Atomic Orientation Detection using Nonlinear Optics and its Application as an Environmental Sensor

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Abstract. Recent advances in theoretical nonlinear optics have enhanced our understanding regarding the origin of the higher harmonic generation in particular interpreting the higher harmonic intensity data from nonlinear spectroscopy. In this work we show that the atomic bond orientation at the surface as well as the bulk of an inversion symmetric material e.g. Silicon (111) facet can be determined from nonlinear spectroscopy alone without the need to apply the conventional X-Ray diffraction method. Our simulation shows that nonlinear spectroscopy data interpreted using bond models can reliably determine atomic orientation almost in a direct way because the model is based on a very simple assumption that the radiations are created from charges along the atomic bonds. In addition we present a brief description of possible application to use nonlinear spectroscopy as an environmental sensor.

Keywords: bond model, second harmonic generation, third harmonic generation, atomic orientation

1. Introduction

Material characterization using nonlinear spectroscopy method posses several advantages compared to its linear counterpart. The nonlinear technique applies femto or pico laser pulses as its incoming source on the sampled material which is nondestructive and does not require vacuum conditions as in linear optics. It has the advantage over the former in that more information can be obtained regarding the material symmetry due to the involvement of higher order (nonlinear) susceptibilities. It has been shown convincingly that linear spectroscopy will not reveal any changes in the output intensity for a Si(111) surface under azimuth rotation because it is linearly isotropic [1]. When using nonlinear spectroscopy however the second harmonic generation (SHG) intensity varies with respect to the rotating azimuth angle because unlike the linear part some elements in the tensor are anisotropic with regard to the azimuthal rotation. This feature provides valuable information regarding the atomic bond orientation at the nanoscale.

The possibility to determine atomic bond orientation using nonlinearity has been made available through the work of Powell et. al. [2] who introduced the bond hyperpolarizability model called simplified bond hyperpolarizability model (SBHM). Their key idea is that the driving nonlinear polarization inside the material creates anharmonic motion along the atomic bonds which produces dipole radiation that can be detected in the far field. This assumption is
valid for linear optics and SHG and to a good approximation also to THG although the latter may (or may not) require further assumption of transverse bond oscillation in addition to the charge oscillation along its atomic bonds. Although the bond model validity has been questioned especially when dealing with vicinal semiconductor surfaces [3] it was shown by Alejo-Molina et. al. [4] that this model is agreeing very well with crystal symmetry principle e.g. Group Theory and withstanding a crucial test when applied to zincblende systems as shown by Hardhienata et. al. [5]. These findings have brought the confidence of SBHM validity into a higher level.

2. Theory of Bond Model

In this work we show that the molecular bond direction of a diamond crystal with (111) orientation can be predetermined both at the interface and bulk using nonlinear spectroscopy simulation taking the assumption of the bond model. When only a single input frequency is applied the general response of the material can be stated macroscopically as:

\[
P(\omega) = \chi^{(1)}(\omega)E(\omega) + \chi^{(2)}(\omega)E^2(\omega) + \chi^{(3)}(\omega)E^3(\omega) + \ldots
\]  

where \(P(\omega)\) is the total polarization produced by the linear (first term in eq. 1) and nonlinear polarizations (second, third, etc. terms) inside the material. The linear and nonlinear susceptibilities are respectfully given by \(\chi^{(1)}\) and \(\chi^{(2)}, \chi^{(3)}\) and so forth. Here \(\chi^{(n)}\) is called the \(n\) – th order nonlinear susceptibility and \(E(\omega)\) is the incoming driving field. Because diamond crystal is centrosymmetric or non-inversion symmetric bulk dipolar contribution at the bulk is disallowed for even order higher harmonics due to parity symmetry when spatial dispersion is not considered. Hence the even order nonlinear susceptibility in eq. (1) is zero. In other words SHG can be used to determine the atomic bond orientation at the surface/ interface because the contribution from dipolar inside the bulk is zero although quadrupolar contribution may have to be taken into account [6-7]. Meanwhile, third harmonic generation (THG) is allowed at the bulk thus later we show how we can use THG to find out the molecular orientation inside the bulk. The advantage of using SHG and THG SBHM model simultaneously is that we can single out and identify different orientation at the interface and bulk.

