io} R_{jp} R_{kq} R_{lr} [\Gamma^{(2),a}_{opqr}]. \quad (2.22)$$

With respect to the final beam coordinates $(\hat{x}, \hat{y}, \hat{z})$, we obtain the bulk anisotropic nonlinear polarization

$$P^{(2\omega),a}_i(\vec{r}) = \Gamma'^{(2)}_{ijkl} \vec{E}'_j(\vec{r}) \nabla'_k \vec{E}'_l(\vec{r}). \quad (2.23)$$

Following Sipe [27, 48], the SH fields outside of the medium generated with a half-space filled with air (or vacuum) are calculated. For simplicity, the polarizations of both the fundamental and harmonic fields are limited to *s* and *p*. The notation *(g, h)* is established to represent *g* polarized fundamental and *h* polarized harmonic radiation, where *g* and *h*=*s* or *p*.

For the (*g, p*) cases, the SH fields $E^{BQ,(2\omega),a}_{g,p}$ arising from bulk anisotropic quadrupole source are

$$E_{g,p}^{BQ,(2\omega),a} = A_0 T_p \zeta \Gamma [b_{00,(g,p)}^{BQ} + \sum_{m=0}^{4} b_{m,(g,p)}^{BQ} \Phi_m(\alpha)\cos(m\psi)][E_g^{(\omega)}]^2 ,$$

(2.24a)

and for the (*g, s*) cases, the SH fields are

$$E_{g,s}^{BQ,(2\omega),a} = A_0 T_s \zeta \Gamma [\sum_{m=1}^{4} b_{m,(g,s)}^{BQ} \Phi_m(\alpha)\sin(m\psi)][E_g^{(\omega)}]^2 . \quad (2.24b)$$

Here, $\Gamma = n\widetilde{\Omega}/8(2w_t + W_t)$. $\Phi_m(\alpha)$ are the angular functions for the specific misorientation as shown in Fig. 2.2, which are listed in Table 2.1 in the same form as that from Lüpke [47]. The coefficients $b_{00,(g,h)}^{BQ}$ and $b_{m,(g,h)}^{BQ}$ are the combinations of Fresnel factors specific to each Fourier coefficient, as listed in Table 2.2. These results are from a complete and systematic calculation rather than a repeat of previous report [47].

Table 2.1. Angular functions $\Phi_m(\alpha)$

$\Phi_0(\alpha)$	$\frac{1}{32}[25 + 4\cos(2\alpha) + 3\cos(4\alpha)]$
$\Phi_1(\alpha)$	$\frac{1}{16}[2\sin(2\alpha) + 3\sin(4\alpha)]$
$\Phi_2(\alpha)$	$-\frac{1}{16}[1 - 4\cos(2\alpha) + 3\cos(4\alpha)]$
$\Phi_3(\alpha)$	$-\frac{1}{16}[14\sin(2\alpha) - 3\sin(4\alpha)]$
$\Phi_4(\alpha)$	$-\frac{1}{32}[7 + 28\cos(2\alpha) - 3\cos(4\alpha)]$

Table 2.2. $b^{BQ}_{00,(g,h)}$ and $b^{BQ}_{m,(g,h)}$ as functions of Fresnel factors

	(s, s)	*(p, s)*	*(s, p)*	*(p, p)*
b^{BQ}_{00}	*0*	*0*	$4f_cF_s$	$4[F_cf_s(-2f_c^2+f_s^2)+F_sf_c(f_c^2-3f_s^2)]$
b^{BQ}_{0}	*0*	*0*	$F_cf_s-4f_cF_s$	$F_cf_s(11f_c^2-4f_s^2)-4F_sf_c(f_c^2-4f_s^2)]$
b^{BQ}_{1}	$3f_c$	$f_c(f_c^2-6f_s^2)$	$-f_cF_c-f_sF_s$	$F_cf_c(10f_s^2-3f_c^2)+F_sf_s(4f_s^2-11f_c^2)]$
b^{BQ}_{2}	f_s	$f_s(5f_c^2-2f_s^2)$	$-2f_cF_s$	$2F_cf_s(f_s^2-3f_c^2)+2F_sf_c(f_c^2-2f_s^2)]$
b^{BQ}_{3}	$-f_c$	$f_c(f_c^2-2f_s^2)$	$f_cF_c+f_sF_s$	$f_c(-f_c^2F_c+2F_cf_s^2-f_cf_sF_s)]$
b^{BQ}_{4}	f_s	$-f_c^2f_s$	$-F_cf_s$	$f_c^2F_cf_s$

