

How Nonlinear Optics can be Simplified to Study Molecular Deposition and Surface Vicinality of a Si(001) Interface

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Abstract. Second-harmonic-generation (SHG) has long been considered as a powerful optical surface diagnostic tool due to its ability to sense optical surface properties in centrosymmetric material. In a series of papers Aspnes et. al. showed that azimuthal measurements of rotated samples can be described by the so called simplified bond-hyperpolarizability model (SBHM) [G. D. Powell, J. F. Wang, and D. E. Aspnes, Phys. Rev. B 65, 205320 (2002)]. In this work, their model is applied to show how small changes in the step hyperpolarizability and vicinal angle of a Silicon (001) interface affects the second harmonic generation (SHG) intensity profile significantly, suggesting that real time surface deposition and interface vicinal angle monitoring using SHG is possible.

1. Introduction

The application of nonlinear optics is not limited in the fields of physics but also in chemistry, material science, and biology [1]. One of the possible and widespread method in studying surface layers using nonlinear optics is second harmonic generation (SHG) in non centrosymmetric crystals [2]. In a recent work, SHG microscopy combined with interferometry can also be used as a nonlinear imaging device to study corrosion effects at material surfaces [3]. All the mentioned technological applications and benefit of nonlinearity cannot be achieved without a firm theoretical understanding of the basic physical laws that can be constructed from a physical model.

Although higher order multipole effects such a quadrupole or magnetic dipole can still contribute to SHG from within the bulk, its effect are usually minor in vicinal centrosymmetric semiconductor due to the large surface anisotropy. Notable work was performed to explain the Rotational Anisotropy (RA) SHG data from a vicinal Si surface using phenomenological model [4] but is still too complex because it requires up to 10 fitting parameters. The model was later modified by Powell et. al. [5] who showed using an anharmonic bond model, assuming that the SHG comes from charges polarized along the atomic bonds that it requires just three independent fitting parameters. Later it was shown that the SHG susceptibility in the previous phenomenological model (group theory) and bond model (bond products) are connected [6] and even developed to explain third harmonic (THG) and electric field induced second harmonic (EFISH) in metal oxide semiconductors [7]. Most recent works that apply the hyperpolarizability model is the investigation of SHG from bulk dipolar contribution in



zincblende structure [8] and interface dipole versus bulk quadrupolar SHG contribution in diamond semiconductor using arbitrary input polarization angle [9]. It will be shown here that such model can also be applied to interpret RASHG intensity during molecular deposition by assigning a change in the effective hyperpolarizability, which will influence the peak profile due to the modification of the interface e.g. filled terrace-steps.

2. Simplified Bond Hyperpolarizability Model

SBHM is a phenomenological model that is based on a classical electrodynamics. As a phenomenology theory, SBHM is still based on the fact that one requires experimental fitting to determine the nonlinear hyperpolarizability. A previous phenomenological model describes the nonlinear polarization source at the surface/interface through a polarization sheet and apply standard transmission and reflection analysis at the boundary of this sheet, deriving the nonlinear susceptibility from group theory (GT) [10]. However it can be shown that GT and SBHM are closely related [6, 11]. In addition, the bond model in [5] handle this source term in a straightforward fashion by viewing it as dipole sources driven by the incoming electric field. Governed by an anharmonic Lorentz model, the charge inside the material experience anharmonic oscillation and producing nonlinear radiation that can be detected in the far field.

Originally, SBHM takes the following assumptions: The nonlinear radiations are only produced by anharmonic dipoles that are oscillating along the bonds. It has to be stated though that other sources can still generate SHG inside the material such as bulk quadrupole, spatial dispersion, and EFISH. Nevertheless, SHG from vicinal diamond semiconductor seems to be very well modelled by assuming only surface dipoles since bulk dipole radiation inside the bulk is forbidden due to parity [12] whereas for a flat (non vicinal) Si surface/interface, bulk quadrupole contribution should be considered too as the *p*-in *p*-out sixfold SHG intensity profile from Rotational Anisotropy SHG can only be fitted if bulk effects such as spatial dispersion and bulk quadrupole effects are applied [13].

