Symmetry Analysis of ZnSe(100)/Air Interface By Second Harmonic Generation

Xiangyang Song\(^1\), Arnold Neumann, Rein Maripuu, Wolfgang Seibt, and Kai Siegbahn\(^*\)

ESCA-Laser Lab., Uppsala University, S-751 21, Uppsala, Sweden

\(^1\)Shanghai Institute of Optics and Fine Mechanics, P. O. Box 800-211, P. R.China

Abstract

We measured the polarized and azimuthal dependencies of optical second harmonics generation (SHG) on polished surfaces of ZnSe(100) single crystal surface in air, using a fundamental wavelength of 1.06\(\mu\)m. By considering both, the bulk- and surface- optical nonlinearities within the electric dipole approximation, we analysed the data for all four combination of \(p\)- and \(s\)-polarized incidence and output. The measurement using \(S_{in} - S_{out}\) is thereby particularly useful in the determining of the symmetry ZnSe(100)/contamination layer-interface, which would lower the effective symmetry of ZnSe(100) from \(C_{4v}\) to \(C_{2v}\). The analysis of \(p\)-incident and \(p\)-output configuration allows us to distinguish the [011] and [0\(\overline{1}\)1]- directions.

I. INTRODUCTION

Optical Second Harmonic Generation (SHG) has matured to be an effective surface- and interface-sensitive technique for probing a large variety of surface- and interface-properties. This technique is a non-destructive. It can be used for \textit{in-situ} measurements in almost any environment, provided that we have optical access to the sample \[\text{[1,2,3]}\]. The method bases on the idea that generally a surface and a bulk have different structural symmetry.
Materials with inversion symmetry, such as Si- and Ge- single crystals have no bulk electric-dipole contribution. Electric quadrupole and magnetic dipole contributions originate the leading source in SHG from the bulk. However, a surface or an interface breaks the inversion symmetry and produces an electric-dipole contribution. Generally the SHG-intensity from a surface or an interface can be compared to be much greater than that from the bulk, depending on the material, the photon energy, and the geometry of the experiment. On the other hand, noncentrosymmetric materials like crystals with the zincblende structure as, e.g. the compound semiconductors GaAs and ZnSe, have intense bulk electric-dipole contributions to the SHG, thus hampering surface observations. Stehlin et al [5] illustrated possible combinations of the polarization of incident and SHG output light and of crystal azimuths for which only the surface contribution may be deduced for typical low index surface, e.g. (001), (110), and (111) and used SHG as effective surface probe with submonolayer sensitivity to monitor the adsorption of Sn on GaAs(001) surface. Later, S. R. Armstrong et al [7] investigated by means of SHG a GaAs(100)/air interface. Similar experiments performed by C. Yamada and T. Kimura [8,?] firstly observed the twofold rotational angle dependence (rotation anisotropy) of SHG in the reflected light from a well prepared and by RHEED characterised noncentrosymmetric single crystal surface of GaAs(100). They interpreted it as the interference of surface SHG and dipole-allowed bulk SHG having fourfold symmetry results in twofold anisotropy, whereby the degree of rotational anisotropy monitors the surface reconstruction. Galeckas et al [10] showed that SHG in reflection is a sensitive and practical method to investigate the departure from perfect crystalline order at the surface by studying the SHG rotational anisotropy of crystalline, polycrystalline and amorphous silicon carbide surfaces. Bottomley et al [11] determined to within $\pm0.1^\circ$ the orientation of vicinal GaAs(001) and Si(111) single crystal wafers using second and third harmonic generation. M. Takebayash et al [12] demonstrated the SHG-measurement of the tilt angle $\theta$ of the crystallographic axis of a vicinal GaAs(100) wafer towards a direction $\xi$ that characterises step direction and step height and forms an angle $\psi$ with respect to [100]-axis and found that the $s$-incident polarization is useful in the
determination of this tilt angle. C. Jordan et al [13] used the azimuthal rotational anisotropy of the SHG for in-situ fingerprint characterisation of various polytypes of SiC and compared with X-ray diffraction (XRD) and identify defect regions in big samples by observing the spatially resolved dependence of the SH-intensity.

In recent years, there has been big interest in wide-band gap II-VI compound semiconductors. In particular, ZnSe is being actively studied due to their electroluminescent properties in blue-light-emitting laser diodes [?]. These devices are fabricated by epitaxial growth on GaAs substrates. The replacement of GaAs substrates by ZnSe ones may decrease the concentration of defects and increase the lifetime of the device. This can be one possible way to improve ZnSe-based laser characteristics. An recent observation in ZnSe/ZnCdSe laser diodes grown onto ZnSe substrates indicates that the growth rate of the defects is much smaller than for layers grown onto GaAs substrates [15]. For the successful growth of II-VI epilayers onto ZnSe layers is very importment to have well ordered substrate surfaces. However, the superiority of ZnSe substrates over GaAs one has not been realised yet, mainly because it is difficult to obtain high-quality ZnSe substrates.

SHG has been successfully applied to the study of semiconductor surfaces semiconductor/semiconductor heterostructures and interfaces, and semiconductor-oxide interfaces [1] and provides a powerful tool for understanding the energetics of various defect formations and surface reconstructions. Although these experiments have been performed mostly for GaAs surface [1,7–9] or SiC surface [10,13], similar symmetric studies were not extend to many other non-centrosymmetric materials, such as ZnSe.