We apply the formalism of the bulk anisotropic SHG to calculate the analogous equations for bulk EFISH in reflection with emphasis on dependence of the EFISH field on crystal symmetry. To our knowledge, a theoretical expression for the EFISH effect in the bulk of a medium has not been developed. The bulk dc field induced dipole polarization can be written phenomenologically as,

$$P_i^{BE,(2\omega)} = \chi^{(3)}_{ijkl} E_j E_k^d E_l \ , \qquad (2.25)$$

where $\vec{E}^d$ is the dc electric field, which is a function of normal position measured from the surface and directed along the surface normal, written as $\vec{E}^{\mathrm{d}}(z) = \hat{z}E^d(z)$.

For a cubic centrosymmetric medium, when the coordinate axes are taken to be the standard cubic axes, $\chi^{(3)}_{ijkl}$ preserves the same symmetry properties as $\Gamma^{(2)}_{ijkl}$, and it is written as,

$$\chi^{(3)}_{ijkl} = (b_0 - 2b_1 - b_2)\delta_{ijkl} + b_1(\delta_{ij}\delta_{kl} + \delta_{il}\delta_{jk}) + b_2\delta_{ik}\delta_{jl} \, . \qquad (2.26)$$

Equation (2.25) can be written in the form

$$P_i^{BE,(2\omega)} = \zeta^d E_i E_i^d E_i + \eta^d E_i (\vec{E}^{\rm d} \cdot \vec{E}) + \gamma^d E_i^d (\vec{E} \cdot \vec{E}), \quad (2.27)$$

where

$$\zeta^d = b_0 - 2b_1 - b_2, \eta^d = 2b_1, \text{ and } \gamma^d = \frac{1}{2} b_2. \quad (2.28)$$

Notice that there is a difference between the bulk quadrupole and the bulk EFISH polarizations. The middle term of the latter is non-zero in general, even for excitation of a homogeneous medium by a single transverse plane wave. The SH polarization arising from the middle term is isotropic, written as

$$\vec{P}^{BE,(2\omega),\eta,i} = \eta^d \vec{E}(\vec{E}^d \cdot \vec{E}) = E^d(z) f_s \eta^d E_p \vec{E}. \quad (2.29)$$

The generated fields at 2ω from this source outside of the medium for either *s*- or *p*-polarized harmonic light are

$$E_s^{BE,(2\omega),\eta,i} = A_0 T_s \Gamma^d f_s \eta^d E_p E_s, \quad (2.30a)$$

$$E_p^{BE,(2\omega),i} = A_0 T_p \Gamma^d f_s F_s \eta^d E_p^2. \quad (2.30b)$$

Here, $\Gamma^d = \int_{-\infty}^{0} E^d(z) \exp[-i(2w_t + W_t)z] dz$ and the integration is over the half infinite medium.

Similarly, the polarization arising from the last term is

$$\vec{P}^{BE,(2\omega),\gamma^d,i} = \gamma^d \vec{E}^d(\vec{E} \cdot \vec{E}) = \gamma^d \vec{E}^d (E_s^2 + E_p^2) e^{2i(\vec{\kappa}\cdot\vec{R} - wz)}, \quad (2.31)$$

and the generated fields at 2ω from this source outside of the medium for either *s*- or *p*-polarized harmonic light are

$$E_s^{BE,(2\omega),\gamma^d,i} = 0, \quad (2.32a)$$

$$E_p^{BE,(2\omega),\gamma^d,i} = A_0 T_p \Gamma^d F_s \gamma^d (E_s^2 + E_p^2). \quad (2.32b)$$