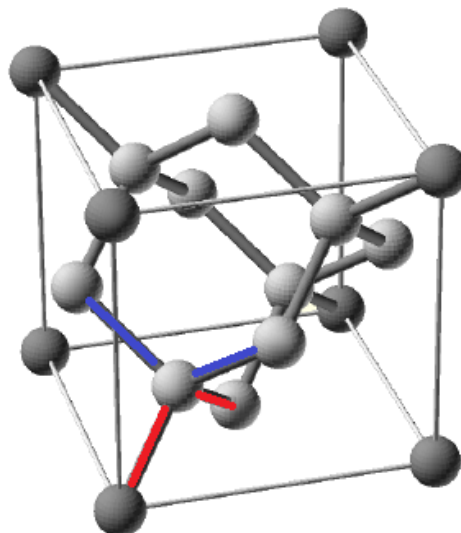


Figure 1. IUPAC unit cell for Si(001) facet and definition of the up bond unit vectors (blue) and down bond unit vectors (red) [14].

It can be seen from Fig. 1 which depict the unit cell according to the International Union of Pure and Applied Chemistry (IUPAC) that a Si(001) surface/interface has the following bond unit vectors:

$$\hat{\mathbf{b}}_1 = \begin{pmatrix} -\frac{1}{\sqrt{2}} \sin \frac{\beta}{2} \\ -\frac{1}{\sqrt{2}} \sin \frac{\beta}{2} \\ -\cos \frac{\beta}{2} \end{pmatrix} \quad \hat{\mathbf{b}}_2 = \begin{pmatrix} \frac{1}{\sqrt{2}} \sin \frac{\beta}{2} \\ \frac{1}{\sqrt{2}} \sin \frac{\beta}{2} \\ -\cos \frac{\beta}{2} \end{pmatrix} \quad \hat{\mathbf{b}}_4 = \begin{pmatrix} -\frac{1}{\sqrt{2}} \sin \frac{\beta}{2} \\ \frac{1}{\sqrt{2}} \sin \frac{\beta}{2} \\ \cos \frac{\beta}{2} \end{pmatrix} \quad \hat{\mathbf{b}}_5 = \begin{pmatrix} \frac{1}{\sqrt{2}} \sin \frac{\beta}{2} \\ -\frac{1}{\sqrt{2}} \sin \frac{\beta}{2} \\ \cos \frac{\beta}{2} \end{pmatrix}$$

where $\beta = 109.47^\circ$ is the angle between two bonds in a Si lattice. In reality the outermost surface layer in Si(001) can differ due to cut roughness by one or two steps of one atomic layer which will change the bond orientation by a shift of $\frac{\pi}{2}$. Therefore we should have to define two times four bond vectors in respect to the double domain nature of the surface:

$$\hat{\mathbf{b}}_5 = -\hat{\mathbf{b}}_1 \quad \hat{\mathbf{b}}_6 = -\hat{\mathbf{b}}_2 \quad \hat{\mathbf{b}}_7 = -\hat{\mathbf{b}}_3 \quad \hat{\mathbf{b}}_8 = -\hat{\mathbf{b}}_4$$

The ratio between the two domains can differ from 50% – 50% to 0% – 100% depending on the puritiness of the cut which can be considered in the calculations by multiplying both groups of four bond vectors with the surface ratio respectively. For the sake of simplicity, the ideal case is assumed thus only one domain consisting of the previous four bond vectors is considered in the simulation.