![Figure 1. Atomic bond Orientation of a Si(111) facet (above, the upward bond is modelled by a different hyperpolarizability than the three down bonds (below).](image)

The theory of the simplified bond hyperpolarizability model (SBHM) has been firmly established and explained lengthily in several research papers, particularly in Refs. [1] and the curious reader is advised to read these works. In SBHM, particularly when doing second harmonic generation one first takes into consideration that the radiation comes from anharmonic oscillation of charges along the atomic bonds. According to the bond model the nonlinear far field for SHG and THG is calculated by:
\[ \vec{E}_{g_{2\omega}}(r) = \frac{k^2 \exp(ikr)}{4\pi\epsilon_0 rV} \left[ (\vec{T} - \hat{\vec{k}}k) \cdot \sum_{j=1}^{4} \vec{\alpha}_j \hat{\vec{b}}_j(\phi)(\vec{b}_j(\phi) \cdot \vec{E}_{loc})^2 \right] \]

\[ \vec{E}_{g_{3\omega}}(r) = \frac{k^2 \exp(ikr)}{4\pi\epsilon_0 rV} \left[ (\vec{T} - \hat{\vec{k}}k) \cdot \sum_{j=1}^{4} \vec{\alpha}_j \hat{\vec{b}}_j(\phi)(\vec{b}_j(\phi) \cdot \vec{E}_{loc})^3 \right] \]

where \( \vec{E}_{loc} \) is the local field and \( \hat{\vec{b}}_j(\phi) \) is the unit vector of the \( j \)th - bond. In principle for the Si case one can assume that the radiation is a sum of four bonds forming a tetrahedral structure (\( sp - 3 \) hybrid orbital). The intensity of the nonlinear radiation can be obtained by multiplying the field in eq. (2-3) with its complex conjugate partner. In addition for the THG case in Si, the correct intensity must also consider Fresnel coefficients because THG dipolar nonlinear radiation comes mainly from within the bulk (it is not symmetry forbidden for odd order nonlinear susceptibilities).

Consider now the case of a diamond Silicon wafer for example, whose orientation is unknown, e.g. we want to determine without other spectroscopic methods whether the orientation is in the 111 or 100 direction. What is needed is to rotate the sample 360° about the vertical axis say the \( -z \) axis and look at their intensity profile. The alerted reader may question the necessity to use nonlinear optics rather than just use linear rotational spectroscopy which is easier and cheaper to set up experimentally. The answer is that the linear radiation profile is isotropic with regard to rotation along the vertical axis for diamond and cubic lattices, the former belongs to Silicon which forms the backbone of modern day microelectronics. This can be traced back by looking at the linear susceptibility which is independent of the azimuthal rotation angle \( \phi \) for an incoming \( p \)-polarized and outgoing \( p \)-polarized light as depicted in figure 1 taken from Ref. [1].

In figure 2, the dashed lines depicts the linear radiation contribution from each of the Si(111) bonds at the surface/interface. Interestingly although the linear susceptibility is anisotropic the field contribution from each bond is not flat but varies harmonically. However, the total sum of the field when squared (intensity) produces a flat intensity profile. Because the experimenter only sees the total intensity the information regarding the atomic bond orientation at the surface is lost.

In contrary the nonlinear radiation – even the first order nonlinear susceptibility already contains some elements in the tensor that is a function of the rotational azimuthal angle \( \phi \). One can straightforwardly see this by computing SHG susceptibility via:
\[
\chi^{(2)}_{ijkl} = \frac{N}{V} \sum_{j=1}^{4} \alpha_j b_j(\phi) \otimes b_j(\phi) \otimes b_j(\phi)
\]  

(4)

where \( N \) and \( V \) are respectively the amount of nonlinear dipoles per volume that radiates the nonlinear field and is just a scaling factor. If we have a Si111 facet the bond orientations are:

\[
\hat{b}_1 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad \hat{b}_2 = \begin{pmatrix} \sin \beta \\ 0 \\ \cos \beta \end{pmatrix} \quad \hat{b}_3 = \begin{pmatrix} -\frac{\sin \beta}{2} \\ \frac{1}{2} \sqrt{3} \sin \beta \\ \cos \beta \end{pmatrix} \quad \hat{b}_4 = \begin{pmatrix} -\frac{\sin \beta}{2} \\ -\frac{1}{2} \sqrt{3} \sin \beta \\ \cos \beta \end{pmatrix}
\]  

(5)

Thus nonlinear optics reveals more information about the symmetry of the material than linear optics. In the following section we will discuss the relevant results to determine the atomic orientation of a Si facet using SHG and THG.