For the anisotropic term and with the polarization of the fundamental and harmonic fields limited to *s* and *p* states, the calculation proceeds the same way as bulk quadrupole SH source. For the (*g, p*) cases, the SH fields $E_{g,p}^{BE,(2\omega),a}$ arising from anisotropic EFISH source are

$$E_{g,p}^{BE,(2\omega),a} = A_0 T_p \zeta^d \Gamma^d [b_{00,(g,p)}^d + \sum_{m=0}^{3} b_{m,(g,p)}^d \Phi_m(\alpha)\cos(m\psi)][E_g^{(\omega)}]^2 \quad ,$$

(2.33a)

and for the (*g, s*) cases, the SH fields are

$$E_{g,s}^{BE,(2\omega),a} = A_0 T_s \zeta^d \Gamma^d [\sum_{m=1}^{3} b_{m,(g,s)}^d \Phi_m(\alpha)\sin(m\psi)][E_g^{(\omega)}]^2 \quad .$$

(2.33b)

Here, $b_{00,(g,h)}^d$ and $b_{m,(g,h)}^d$ are the combinations of Fresnel factors specific to each Fourier coefficient, as listed in Table 2.3.

Table 2.3. $b_{00,(g,h)}^d$ and $b_{m,(g,h)}^d$ as functions of Fresnel factors

	(s, s)	*(p, s)*	*(s, p)*	*(p, p)*
b_{00}^d	*0*	*0*	$4F_s$	$4(-2F_c f_c f_s + f_c^2 F_s - f_s^2 F_s)$
b_0^d	*0*	*0*	$-4F_s$	$-4(-2F_c f_c f_s + f_c^2 F_s - 2f_s^2 F_s)$
b_1^d	*3*	$f_c^2 - 4f_s^2$	$-F_c$	$-3f_c^2 F_c + 4F_c f_s^2 - 8f_c f_s F_s$
b_2^d	*0*	$4f_c f_s$	$-2F_s$	$2f_c(-2F_c f_s + f_c F_s)$
b_3^d	$f_c^{\ 2}$	f_c^2	F_c	$-f_c^2 F_c$

Symmetry properties of the bulk SH contribution are predicted from the above calculation. Now we consider the surface SH contribution. The SH polarization arising from the surface dipole response is given by

$$P_i^{SD,(2\omega)} = \chi_{ijk}^{S,(2)} E_j E_k \tag{2.34}$$

For a surface with one mirror plane of symmetry, with the $\hat{y}$ axis perpendicular to the plane of symmetry, Eq. (2.34) can be rewritten in the usual piezoelectric contracted notation as [49, 50]

$$\begin{bmatrix} P_x^{(2\omega)} \\ P_y^{(2\omega)} \\ P_z^{(2\omega)} \end{bmatrix} = \begin{bmatrix} \partial_{11} & \partial_{12} & \partial_{13} & 0 & \partial_{15} & 0 \\ 0 & 0 & 0 & \partial_{24} & 0 & \partial_{26} \\ \partial_{31} & \partial_{32} & \partial_{33} & 0 & \partial_{35} & 0 \end{bmatrix} \times \begin{bmatrix} E_x^{\ 2} \\ E_y^{\ 2} \\ E_z^{\ 2} \\ 2E_yE_z \\ 2E_xE_z \\ 2E_xE_y \end{bmatrix}, \tag{2.35}$$

where ∂_{mn} are independent tensor elements of $\chi_{ijk}^{S,(2)}$. Note that the $\hat{x}$ axis should also be specified to relate the surface to the bulk susceptibilities. For the vicinal Si surface, the $\hat{x}$ axis is toward the downward miscut direction when ψ =0, as shown in Fig. 2.2.

For the ideal low-index (001) surface under perfect flatcut condition, the ∂_{mn} simplify considerably to only the nonzero elements, $\partial_{31}, \partial_{32}, \partial_{15}, \partial_{24}$, and ∂_{33}. For a practical Si(001) surface, to a good approximation it is macroscopic fourfold symmetric; therefore, these nonzero elements can be simplified again to $\partial_{31} = \partial_{32}, \partial_{15} = \partial_{24}$, and ∂_{33} [27].