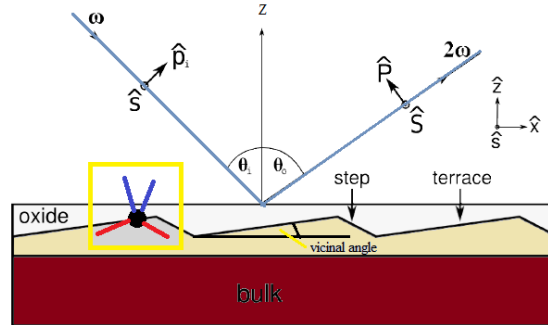


Figure 2. Vicinal Si(001) interface and optical axis of the system for a *p* polarized fundamental input and *p* polarized second harmonic output. The yellow box shows that the two down bonds are affected by the terrace and steps and thus its hyperpolarizability must be modified. Image extended from Ref. [15].

To account for the vicinality of the surface the rotation matrix around the *y*-axis is introduced:

$$R_y(\gamma) = \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ 0 & 1 & 0 \\ -\sin \gamma & 0 & \cos \gamma \end{pmatrix} \quad (1)$$

where γ is the vicinal angle. Considering that the sample can be rotated about the *z* axis, rotation of the bond direction along this axis for an angle ϕ gives:

$$\hat{\mathbf{b}}_j(\phi) = \mathbf{R}_z(\phi) \cdot \hat{\mathbf{b}}_j \quad (2)$$

where $R_z(\phi)$ is the common rotation matrix:

$$R_z(\phi) = \begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (3)$$

The SHG polarization produced by dipolar interfacial sources can be modelled in the SBHM via [5, 13]:

$$\begin{aligned} \mathbf{P}_D^{(2),\text{interface}} &= \chi_D^{(2)} \cdot \mathbf{E}_{\text{int}} \mathbf{E}_{\text{int}} \\ &= \frac{1}{V} \sum_{j=1}^n \left(\alpha_{2j} \hat{\mathbf{b}}_j \hat{\mathbf{b}}_j \hat{\mathbf{b}}_j \right) \cdot \mathbf{E}_{\text{int}} \mathbf{E}_{\text{int}} \end{aligned} \quad (4)$$

where $\chi_D^{(2)}$ is the third rank susceptibility tensor; \mathbf{E}_{int} , is the field on the interface, α_{2j} is the interface dipolar SHG hyperpolarizability, V is the volume, n is the total number of bonds inside the considered conventional cell, and $\hat{\mathbf{b}}_j$ is the bond unit vector. For a non vicinal surface there are two hyperpolarizabilities namely *up* hyperpolarizability labelled as α_u for the two *up* bond ($\hat{\mathbf{b}}_1, \hat{\mathbf{b}}_2$) and a hyperpolarizability α_d for the two *down* bonds ($\hat{\mathbf{b}}_3, \hat{\mathbf{b}}_4$), whereas we only use one bulk hyperpolarizability for all of the bulk bonds because of symmetry. All hyperpolarizabilities can generally have a real and imaginary term. For a vicinal surface the two down bond hyperpolarizability are clearly affected by the cut as can be seen in Fig. 2. Therefore the two down hyperpolarizability should be changed accordingly to [16]:

$$\alpha_{eff,int} = (1 - |\tan \gamma|) \alpha_{terrace} + |\tan \gamma| \alpha_{step} \quad (5)$$

which reduces immediately to the initial hyperpolarizability if the surface is flat (e.g. $\gamma = 0$)

With the assumption before that the bond charges oscillate only along the bonds, the far-field radiation E_{ff} at the interface is [13, 5]:

$$\mathbf{E}_{ff,int}(\mathbf{r}) \propto [(\bar{\mathbf{I}} - \hat{\mathbf{k}}_{\mathbf{0}2\omega,int} \hat{\mathbf{k}}_{\mathbf{0}2\omega,int}) \cdot \mathbf{P}] \quad (6)$$

where $\hat{\mathbf{k}}_{\mathbf{0}2\omega,int}$ is the outgoing SHG vector from the interface.

3. Results and Discussions

Using Eq. (6) the far field can be obtained for a *p*-in *p*-out polarization because *pp* gives the most accurate changes in the SHG intensity profile compared to the other three polarization (e.g. *ps*, *sp*, and *ss*).