In this paper, we have measured the SH intensity from ZnSe(100) as a function of the light polarization and as a function of the azimuthal angle. We have also calculated the intensity of SHG from the surface electric dipoles and the the second-order nonlinear polarization arising from the bulk response. We use optical SHG to determine the macroscopic symmetry properties of the ZnSe(100)/air interface. The remainder of the paper is organized as follows. In Sec. II, the theory for SHG in reflection from the bulk and surface of nonsymmetric crystals is briefly introduced. Then the experimental apparatus is described in Sec. III, and
finally the results are analyzed in terms of symmetry.

II. THEORY

A. General

We can express the induced nonlinear surface polarization at an interface in the following manner: [5]

\[ P_{\text{eff}}(2\omega) = P_{\text{surf}} + P_{\text{bulk}} F(\omega) F(2\omega) L_{\text{eff}}, \]  

(1)

where \( F(\omega) \) and \( F(2\omega) \) are the Fresnel factors for the incident input and output fields, and \( L_{\text{eff}} = (W + 2w)^{-1} \) is the effective phase-matching distance of the substrate with \( W = k_{\omega,z} \) and \( 2w = k_{2\omega,z} \) representing the \( z \) component of the wave vectors of the fundamental and SH light, respectively, \( P_{\text{surf}} \) is the surface nonlinear polarization of the interfacial layer, and \( P_{\text{bulk}} \) is the bulk nonlinear polarization in medium.

The bulk nonlinear polarization can generally be expressed by a series of multipole terms: [16]:

\[ P_{\text{bulk}}(2\omega) = P^{(2)}(2\omega) - \nabla \cdot Q^{(2)}(2\omega) + \frac{c}{2i\omega} \nabla \times M^{(2)}(2\omega), \]  

(2)

where \( P^{(2)}, Q^{(2)}, \) and \( M^{(2)} \) describe the electric-dipole polarization, electric-quadrupole polarization and magnetic-dipole polarization respectively. Up to the first derivative in \( P_{\text{eff}} \), the three polarization sources are the following:

\[ P^{(2)}(2\omega) = \chi^D : E(\omega) E(\omega) + \chi^P : E(\omega) \nabla E(\omega), \]  

(3)

\[ Q^{(2)}(2\omega) = \chi^Q : E(\omega) E(\omega), \]  

(4)

\[ M^{(2)}(2\omega) = \chi^M : E(\omega) E(\omega). \]  

(5)

We neglect \( M \) and higher-order multipole in our discussion here, because these contributions are thought to be orders of magnitude smaller than the electric dipolar contribution. The
second terms in eq. (2) and (3) arises from the gradient of the field $E(\omega)$. Since the penetration depth in crystals ($\sim 100 \text{Å}$) is much smaller than the spatial variation of the field ($\sim 10,000 \text{Å}$ for optical frequencies), this bulk contribution is small under nonresonant conditions. [17]

The surface contribution of the SH field arises from two effects. First, at the interface between the dissimilar media, inversion symmetry is broken for centrosymmetric crystals and symmetry is changed for noncentrosymmetric crystals, and so a dipolar contribution to SHG can exist. In addition, there is a discontinuity in the fundamental electric field normal to the surface. This can generate a sizable SH contribution through higher-order multipole terms. So the surface contribution to the nonlinear polarization can be expressed as:

$$P_{\text{surf}}^{(2)}(2\omega) = \chi^D : E(\omega)E(\omega) + \chi^D : E(\omega)\nabla E(\omega) - \chi^Q : \nabla E(\omega)E(\omega).$$  

Since the tangential components of the incident electric field are continuous across the interface, all terms in eq. (6) involving a gradient that can be neglected when describing an in-plane surface response and only the first term should be considered:

$$P_{\text{surf}}^{(2)}(2\omega) = \chi^D : E(\omega)E(\omega).$$  

If the nonlinear susceptibilities are all defined in terms of the input field $E(\omega)$, in the interfacial layer by $P(\omega) = \chi^{(2)} : E(\omega)E(\omega)$, then from (2), the corresponding effective surface nonlinear susceptibility is given by

$$\chi_e^{(2)} = \chi_{\text{surf}}^{(2)} + \chi_{\text{bulk}}^{(2)}L_{\text{eff}}F(\omega)F(2\omega),$$  

where $\chi_{\text{surf}}^{(2)}$ and $\chi_{\text{bulk}}^{(2)}$ are the surface and bulk nonlinear susceptibility tensors, respectively.

The tensorial properties of $\chi_e^{(2)}$ can be exploited as: if the SH intensity is recorded as a function of azimuthal angle of rotation, the variation in intensity reflects the overall symmetry of the surface of interface.