With the fundamental and SH beams limited to *s*- or *p*-polarized states, the SH fields $E_{g,h}^{SD,(2\omega)}$ for the (*g, p*) cases are

$$E_{g,p}^{SD,(2\omega)} = A_0 T_p [\sum_{m=0}^{3} s_{m,(g,p)}^{SD} \cos(m\psi)][E_g]^2 , \qquad (2.36)$$

and for the (*g, s*) cases are

$$E_{g,s}^{SD,(2\omega)} = A_0 T_s [\sum_{m=1}^{3} s_{m,(g,s)}^{SD} \sin(m\psi)][E_g]^2 . \qquad (2.37)$$

Here, $s_{m,(g,h)}^{SD}$ are the combinations of Fresnel factors and independent tensor elements, as listed in Table 2.4. In the table, the following expressions have been introduced for notational convenience [47]:

$$\begin{aligned} \partial_{11}^{(1)} &= \frac{1}{4}(3\partial_{11} + \partial_{12} + 2\partial_{26}), \\ \partial_{12}^{(1)} &= \frac{1}{4}(\partial_{11} + 3\partial_{12} - 2\partial_{26}), \\ \partial_{11}^{(3)} &= \frac{1}{4}(\partial_{11} - \partial_{12} - 2\partial_{26}). \end{aligned} \qquad (2.38)$$

Table 2.4. $s_{m,(g,h)}^{SD}$ as combinations of Fresnel factors and tensor elements

	(s, s)	*(p, s)*	*(s, p)*	*(p, p)*
s_0^{SD}	*0*	*0*	$\frac{1}{2}\varepsilon(2\omega)F_s(\partial_{31} + \partial_{32})$	$\varepsilon(2\omega)F_s[f_s^2\partial_{33} + \frac{1}{2}f_c^2(\partial_{31} + \partial_{32})] - F_c f_c f_s(\partial_{15} + \partial_{24})$
s_1^{SD}	$\partial_{11}^{(1)}$	$f_c^2\partial_{12}^{(1)} + f_s^2\partial_{13}$	$-F_c\partial_{12}^{(1)}$	$2\varepsilon(2\omega)F_s f_c f_s\partial_{35} - F_c[f_s^2\partial_{13} + f_c^2\partial_{11}^{(1)})$
s_2^{SD}	*0*	$f_c f_s(\partial_{15} - \partial_{24})$	$-\frac{1}{2}\varepsilon(2\omega)F_s(\partial_{31} - \partial_{32})$	$\frac{1}{2}\varepsilon(2\omega)F_s f_c^2(\partial_{31} - \partial_{32}) - F_c f_c f_s(\partial_{15} - \partial_{24})$
s_3^{SD}	$-\partial_{11}^{(3)}$	$f_c^2\partial_{11}^{(3)}$	$F_c\partial_{11}^{(3)}$	$-f_c^2F_c\partial_{11}^{(3)}$

If there is a dc electric field at the surface (or interface), SHG has a contribution from the surface EFISH polarization $\vec{P}^{SE,(2\omega)}$, given by

$$P_i^{SE,(2\omega)} = \chi_{ijkl}^{S,(3)} E_j E_k^d E_l \,. \qquad (2.39a)$$

At the surface or interface, the symmetry is different from in the bulk. The dc field here is limited to the surface normal direction. Considering the small size of the interfacial region, we treat the EFISH polarization as a surface effect by integrating the *z*-dependent variables across the interfacial layer, written as

$$P_i^{d,s,(2\omega)} = \int_I \chi_{ij3k}^{s,(3)}(z) E_3^d(z) dz E_j E_k = M_{ijk}^{S,(2)} E_j E_k \,. \qquad (2.39b)$$

If $\chi_{ijkl}^{S,(3)}$ is a mathematical tensor, the new variable $M_{ijk}^{S,(2)}$ is not a tensor, strictly speaking; however, it possesses the same symmetry properties as $\chi_{ijk}^{S,(2)}$ when the symmetry operation is limited to rotation about the surface normal. Therefore, the surface EFISH effect can be combined into the surface SH without the dc field by defining a new set of field-dependent tensor elements ∂_{mn}^d and adding them one by one to the field-independent tensor ∂_{mn}, written as $\partial_{mn} + \partial_{mn}^d$. The symmetry properties of the rotational-anisotropy SHG should be the same with or without the EFISH effect.