3. Results and Discussion

The intensity for SHG is plotted for a Si(111) orientation can be obtained by squaring the far field in eqs. (2) and is presented in figure 3.

3.1 Results

The SHG intensity peaks can be explained as follows. When the Si(111) facet is shined by a \( s \) (fundamental) \(-\)incoming and \( s \) (SHG) \(-\)outgoing polarized light 6 intensity peaks are obtained. This can be explained from the basic assumption that each down bonds contribute twice to the peak, namely when the \( s \) incoming field is parallel to the bond direction which happens twice. Because there are 3 down bonds there are 6 peaks with equal height where each peak differ by a phase of \( \pi/3 \). Now assume that we do not know exactly how the atoms are oriented at the surface. By knowing experimentally that there are 6 equal peaks for the ss polarization we can guess using SBHM that the surface has \( C_{3v} \) symmetry so the orientation of the Si should be (111). If experimentally we have for the \( p \) \(-\)incoming and \( p \)\(-\)outgoing polarization 4 peaks instead it can analogously be shown using
SBHM that the orientation is Si(001) because the two bonds pointing upwards contribute 2 peaks whereas the two down bonds also contribute to 2 peaks this contrary to the case of a Si(111) $pp$ SHG intensity because we expect only 3.

It is also notable that using SBHM we can determine the azimuthal orientation of the atoms inside a material by looking at which azimuthal angle the peaks occur. For the sake of clarity it is instructive to look at figure 4 which depicts a top view of the Si(111) surface. The blue line indicates the direction of the s-field. By careful analysis of the ss peaks it can be inferred that the first peak occurs after a rotation of $\frac{\pi}{6}$ so the down bond orientation at the surface before the rotation has to be as depicted. It must be stated that one cannot distinguish between any of the three down bonds so in this case the $b_3$ down bond can also be arbitrarily labelled as $b_2$ or $b_4$. Thus nonlinear optic RASHG can also serve as a direct method to access the molecular orientation especially for low symmetry structures such as Si.

![Figure 4](image.png)

**Figure 4.** Top view orientation of the atomic bonds at the interface and bulk (in this case it is the same) for Si(111) (left).

The before mentioned discussion applies SHG to investigate surface atomic bond orientation which is valid because dipolar contribution are forbidden from within the bulk. Although this statement is not strictly correct because quadrupolar contribution from within the bulk also fairly contributes to the total SHG intensity, for certain cases such as Si(111) it does not produce significant change as to shift the phase of the peaks but only interferes with the dipolar contribution to increase or decrease the intensity peaks [6-7] as long as the atomic orientation at the surface and bulk are the same. Otherwise, one can still determine the atomic orientation but require a more complex model by assuming a different bond orientation for the quadrupolar SBHM model and add the fields with the dipolar surface radiation which is beyond the scope of our discussion.
Another nice feature of nonlinear optics is the ability to use other harmonics in this case third harmonic generation (THG) to investigate the atomic orientation inside the bulk. It is well known that THG and other odd order nonlinear radiations are not dipole forbidden in centrosymmetric materials such as Si(111) so THG can be applied in analogy with SHG but in this case for guessing bulk atomic bond orientation. The THG intensity obtained by squaring eq. (3) is presented in figure 5. The simulation result that were obtained are in excellent agreement with the RASHG experimental data for a Si(111) orientation [8]. In a similar way, one can construct the SBHM model for THG and compare it with the experimental data to determine the atomic orientation as well as its position azimuthally before the rotation.

As a side note, we would also describe briefly the future potential of RASHG experiment backed by SBHM model to detect molecular deposition at the surface using nonlinear optics. Nonlinear optics offers many advantages in this regard because one can monitor atomic deposition such as oxygen gas in real time, without the need for ultra high vacuum, and in a non-destructive way. It has been relatively well understood that SHG can be applied to describe the surface kinetics of simple gas such as the dissociation of molecular oxygen at the Si/SiO$_2$ surface [9]. SBHM simulation can very well model SHG radiation from vicinal surfaces where it has also been shown by one of us recently using SBHM [10] that such configuration can sensitively detect atomic deposition and the vicinal angle. It is therefore suggested to modify this model accordingly e.g. include dimmer bonds for surface atoms opening the possibility to construct an environmental sensor especially using thin film semiconductors as substrate.

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