Fig. 3a depicts the SHG intensity for variation in the vicinity of the surface for a fix hyperpolarizability which we take for simplicity to be one. It can be seen that the vicinity will produce a change in the middle peak for an azimuthal angle of $\frac{\pi}{2}$ which is sensitive even to a 1° of change. For $\gamma = 0^\circ$ it is obvious that the simulation produces four equal heighted peaks corresponding to a C_{2v} surface symmetry whereas the bulk has T_d symmetry thus producing no even harmonic dipolar contribution. Therefore, using Rotational Anisotropy Spectroscopy (RA) SHG one can determine the vicinity of an unknown diamond sample by looking at the SHG intensity. However after the vicinity reaches 8° the middle peak vanishes and the simulation cannot distinguish further inclinations. Results for $\gamma = 9^\circ$ looks quite similar to experimental result given in Fig. 3 of Ref. [5] where there is a small asymmetry between the two peaks arising from a small difference in the terrace and step hyperpolarizability in the effective hyperpolarizability of the down bonds and in addition the middle peak is higher than in the simulation but can in principle be fitted. The point is nevertheless, that even small changes in vicinity can be observed from the peak profile height variation at the middle.

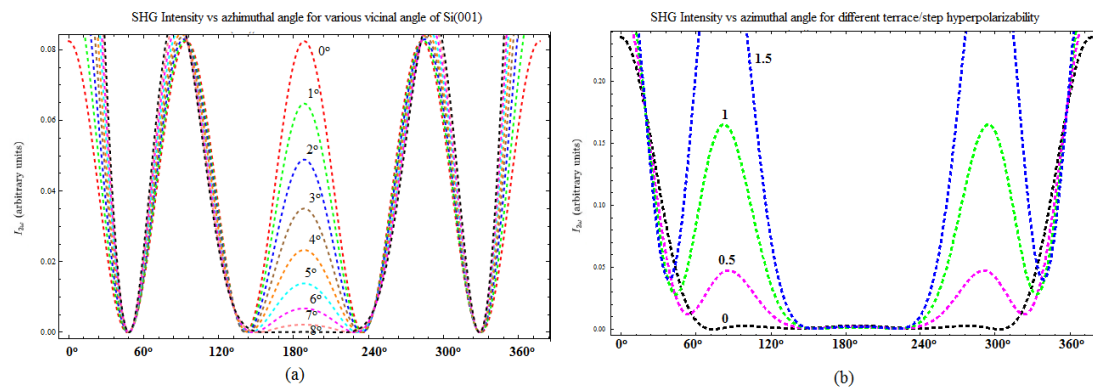


Figure 3. SBHM simulation for a Si(001) vicinal interface with (a) variations of the vicinal angle and (b) effective hyperpolarizability.

To investigate the effect of changes in the step and terrace hyperpolarizability, for example due to depositions of molecules on the surface of a vicinal diamond semiconductor, the effective hyperpolarizability is changed gradually by setting the $\alpha_{terrace} = \alpha_{step}$ respectively from 0, 0.5, 1 and 1.5. It can be seen from Fig. 3b that the peaks between $120^\circ - 160^\circ$ and $240^\circ - 300^\circ$ varies accordingly in a symmetric manner if we assume that the effective hyperpolarizability of the two down bonds are the same. An asymmetric peak will result if the hyperpolarizabilities of the two down bonds are not similar. Therefore one can use SBHM to determine possible surface contamination in vicinal structures. Finally, this method can also be applied for other different Si interface orientation such as Si(111) or Si(011) with different polarizations. Further work will be performed to investigate whether bulk effects such as spatial dispersion or quadrupole effects also play a significant role in vicinal centrosymmetric semiconductors.

4. Conclusions

It is demonstrated that for a Si(001) vicinal semiconductor that the *pp* polarization RASHG data can be combined with SBHM simulation to determine the surface vicinal angle and possible molecule deposition by monitoring the change in the SHG intensity peak profile.

5. References

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