A tensorial expression for the second-order polarization can be written as: [17]
\[
\begin{pmatrix}
\hat{x}(2\omega) \\
\hat{y}(2\omega) \\
\hat{z}(2\omega)
\end{pmatrix}
= \chi\begin{pmatrix}
\chi_{x\chi\chi} & \chi_{x\chi\psi} & \chi_{x\chi\zeta} & \chi_{x\psi\chi} \\
\chi_{\psi\chi\chi} & \chi_{\psi\chi\psi} & \chi_{\psi\chi\zeta} & \chi_{\psi\psi\chi} \\
\chi_{\zeta\chi\chi} & \chi_{\zeta\chi\psi} & \chi_{\zeta\chi\zeta} & \chi_{\zeta\psi\chi} \\
\chi_{\zeta\psi\chi} & \chi_{\zeta\psi\psi} & \chi_{\zeta\psi\zeta} & \chi_{\zeta\zeta\chi}
\end{pmatrix}
\begin{pmatrix}
E_x(\omega)E_y(\omega) \\
E_y(\omega)E_y(\omega) \\
E_z(\omega)E_z(\omega) \\
2E_y(\omega)E_z(\omega) \\
2E_x(\omega)E_z(\omega) \\
2E_x(\omega)E_y(\omega)
\end{pmatrix},
\tag{9}
\]

This is the general expression describing the interaction of the two EM driving fields being coupled through a dyadic product.

**B. Bulk contribution**

We now define a new set of coordinates \((\hat{x}', \hat{y}', \hat{z}')\) for each of the three crystal orientations such that \(z\) axis is perpendicular to each crystal face. For the (111) crystal face, we therefore have, in terms of the standard crystal axes \((\hat{x}, \hat{y}, \hat{z})\)

\[
\begin{pmatrix}
\hat{x}' \\
\hat{y}' \\
\hat{z}'
\end{pmatrix}
= R_1 \begin{pmatrix}
\hat{x} \\
\hat{y} \\
\hat{z}
\end{pmatrix} = \begin{pmatrix}
2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\
0 & 1/\sqrt{2} & -1/\sqrt{2} \\
1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3}
\end{pmatrix} \begin{pmatrix}
\hat{x} \\
\hat{y} \\
\hat{z}
\end{pmatrix},
\tag{10}
\]

where the new \(\hat{x}'\) axis is projected on to the original crystal \(\hat{x}\) axis in the plane of the crystal surface, and \((\hat{x}, \hat{y}, \hat{z})\) represents the principal-axis system of the crystal ([100], [010], [001]). For the (100) face we simply choose the \(\hat{x}\) axis to lie normal to the surface, the transformation matrix can be expressed by

\[
R_1 = \begin{pmatrix}
0 & 1/\sqrt{2} & -1/\sqrt{2} \\
0 & 1/\sqrt{2} & 1/\sqrt{2} \\
1 & 0 & 0
\end{pmatrix},
\tag{11}
\]

and for the (110) face crystal

\[
R_1 = \begin{pmatrix}
-1/\sqrt{2} & 1/\sqrt{2} & 0 \\
0 & 0 & 1 \\
1/\sqrt{2} & 1/\sqrt{2} & 0
\end{pmatrix}.
\]
We can define a set of unit vectors for the incident light beam $\hat{s}$, $\hat{k}$, and $\hat{z}$ such that $\hat{s}$ and $\hat{k}$ lie on the crystal face, perpendicular and parallel to the plane of incidence, respectively, and $\hat{z} = \hat{z}'$ is the surface normal,

$$
\begin{pmatrix}
\hat{s} \\
\hat{k} \\
\hat{z}
\end{pmatrix}
= 
R_0 
\begin{pmatrix}
\hat{x} \\
\hat{y} \\
\hat{z}
\end{pmatrix}
= 
\begin{pmatrix}
\sin \phi & - \cos \phi & 0 \\
\cos \phi & \sin \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\hat{x} \\
\hat{y} \\
\hat{z}
\end{pmatrix}.
$$

(12)

Here $\phi$ is the angle between $\hat{k}$ and $\hat{x}$, the azimuthal angle.

In many of the experiments, the single surface is rotated about its azimuthal angle $\phi$ and the SH response is analyzed with respect to the beam coordinates. Therefore, one needs to transform $\chi^{(2)}$ from crystal coordinates into beam coordinates, as shown in figure 1, with the appropriate transformation operations. The transformation rule for third rank tensors is the following:

$$
\chi_{ijk} = \sum_{l,m,n} R_{il} R_{jm} R_{kn} \chi_{lmn},
$$

(13)

where $R = R_0 R_1$ is the transformation operator from the crystal $(\hat{x}, \hat{y}, \hat{z})$ to beam $(\hat{s}, \hat{k}, \hat{z})$ coordinates.