The total SH field $E_{g,h}^{(2\omega)}$ arising from both the bulk and surface for the (*g, p*) cases are

$$E_{g,p}^{(2\omega)} = [\sum_{m=0}^{4} C_{m,(g,p)} \cos(m\psi)][E_g]^2 \,, \qquad (2.40a)$$

and for the (*g, s*) cases are

$$E_{g,s}^{(2\omega)} = [\sum_{m=1}^{4} C_{m,(g,s)} \sin(m\psi)][E_g]^2 . \qquad (2.40b)$$

The fourfold Fourier coefficient C_4 is unique in that it originates from only anisotropic bulk quadrupole contribution. The SH intensity $I^{(2\omega)}$ is proportional to the magnitude squared of the SH field, written as $I^{(2\omega)} \propto |E^{(2\omega)}|^2$.

2.3.3 RA-SHG from the Si(001) face

In calculating SHG from vicinal Si surfaces, the polarizations of both the fundamental and the SH fields are limited to either *s* or *p* in order to simplify the expressions of the SH fields for a complicated surface susceptibility tensor. In contrast, for the Si(001) surface, the surface susceptibility tensor is much simpler than that of vicinal surfaces; therefore, we consider a general linear polarization configuration for both the fundamental and the SH fields. The notation $(\Delta\alpha, \Delta\beta)$ is introduced to represent a specific linear polarization configuration, as shown in Fig. 2.3, where $\Delta\alpha$ represents the polarization direction of the incident field $\vec{E}_0(\Delta\alpha)$ that is an angle $\Delta\alpha$ counterclockwise from its *s*-polarization, and $\Delta\beta$ represents the polarization of the SH field $\vec{E}^{(2\omega)}(\Delta\beta)$ that is an angle $\Delta\beta$ counterclockwise from its *s*-polarization. Here, counterclockwise is with respect to the forward beam propagation direction.

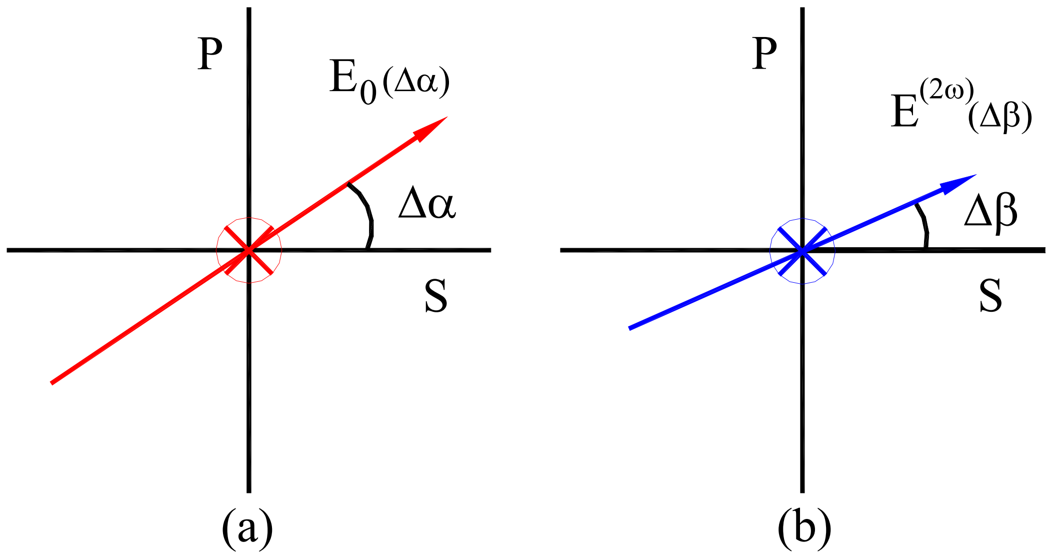

Fig. 2.3. Definition of the linear polarization configuration with the incident fundamental beam (a) and the reflected SH beam (b).