Wide-gap zinc-blende II-VI semiconductors with symmetry $T_d(\overline{T}3m)$ are optically isotropic, but do not possess a center of inversion. The bulk second-order susceptibility tensor has only one component, $\chi_{xyz} = \chi_{yzx} = \chi_{zxy} = d$. Using the rule in Eq. (13), this tensor for the (100) face in beam coordinates can be written as

$$
\chi_{\text{bulk}}^{(2)}(\phi) = 
\begin{pmatrix}
0 & 0 & 0 & -\sin(2\phi)d & \cos(2\phi)d & 0 \\
0 & 0 & 0 & -\cos(2\phi)d & -\sin(2\phi)d & 0 \\
\cos(2\phi)d & -\cos(2\phi)d & 0 & 0 & 0 & -\sin(2\phi)d
\end{pmatrix},
$$

(14)

and for (111) face we have

$$
\chi_{\text{bulk}}^{(2)}(\phi) = 
\begin{pmatrix}
-\sqrt{\frac{2}{3}} \sin(3\phi)d & \sqrt{\frac{2}{3}} \sin(3\phi)d & 0 & 0 & -d/\sqrt{3} & -\sqrt{\frac{2}{3}} \cos(3\phi)d \\
-\sqrt{\frac{2}{3}} \cos(3\phi)d & \sqrt{\frac{2}{3}} \cos(3\phi)d & 0 & -d/\sqrt{3} & 0 & \sqrt{\frac{2}{3}} \sin(3\phi)d \\
-d/\sqrt{3} & -d/\sqrt{3} & 2d/\sqrt{3} & 0 & 0 & 0
\end{pmatrix}.
$$

(15)
The components of the fundamental field in the medium expressed in the beam coordinate axes are

\[ E_s t_s, \]
\[ E_k = f_c E_p t_p, \]
\[ E_z = f_s E_p t_p, \]

where \( f_{c,s} \) are the Fresnel factors and \( t_{s,p} \) are the linear transmission coefficients for the fundamental field, given by

\[ f_s = \frac{\sin \theta}{n(2\omega)}; \quad f_c = (1 - f_s^2)^{1/2}; \quad t_s = \frac{2 \cos \theta}{\cos \theta + n f_c}; \quad t_p = \frac{2 \cos \theta}{n \cos \theta + f_c}, \]

with \( f_c \) taken such that \( \text{Im} f_c \geq 0 \), and \( \text{Re} f_c \geq 0 \) if \( \text{Im} f_c = 0 \); \( n(\omega) \) is the complex refractive index of the medium in which the beam is propagating. \( \theta \) is the angle of the beam propagation in this medium. For the SH field, the corresponding \( F_s, F_c, T_s, T_p \) are similar with refractive index \( N(2\omega) \) of SH light.

Through combining Eq. (13) and Eqs. (14)-(17), one obtains the second-order polarization from the (100) face crystal,

\[ P_{bulk}^s = -2d[\sin(2\phi)f_c f_s t_s^2 E_p^2 - \cos(2\phi)f_s t_p t_s E_p E_s], \]
\[ P_{bulk}^k = -2d[\cos(2\phi)f_c f_s t_s^2 E_p^2 + \sin(2\phi)f_s t_p t_s E_p E_s], \]
\[ P_{bulk}^z = d[\cos(2\phi)t_s^2 E_s^2 - \cos(2\phi)f_c^2 t_p^2 E_p^2 - 2\sin(2\phi)f_c t_p t_s E_p E_s], \]

and for the (111) crystal,

\[ P_{bulk}^s = -\sqrt{\frac{2}{3}}d[\sin(3\phi)t_s^2 E_s^2 - \sin(3\phi)f_c^2 t_p^2 E_p^2 + 2(\cos(3\phi)f_c + \sqrt{2}f_s)t_p t_s E_p E_s], \]
\[ P_{bulk}^k = -\sqrt{\frac{2}{3}}d[t_s^2 \cos(3\phi)E_s^2 + (\sqrt{2}f_c f_s - \cos(3\phi)f_c^2)t_p^2 E_p^2 - 2\sin(3\phi)f_c t_p t_s E_p E_s], \]
\[ P_{bulk}^z = -\frac{d}{\sqrt{3}}[t_s^2 E_s^2 - (f_c^2 - 2f_s^2)E_p^2]. \]

The SH fields generated by polarization are decomposed into s- and p-polarized components,

\[ E_{bulk}^s = A_s \Omega \epsilon_{eff} P_{s}^{bulk} \]
and

\[ E_p^{bulk} = A_p \Omega L_{\text{eff}} [F_s P_{z}^{bulk} - F_c P_k^{bulk}] \]  \tag{20}  

where \( \Omega = 2\omega/c \) is the magnitude of the wave vector of the SH light. \( A_s \) and \( A_p \) (given in Ref. [20]) are independent of the angle of rotation, but are dependent on the incident angle and the optical frequency through a change in the index of refraction. The SH intensity is proportional to the absolute square of \( E(2\omega) \), which for either \( s \)- or \( p \)-polarized pump beam, from (100), (110) and (111) face crystals are found from Table I (only the bulk susceptibility is included).

| TABLE I. The second-harmonic field for bulk contribution |
|----------------------------------------------------------|
| **(100) face**                                           |
| \( E_{p,s} = -2d \Omega L_{\text{eff}} f_c f_s t_p^2 \cos(2\phi)A_s E_p^2 \) |
| \( E_{p,p} = d \Omega L_{\text{eff}} f_c t_{p}^{2}(2f_s F_c - f_c F_s) \cos(2\phi)A_p E_p^2 \) |
| \( E_{s,s} = 0 \)                                          |
| \( E_{s,p} = d \Omega F_s L_{\text{eff}} t_s^2 \cos(2\phi)A_p E_s^2 \) |
| **(110) face**                                           |
| \( E_{p,s} = \frac{1}{2}d \Omega L_{\text{eff}} [(3 \cos(2\phi) - 1) f_c^2 - 2 f_c^2] \cos(\phi)A_s E_p^2 \) |
| \( E_{p,p} = d \Omega L_{\text{eff}} [3 \cos^2 \phi f_c^2 F_c - f_s^2 F_c + 2 f_c f_s F_s] \sin(\phi)A_p E_p^2 \) |
| \( E_{s,s} = 3 d \Omega \cos \phi \sin^2 \phi A_s E_s^2 \) |
| \( E_{s,p} = \frac{1}{4}d \Omega L_{\text{eff}} F_c [\sin \phi - 3 \sin(3\phi)]A_p E_s^2 \) |
| **(111) face**                                           |
| \( E_{p,s} = \sqrt{\frac{2}{3}} d \Omega L_{\text{eff}} f_c^2 t_p^2 \sin(3\phi)A_s E_p^2 \) |
| \( E_{p,p} = \sqrt{\frac{2}{3}} d \Omega L_{\text{eff}} [\sqrt{2} f_c^2 F_c \cos(3\phi) + f_c^2 F_s - 2 f_c f_s F_c - 2 f_s F_s] t_p^2 A_p E_p^2 \) |
| \( E_{s,s} = -\sqrt{\frac{2}{3}} d \Omega L_{\text{eff}} t_s^2 \sin(3\phi)A_s E_s^2 \) |
| \( E_{s,p} = \sqrt{\frac{2}{3}} d \Omega L_{\text{eff}} [\sqrt{2} F_c \cos(3\phi) - F_s] t_s^2 A_p E_s^2 \) |

The SH intensity is proportional to the absolute square of \( E(2\omega) \). Figure 2 shows the rotation-angle dependence of the SH intensity \( P_{in} - S_{out} \) for singular ZnSe(100) and
ZnSe(111) with only the bulk susceptibility. For ZnSe(100), the SH intensity distribution shows a fourfold symmetry, but for ZnSe(111) a full sixfold symmetry.

C. Surface or Interface Contribution

The surface or interface nonlinear susceptibility $\chi_{\text{surf}}^{(2)}$ is a third rank tensor with 27 elements, which reflect the symmetry of the interface. For SHG the last two indices may be permuted at will, thus, the nonlinear susceptibility tensor may have a maximum of 18 independent nonvanishing elements (e.g. $C_1$), and higher symmetries lead to a reduction in the number of independent and nonvanishing tensor elements. Table II summarizes the results for the form of the surface nonlinear susceptibility tensor $\chi_{\text{surf}}^{(2)}$ for various symmetry classes.

| Point Group | Nonvanishing independent tensor elements |
|-------------|-----------------------------------------|
| $C_1 - 1$   | $xxx, yxy, xzz, yxz=xzy, xzx=xxz, xxy=xyx, yyy=yyy, yzz=yyz, yyz=zyz, yxz=yzx, yzx=zyx$ |
| $C_s - m$   | $xxx, xyy, xzz, xzx=xxz, yxz=yzx, yzy=yyz, zxx=zzz, zyy=zzz, zzz=zzz$ |
| $C_2 - 2$   | $xyz=zyx, xzx=xxz, yxz=yzx, yzy=yyz, zxx=zzz, zyy=zzz, zxz=zzx$ |
| $C_{2v} - mm2$ | $xxx=xxz, yyy=yyz, zxx=zzz$ |
| $C_3 - 3$   | $xxx=xxy=-yxy, yyy=-yxx=-xxz=-yzy, yyy=-yxx=-xxz=-yzy, zxx=zzz$ |
| $C_{3v} - 3m$ | $xxx=-xxy=-yxy=-yxx, yyy=-yxx=-xxz=-yzy, zxx=zzz$ |
| $C_4 - 4, C_6 - 6$ | $xxx=xxz=yyy=yyz, xzx=xxz=yyz, zxx=xxz=yzx, yyy=-yxx=-xxz=-yzy, zxx=zzz$ |
| $C_{4v} - 4mm$ | $xxx=xxz=yyy=yyz, xxx=zzz$ |
| $C_{6v} - 6mm$ | $xxx=xxz=yyy=yyz, xxx=zzz$ |
We use the symbol $\chi_{xyz}^{surf}$ to denote the surface (dipolar) second-order susceptibility, and $P_{x,y,z}^{surf}$ for surface polarization, e.g.,

TABLE III. Rotation-angle dependences of the second-order susceptibility tensor components for different symmetry.