Under the excitation of a $\Delta\alpha$ polarized fundamental beam, the generated *s*-polarized SH field due to the bulk anisotropic source is

$$E_{\Delta\alpha,s}^{(2\omega),ani} = A_0 T_s \Gamma \zeta f_s \{-f_c t_s t_p \sin(2\Delta\alpha) + [t_s^{\ 2}\cos^2(\Delta\alpha) - f_c^{\ 2} t_p^{\ 2}\sin^2(\Delta\alpha)]\sin(4\phi) + f_c t_s t_p \sin(2\Delta\alpha)\cos(4\phi)\}[E_0]^2, \quad (2.41a)$$

and the generated *p*-polarized SH field is

$$E_{\Delta\alpha,p}^{(2\omega),ani} = A_0 T_p \Gamma \zeta f_s \{[F_c t_s^{\ 2}\cos^2(\Delta\alpha) + (3F_c f_c^{\ 2} + 4F_s f_s f_c) t_p^{\ 2}\sin^2(\Delta\alpha)] + f_c F_c t_s t_p \sin(2\Delta\alpha)\sin(4\phi) - F_c[t_s^{\ 2}\cos^2(\Delta\alpha) - f_c^{\ 2} t_p^{\ 2}\sin^2(\Delta\alpha)]\cos(4\phi)\}[E_0]^2.$$

(2.41b)

Here, ϕ is the azimuthal angle between the [100] crystal axis and the incident plane.

For the $(\Delta\alpha, \Delta\beta)$ polarization, the total SH field arising from bulk anisotropic source is

$$E_{\Delta\alpha,\Delta\beta}^{(2\omega),ani} = E_{\Delta\alpha,s}^{(2\omega),ani}\cos(\Delta\beta) + E_{\Delta\alpha,p}^{(2\omega),ani}\sin(\Delta\beta). \quad (2.42)$$

The isotropic SH field arising from both bulk and surface sources is written together as

$$E_{\Delta\alpha,\Delta\beta}^{(2\omega),iso} = (A_0 T_s \partial_{15} f_s t_s t_p \sin(2\Delta\alpha)\cos(\Delta\beta) + A_0 T_p \{[\varepsilon(2\omega)\partial_{31} + \gamma] F_s [t_s^{\ 2}\cos^2(\Delta\alpha) + t_p^{\ 2}\sin^2(\Delta\alpha)] + [\varepsilon(2\omega)(\partial_{33} - \partial_{31}) F_s f_s^{\ 2} - 2\partial_{15} f_s F_c f_c] t_p^{\ 2}\sin^2(\Delta\alpha)\}\sin(\Delta\beta))[E_0]^2.$$

(2.43)

Thus, the total SH field under the $(\Delta\alpha, \Delta\beta)$ polarization is

$$E_{\Delta\alpha,\Delta\beta}^{(2\omega)} = E_{\Delta\alpha,\Delta\beta}^{(2\omega),ani} + E_{\Delta\alpha,\Delta\beta}^{(2\omega),iso}. \quad (2.44)$$

In case that there is an EFISH effect, we treat it as an additional SH contribution. The surface EFISH field is easily treated by replacing ∂_{15}, ∂_{31}, and ∂_{33} with $\partial_{15} + \partial_{15}^d$, $\partial_{31} + \partial_{31}^d$, and $\partial_{33} + \partial_{33}^d$, respectively.

For the $(\Delta\alpha, \Delta\beta)$ polarization, the bulk EFISH field is calculated following Green's function formalism [48, 51], written as

$$E^{BE,(2\omega)}_{\Delta\alpha,\Delta\beta} = (A_0 T_s \Gamma^d \eta^d f_s t_s t_p \sin(2\Delta\alpha)\cos(\Delta\beta) + A_0 T_p \Gamma^d F_s \{\gamma^d [t_s{}^2 \cos^2(\Delta\alpha) + t_p{}^2 \sin^2(\Delta\alpha)] + (2\eta^d f_s + f_s{}^2 \zeta^d) t_p{}^2 \sin^2(\Delta\alpha)\} \sin(\Delta\beta))[E_0]^2 .$$

(2.45)

2.4 Separation of bulk and surface SH contributions

Using SHG as a surface-specific probe for centrosymmetric materials is based on the fact that SHG is forbidden under the dipole approximation in the bulk but allowed at the surface. The involvement of a bulk SH contribution complicates the interpretation of SHG data. Separation of bulk and surface contributions is a problem of fundamental importance if one intends to use SHG as a strict surface probe. Great effort has been put on the bulk-surface discrimination [26, 52, 53], but it has been shown that it is fundamentally difficult under certain circumstances, even for static medium properties [28]. If there exists any time-dependence of SHG or EFISH effect, discrimination of different SH contributions would be considerably complicated. The theoretical predictions also show that there is no advantage in using vicinal Si surfaces to distinguish different SH contributions because the surface susceptibility tensor for vicinal surfaces is much complicated.