| Surface symmetry (100) face xyz $^a$ | $P_{in} - P_{out}$ | $P_{in} - S_{out}$ | $S_{in} - P_{out}$ | $S_{in} - S_{out}$ |
|-------------------------------------|-------------------|-------------------|-------------------|-------------------|
| $C_{4v}, C_{6v}$ $^{xxz=yyz,zzz}$  | $\cos(2\phi)$    | $\cos(2\phi)$    | $\cos(2\phi)$    | $-$               |
| $^{zzz=zyy}$                       | isotropic         | $-$               | $-$               | $-$               |
| $C_{3v}^{b}$ $^{xxx}$              | $\cos(3\phi)$    | $\sin(3\phi)$    | $\cos(3\phi)$    | $\sin(3\phi)$    |
| $C_{3}^{b}$ $^{xxx}$               | $\cos(3\phi)$    | $\sin(3\phi)$    | $\sin(3\phi)$    | $\sin(3\phi)$    |
| $^{yyy}$                           | $\sin(3\phi), \sin\phi$ | $\cos\phi$ | $\cos(3\phi), \sin\phi$ | $\cos(3\phi), \cos\phi$ |
| $C_{2v}$ $^{xxz+zyy}$              | isotropic         | $-$               | isotropic         | $-$               |
| $^{xxz+yzy}$                       | isotropic         | $-$               | $-$               | $-$               |
| $^{xxx-yyz}$                       | $\sin(2\phi)$    | $\sin(2\phi)$    | $-$               | $-$               |
| $^{zzz-zyy}$                       | $\sin(2\phi)$    | $-$               | $\sin(2\phi)$    | $-$               |
| $^{zzz}$                           | isotropic         | $-$               | $-$               | $-$               |
| $C_{s}^{b}$ $^{xxx, yyy, yxz}$     | $\cos(3\phi), \cos\phi$ | $\sin(3\phi), \sin\phi$ | $\cos(3\phi), \cos\phi$ | $\sin(3\phi), \sin\phi$ |
| $^{xxx, yyz}$                      | $\cos(2\phi)$    | $\sin(2\phi)$    | $-$               | $-$               |
| $^{xxx}$                           | $\cos\phi$       | $\sin\phi$       | $-$               | $-$               |
| $C_{1}^{b}$ $^{xxx, yyy, yxz}$     | $\cos(3\phi), \cos\phi$ | $\sin(3\phi), \sin\phi$ | $\cos(3\phi), \cos\phi$ | $\sin(3\phi), \sin\phi$ |
| $^{yyy, xyy, yxz}$                 | $\sin(3\phi), \sin\phi$ | $\cos(3\phi), \cos\phi$ | $\sin(3\phi), \sin\phi$ | $\cos(3\phi), \cos\phi$ |
| $^{xyz, yxz}$                      | $\sin(2\phi)$    | $\cos(2\phi)$    | $-$               | $-$               |
| $^{xxx}$                           | $\sin(2\phi)$    | $-$               | $\sin(2\phi)$    | $-$               |
| $^{xzz}$                           | $\sin\phi$       | $-$               | $\sin\phi$       | $-$               |

$^a$ Only the bulk susceptibility is included.

$^b$ The isotropic terms are not shown.
\[ P_{x}^{surf} = \chi_{xys}^{surf} E_y E_z, \text{ etc.,} \] (21)

in the \((x, y, z)\) system. The transformation rule Eq. (13) is used to transfer the tensor \(\chi_{xyz}^{surf}\) from crystal coordinates to beam coordinates \(\chi_{skz}^{surf}\). Following Sipe [18], the SH field induced by the sheet of polarization can be written as

\[
E_{s}^{surf} = A_s \Omega P_{s}^{surf},
\]

\[
E_{p}^{surf} = A_p \Omega \left[ F_s \varepsilon(2\omega) P_{s}^{surf} - F_k P_{k}^{surf} \right],
\] (22)

where \(\varepsilon(2\omega)\) is the dielectric constant at frequency \(2\omega\).

We assume for simplicity that the surface has a simple unreconstructed structure, and thus for a particular face it has the same symmetry as the bulk. Therefore we use \(C_{3v}\) symmetry for the (111) surface and \(C_{4v}\) symmetry for the (100) face [18]. In fact, there exist many local microscopic structures, even in a nominally single surfaces, and in such cases, the microscopic symmetry of the structures, such as monoatomic steps, etc. would allow some specific tensor element to exist. That is, we may observe a lower symmetry than expected if the newly introduced tensor is of different symmetry. Table III summarizes the results in cases where surface susceptibility is presented.

From Table III, we see that there are always plural tensor elements which cause the same rotational symmetry. Therefore, the determination of the relevant tensor elements must depend on other sources of information, which may be obtained experimentally. Note that because SHG is described by a third rank tensor, all surface symmetries higher than \(C_{3v}\) yield an isotropic response.

III. EXPERIMENTAL METHODS

The experimental setup for SHG measurement is shown in Fig. 3. The light source of the fundamental frequency is a picosecond mode-locked Nd:YAG (yttrium aluminum garnet) laser (Light Conversion Ltd. EKSPLA 2143A) with light pulses of wavelength 1.06\(\mu m\), duration time 20 ps, and repetition rate 10 Hz. The linear polarization of the
fundamental beam is rotated to the desired angle by the combination of the half wave plate ($\lambda/2$) and the input Glan-Taylor polarizer prism P1. The polarized beam is focused into a spot of 3 mm diameter on the sample surface at an incident angle of 45°. In order to avoid damaging the sample, the pulse energy was set to about 0.5-0.3 mJ per pulse throughout the experiment. The visible-cut filter F1 situated immediately before the sample surface removes the visible light component, especially SH signals which are generated in the preceding polarizer and lens. The reflected fundamental beam and the SH signal from the surface are collinear beyond the sample surface, and the former is eliminated from the beam by an IR-cut filter F2 and an interference filter F3 (Melles Griot 03FIB008, $\lambda = 550$ nm, FWHM=70 nm). The linear polarization of the SH signal to be measured by the detection system was selected by rotation of the analyzer P2. The signal was finally detected by a photomultiplier (Hamamatsu R1464). About 4% of the reflected laser beam is directed through the reference arm containing a crystalline quartz plate. The SH intensity from quartz plate can be used for providing a reference to remove laser intensity fluctuations. This signal is detected by another photomultiplier (Hamamatsu R928) through an interference filter F3. Both electronics signals from the two PMT outputs were fed into a BOXCAR (SRS 250) averaged over 50 pulses and then recorded using a computer.

The ZnSe(100) and ZnSe(111) crystals grown by the Markov method were commercially purchased from Ma Teck Material Technologie & Kristalle GmbH, Germany [23]. Their surfaces are chemical and mechanically polished. The samples were mounted on a rotation stage, with the surface normal set parallel to the rotating axis of the stage and could be rotated freely.

**IV. RESULTS AND DISCUSSION**

In Figure 4(a)-(d), the intensity from ZnSe(100) is shown as a function of the azimuthal orientation for the four different polarization combinations: $P_{in} - P_{out}$, $P_{in} - S_{out}$, $S_{in} - P_{out}$, $S_{in} - S_{out}$. All experiments were made under the same conditions which makes it possible
to compare the intensities of the different combinations. Fig. 4(a) [Fig. 4(b)] displays the
the p-[s]-polarized SH intensity $I_{pp}$ [$I_{sp}$] with p-[s]-polarized incident light, whereas Fig. 4(c)
[Fig. 4(d)] shows the s-polarized SH intensity $I_{ps}$ [$I_{ss}$] with p-[s]-polarized incident light.
All plots clearly exhibit twofold symmetry. It seems to be consistent with a $C_s$ symmetry. A
more detailed analysis of the experimental results (see below) shows the interference of the
surface $C_s$ symmetry with the underlying $C_{4v}$ symmetry of the ZnSe(100). The data for the
four cases are fit by the trigonometric function square plus a constant, this small constant
can be due to light at other frequencies leaking through the filters. We might be able to
obtain relative values for the surface and bulk contributions if the function of the incident
angle multiplying the different surface and bulk contributions would change significantly
with $\theta$ (see Eq. (17) and TABLE I). However, with the experimental conditions used here,
changing from normal to grazing incidence decreases $f_c$ and $F_c$ by 5%, whereas $f_s$ and $F_s$
remain small. Hence any attempt to separate bulk and surface contribution by the use of
this method seems to be inappropriate. It is for this reason that in all experiments a fixed
angle of incidence of 45° was used.

For simplicity we concentrate on the s-polarized SHG response for an s-polarized pump
beam, because this signal only contains anisotropic terms and will be most sensitive for
the surface symmetry. This conclusion arises because the bulk contribution is forbidden, as
seen in Table III. According to [18], for the (100) face, we see that the surface in general
has $C_{4v}$ symmetry. However, such a mechanism should lead no $\phi$-angle dependence. Even
though we replace the symmetry $C_{4v}$ with lower symmetry $C_{2v}$, we cannot obtain any $\phi$-angle
dependent signal. Thus we must allow the effective symmetry of the surface to lower from
$C_{2v}$ to $C_s$, corresponding to the observed symmetry of the rotation angle dependence. From
Table III, for $C_s$ symmetry only the following components of surface or interface nonlinear
susceptibility do not vanish

$$\chi_{xxx}, \chi_{xyy}, \text{and } \chi_{yxy} = \chi_{yyx}. \quad (23)$$

And a similar expression for the $S_{in} - S_{out}$ case is derived as
\[ E_{s,p}(2\omega)/E_{sp}^2(\omega) \propto \chi_{xxx} \sin^3 \phi - (\chi_{xyy} + 2 \chi_{yyx}) \sin \phi \cos^2 \phi . \]  

The solid line in Fig. 4(d) is a least-squares fit of SHG intensity to the data, from which we obtain the ratio

\[ \frac{\chi_{xxx}}{\chi_{xyy} + 2 \chi_{yyx}} = 0.276, \]

the agreement with experimental result justifies our choice of \( C_s \) symmetry. There is a large scatter in the data for \( S_{in} - S_{out} \) polarization combination, because its absolute SH intensity is small, thus we cannot obtain a complete fit to every data point in this configuration. In Ref. [24], value of \( \chi_{xxx} / (\chi_{xyy} + 2 \chi_{yyx}) = 1.10 \) was obtained from the NaCl(100)-air interface. This difference is not surprising given the fact that the absorption depth in the oxide layers of the NaCl(100) is more than that of ZnSe(100) in our experiment.