For simplicity, we consider SHG from a flatcut Si(001) face without any time-dependent effect of SHG and EFISH effect. If all of the five independent tensor elements ζ, γ, ∂_{15}, ∂_{31}, and ∂_{33} are known, SH response from the Si(001) surface would be fully determined, and then different SH contributions would be neatly separated. We consider here the possibilities of separation of these elements by combining polarization selection and RA-SHG. From our theoretical predictions, the *h*-polarized SH fields $E_{g,h}^{(2\omega)}$ are related to the *g*-polarized incident fundamental fields E_g by the following equations,

$$E_{g,s}^{(2\omega)} = a_{4,(g,s)} \sin(4\phi) e^{i\delta_{g,s}} E_g^2 , \tag{2.46}$$

$$E_{g,p}^{(2\omega)} = [a_{0,(g,p)} + a_{4,(g,p)} \cos(4\phi)] e^{i\delta_{g,p}} E_g^2 , \tag{2.47}$$

where the polarization (*g* or *h*) of both fields is limited to be *s* or *p*. On the other hand, for a special polarization (*q, s*), this relation takes the form,

$$E_{q,s}^{(2\omega)} = [a_{0,(q,s)} + a_{4,(q,s)}^{s} \sin(4\phi) + a_{4,(q,s)} \cos(4\phi)] e^{i\delta_{q,s}} E_q^2 . \tag{2.48}$$

Here, the letter *q* (-*q*) represents the linear polarization that is 45^{o} counterclockwise (clockwise) from *s* when facing in the propagation direction.

The Fourier coefficients in Eqs. (2.46)-(2.48) are functions of susceptibility tensor elements and linear optical preparation factors, as shown in Eqs. (2.41)-(2.43). We choose the anisotropic coefficient a_4 be positive and real (with its phase included in $\delta_{g,h}$), then the isotropic term a_0 is complex in general and can be split into real and imaginary parts, written as $a_0 = a_{0,r} + ia_{0,i}$. Because all of the a_4's for different polarizations are a function of the bulk anisotropic tensor element ζ, they are related by linear optical coefficients. The SH intensity is proportional to the magnitude square of the SH field. For cubic centrosymmetric media, ζ is usually nonzero, so is a_4. From Eq. (2.46), the (*p, s*) or (*s, s*) RA-SHG intensity should show eightfold symmetry. From Eqs. (2.47) and (2.48), the (*p, p*), or (*s, p*), or (*q, s*) RA-SHG intensity may show either eightfold or fourfold symmetry, depending on whether $a_{0,r}$ is zero or not. For the (*p, p*) polarization, if the RA-SHG intensity shows fourfold symmetry, the peak locations of RA-SHG discerns the sign of $a_{0,r}$, i.e., if a peak appears at ϕ=0°, $a_{0,r} > 0$, and if a peak appears at ϕ=45°, $a_{0,r} < 0$.

From one scan of either (*s, s*) or (*p, s*) RA-SHG signal, the absolute value of ζ can be determined by fitting the RA-SHG to Eq. (2.46). We note that it also possible to avoid the ζ SH contribution by combining polarization and RA-SHG, for example, by measuring the (*s, p*) polarized SH signal at a fixed azimuthal angle ϕ=0°. The relative phase between the SH field and fundamental field is unknown from only intensity measurement. The surface tensor element ∂_{15} is determined from the (*q, s*) RA-SHG signal with the known ζ. For the (*q, s*) polarized RA-SHG, bulk and surface SH contributions can be strictly separated in theory. As shown in Eq. (2.43), ∂_{31} and γ are always together, thus thorough separation of ∂_{31}, γ, and ∂_{33} is impossible from this theory. However, if the γ contribution is negligible, ∂_{31} is determined from (*s, p*) RA-SHG, and then ∂_{33} is determined from (*p, p*) RA-SHG.