This \( C_s \) symmetry may be caused by (1) the interface between oxide absorbate and sample [24], (2) a nonideal cut of the crystal, the domain formation with different symmetry axis [11]. When one only consider the bulk susceptibility, \( \phi \) dependence for \( S_{in} - S_{out} \) is very sensitive to the miscut angle of the crystal axis, even its absolute SH intensity is very small. If we consider that the surface tensor elements \( \chi_{xxx}, \chi_{xyy}, \) and \( \chi_{yxy} \) have relevance to the miscut angle of ZnSe(100) crystal, which is less than 0.5\(^\circ\) [23], the response of \( S_{in} - S_{out} \) is determined to be more than an order of magnitude smaller than other corresponding cases [12,11]. C. Yamada and K. Kimura [8] found it was very difficult to measure \( S_{in} - S_{out} \) rotational-angle dependence because the signal was poor under UHV condition. However, we observed that the output was about half of the other cases. So we concluded that in our experiment the interface plays an important role for producing the anisotropic in \( S_{in} - S_{out} \) configuration. This is supported in part by similar measurements made for GaAs(100) surfaces contaminated with carbon and oxygen which revealed a high degree of anisotropy in the SHG signal [25]. The anisotropy cannot be ascribed to any particular surface symmetry. One possible explanation may be suggested: the anisotropy may arise due to variations in oxide layer thickness which could be regarded as generating a stepped buried ZnSe(100)/oxide layer interface.
For three configurations ($P_{in} - P_{out}$, $S_{in} - P_{out}$, $P_{in} - S_{out}$), the SHG intensity distribution shows a $C_{4v}$ symmetry if we only consider the bulk susceptibility. Further, we notice that the oxide layer interface would lower the effective symmetry of the surface from $C_{4v}$ to $C_{2v}$. In Fig 4.(a)-(c), we observe twofold symmetries not fourfold for three configurations, which is the result of interference of bulk SHG with surface SHG. Therefore, the observed rotation-angle dependence can be described as

$$I_{s.p} \propto |A + B \cos(2\phi) + C \sin(2\phi)|^2,$$

(26)

where $A$ represents the isotropic surface contribution, $B$ is the bulk dipole term and $C$ the surface anisotropic term. We least-square fitted the observed rotation-angle dependence for three configurations by Eq. (26) with $A$, $B$ and $C$ used as adjustable parameters. These fitting parameters are summarized in Table IV for the SHG data. As shown in Fig. 4(a)-(c), the fit was satisfactory.

| Configuration | A     | B     | C     |
|---------------|-------|-------|-------|
| $P_{in} - P_{out}$ | -0.034 | 0.203 | 1.201 |
| $P_{in} - S_{out}$  | 0.046 | 1.200 | -0.126 |
| $S_{in} - P_{out}$  | 0.062 | 0.039 | 1.150 |

In the $P_{in} - P_{out}$ combination (Fig 5.), the peak at $\phi = 135^\circ$ is higher than that at $\phi = 45^\circ$, and the peak at $\phi = 315^\circ$ is higher than that at $\phi = 225^\circ$. These differences arise from the interference between the isotropic surface SHG and the bulk SHG. The signs of the nonlinear susceptibility components for the exciting electric fields in the (011) and (0\bar{1}1) planes are opposite. This is because the bulk Zn-Se-Zn-Se- chain along the [011] has Zn atoms higher than Se atoms and Zn-Se-Zn-Se- chain along [0\bar{1}1] has Se atoms higher than Zn atoms. This phase difference of $180^\circ$ between the electronic wave functions of the two bulk chains leads to the difference in the interference between the bulk and surface SHG and to the change of the SHG peak intensities.
V. SUMMARY

We have developed a phenomenological model and performed experiments to determine the symmetry of the noncentrosymmetric semiconductor crystal ZnSe(100) covered with an oxide layer. Under the four combinations of fundamental and harmonic linear polarization states considered, the harmonic intensity can be expressed as a function of the light polarization and as a function of the azimuthal angle. Using the calculated sensitivity to rotation angle of the SHG signal from the bulk and surfaces, we have been able to deduce the symmetry of the noncentrosymmetric crystal surfaces. We found that the measurement using $S_{in} - S_{out}$ is particularly useful in determining the symmetry of the oxidized layer interface, which would lower the effective symmetry of the surface from $C_{4v}$ to $C_{2v}$. The separation between bulk and interface or surface SHG demonstrated here is promising for the application of this technique to the study of surface and interfacial properties. This way can be used to detect the quality of the substrate surface for growth of II-VI epilayers on ZnSe layers.

In addition, we have shown that the [011] and [011] directions can be distinguished through the analysis of $p$-incident and $p$-output configuration.
FIGURES

FIG. 1. Principal geometry for SHG in reflection. In the experiment the surface is rotated its normal Z (azimuthal angle $\phi$), and the polarization of both fundamental and SH can be varied to any direction between $s$ and $p$.

FIG. 2. The rotation-angle dependence of the SH intensity $P_{in} - S_{out}$ for singular ZnSe(100) and ZnSe(111) with only the bulk susceptibility.

FIG. 3. Schematic diagram of the experimental configuration used to measure the SHG from ZnSe single crystal surfaces.

FIG. 4. Rotational anisotropy of SHG from ZnSe(100) surface in free air for a set of input and output polarization combinations. The circles are the experimental points, and the solid lines are least-squares fit to theoretical calculation.

FIG. 5. Polar plot of the SHG intensity from ZnSe(100). The pump and SHG beam were both $p$ polarized.

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