The anisotropic coefficient $a_{4,(p,s)}$ can be obtained from fitting the measured (*p, s*) RA-SHG signal to Eq. (2.46), the remaining $a_{4,(g,h)}$ of other polarizations and $a^{s}_{4,(q,s)}$ are derived using optics coefficients that take into account linear propagation and beam geometry. Both the real part ($a_{0,r}$) and the imaginary part ($a_{0,i}$) of a_0 can be extracted from the measured RA-SHG signals using Eqs. (2.47) and (2.48); however, the value of a_0 can not be uniquely determined by only one scan of RA-

SHG. For example, both $a_{0,r} \pm i a_{0,i}$ give the same RA-SHG intensity as shown from Eq. (2.47), i.e.,

$$|E_{g,p}^{(2\omega)}|^2 = |[a_{0,r,(g,p)} \pm i a_{0,i,(g,p)} + a_{4,(g,p)} \cos(4\phi)]E_g^2|^2 \quad (2.49)$$

We present a theoretical method to solve the ambiguity in fit coefficients by combining two scans of differently polarized RA-SHG signals. By subtracting the *(-q, s)* RA-SHG signal from the (*q, s*) RA-SHG signal, as shown from Eqs (2.41)-(2.44), we obtain the difference between these two scans of RA-SHG signal, which is proportional to

$$\begin{aligned} &|E_{q,s}^{(2\omega)}|^2 - |E_{-q,s}^{(2\omega)}|^2 = \{4[a_{0,r,(q,s)} + a_{4,(q,s)} \cos(4\phi)]a_{4,r,(q,s)}^s \sin(4\phi) \\ &+ 4a_{0,i,(q,s)} a_{4,i,(q,s)}^s \cos(4\phi)\} |E_q^4| \end{aligned} . \quad (2.50)$$

This is a linear function of the fit coefficients $a_{0,r,(q,s)}$ and $a_{0,i,(q,s)}$; therefore, ∂_{15} can be uniquely determined. To determine ∂_{31} uniquely, which is impossible from only one scan of the (*s, p*) RA-SHG, we need combine a differently polarized scan of RA-SHG. A convenient example is subtracting the (*s, -q*) polarized RA-SHG signal from the (*s, q*) polarized RA-SHG signal, then we obtain a similar linear fit equation as Eq. (2.50). Similarly, by combining appropriate RA-SHG scans ∂_{33} can be determined uniquely.

2.5 Summary

We have used a phenomenological theory of SHG to predict the symmetry properties of RA-SHG from Si surfaces. Four SH sources (surface dipole, bulk quadrupole, surface EFISH, and bulk EFISH) have been systematically calculated. For vicinal Si(001) surfaces, the polarizations of both the fundamental and harmonic fields were limited to *s* or *p* in the calculation. For the Si(001) surface, we considered configurations of mixed linear polarization.

Both the surface dipole and surface EFISH contributions can be combined into an effective surface dipole response, which is isotropic for the Si(001) surface but anisotropic for vicinal Si(001) surfaces. The bulk EFISH effect, which is characterized by ζ^d, η^d, and γ^d, can not be combined into the bulk quadrupole response, which is characterized by ζ and γ. The ζ contribution is anisotropic for both major and vicinal Si(001) surfaces, but the ζ^d contribution is anisotropic for vicinal Si(001) surfaces but isotropic for the Si(001) surface. The remaining tensor elements η^d, γ^d, and γ are all isotropic.

For the Si(001) surface, we showed that bulk and surface SH contributions can be separated exactly both in theory and in experiment by combining polarization selection and RA-SHG. In addition, we presented methods of uniquely determining both the amplitude and the phase of individual susceptibility tensor elements from RA-SHG scans.

Compared with other crystalline Si surfaces, the Si(001) surface is characterized by the simplest surface susceptibility tensor. Furthermore, for the Si(001) surface, it is possible to separate out or eliminate the bulk anisotropic SH contribution, which is independent of surface conditions and can be used as a reliable reference signal for surface SHG. Both properties are significant advantages of using the Si(001) surface for SHG studies.