PHOTONIC PROBE OF CRYSTALLINE SURFACE BY SECOND HARMONIC GENERATION

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Abstract: The nonlinear optical processes of second harmonic generation (SHG) have become very powerful spectroscopic tools of high sensitivity for probing surfaces and interfaces of centrosymmetric materials. However, for materials whose structure lacks inversion symmetry, a bulk contribution to SHG is present. Many studies were carried out to separate surface contribution versus bulk contribution in surface of these materials. Our studies focus on the II-VI semiconductors of zincblende structure, in particular, ZnSe crystals. We calculated the rotation - angle dependence of the intensity of surface reflection SHG for the single crystalline ZnSe and carried out experiments to compare. Our results and discussion will be represented in this paper.

1. Surface SHG of ZnSe crystal

In the case of sum frequency generation (SFG) from an interface between two centrosymmetric materials in the reflected direction by the mixing of two input beams at frequencies ω_1, ω_2 the expression for intensity of the radiated SF signal may be obtained by solving the Maxwell equations for the nonlinear source polarization.

$$I^{\Omega} = \frac{8\pi^3\Omega^2 \sec^2\theta^{\Omega}}{c^3\sqrt{\varepsilon_1(\Omega)\varepsilon_1(\omega_1)\varepsilon_1(\omega_2)}} \left| e^{\Omega}.\chi_S^{(2)} e^{\omega 1}.e^{\omega 2} \right|^2 I^{\omega 1}.I^{\omega 2}\,, \tag{1}$$

where $\Omega = \omega_1 + \omega_2$, $\chi_S^{(2)}$ is surface nonlinear susceptibility and $e^{\Omega}.e^{\omega 1}.e^{\omega 2}$ are the transformed polarization vectors at the interface. SHG is a special case with $\omega_1 = \omega_2$. Since materials with crystalline order are not invariant under arbitrary rotations, the SH/SF response of the material will generally vary under rotations about the surface normal but recover the same value under any allowable symmetry operation. Considerations of the symmetry are helpful to simplify measurement and the form of the tensor $\chi_S^{(2)}$ may give information about distinctive properties of the surface. Since the symmetry of the tensor $\chi_S^{(2}$ reflects the order of the surface, it can also give information on the orientation of adsorbates at a surface.

2. Calculation results

The crystal structure of ZnSe belongs to the point group $\bar{4}3m$. There is only one component in the bulk second-order susceptibility tensor of ZnSe: $\chi^{(2)}_{xyz} = \chi^{(2)}_{yzx} = \chi^{(2)}_{zxy} = \chi^{(2)}_{xzy} = \chi^{(2)}_{yxz} = \chi^{(2)}_{zxy}$

Where (x,y,z) represent the principal-axis system of the crystal ([100], [010], [001]). The Fig 1 shows the coordinate system. In the beam coordinate system (s, k, z) the SH polarization of the crystal is given by:

$$P_i^{(2\omega)}(\varphi) = \sum\sum \chi_{ilm}^{(2)}(\varphi) E_l^{(\omega)} . E_m^{(\omega)} \qquad (2)$$

Where i, l and m run through s, k and z.

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

$$E_s^{(2\omega)} = A_s \Omega L_{eff} P_s^{(2\omega)} \qquad (3)$$

$$E_p^{(2\omega)} = A_p \Omega L_{eff} \left[F_s P_z^{(2\omega)} - F_c P_k^{(2\omega)} \right] \qquad (4)$$

where $L_{eff} = (K+2k)^{-1}$ is the effective phase-matching distance in which K and k are the z component of the wave vectors of SH and fundamental light,respectively.

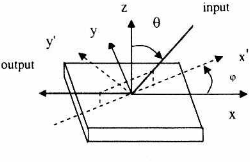
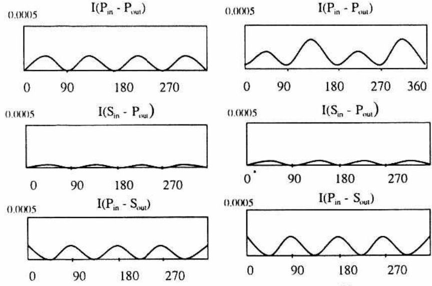


Fig.1. Rotation angle for the (001) face of single crystalline ZnSe.

A_s and A_p are dependent on the incident angle and optical frequency. The surface second order susceptibility tensor elements were classified [2]. The (001) face has two mirror planes perpendicular to each other in the direction of [110] and [110] which are 45° off from the x [100] and y [010] axes. We call the intersections of the mirror planes with the crystal face ξ and η. In the (ξ,η,z) coordinates system, the SH field induced by the sheet of polarization can be decomposed in s- and p- polarized components as follows:

$$E_{Surf,s}^{(2\omega)} = A_s \Omega P_{S,s}^{(2\omega)} \ ; \quad E_{Surf,p}^{(2\omega)} = A_p \Omega \left[F_s . \varepsilon(2\omega) P_{S,z}^{(2\omega)} - F_c P_{S,k}^{(2\omega)} \right] \qquad (5)$$



(a) (b)

Fig.2: The rotation-angle dependence of the surface SH intensity from single crystalline ZnSe (001) by input laser beam of 1064nm wavelength. The incident angle is 45°. a-bulk contribution only b- bulk and surface contributions with surface susceptibility of $\chi^{(2)}_{s,\xi\xi z} = -0{,}04$

The SH intensity was calculated for the possible combinations of the polarization of incident and SH light. The combination (S_{in}-S_{out}) is forbidden for SHG. The SH intensity distribution of three combinations (P_{in}-P_{out}) (S_{in}-P_{out}) (P_{in}-S_{out}) is shown in Fig.2. For comparison, we first calculated the surface SH intensity with bulk contribution only (Fig 2a) and then with both surface and bulk contribution (Fig.2b). In general, the SH intensity from bulk contribution is larger than that from surface. The surface contribution to surface-reflection SHG is very small. That is reasonable because ZnSe is one of compound semiconductors having large second order susceptibility. However, in the (P_{in}-P_{out}) case, the intensity difference of the strong and the weak peaks is clear. It was explained by the interference of bulk SHG and surface SHG.

3. Experimental results

Taking the advantage of the theoretical results of rotational symmetry, we carried out experiments to observe the rotation-angle dependence of the surface-reflection SH intensity from single crystalline ZnSe (001). We used a Q-switched Nd:YAG laser (Continuum NY81-50) which delivers 8 ns pulses at 1064 nm wavelength with pulse energy of up to 600 mJ and repetition rate of 50 Hz. The incidence angle of laser beam was fixed at 45°.The surface-reflection SH signal was detected by a photo-multiplier tube (Hamamatsu R 928). We selected SH signal by high-pass optical filers including an interference filter with a bandwidth of 10 nm (Melles Griot FIV 111) and a blue filter. The SH signal was monitored by a digital real time oscilloscope (Textronix TDS 360, 2 channels, 200 MHz. The rotation -angle dependence of the SH intensity in the (P_{in}-P_{out}) case is shown in the fig.3. There is a notable difference between the peaks. In the (S_{in}-P_{out}) case, the surface-reflection SH signal was so small that we can not distinguish the SH signal with noises. Our experimental results were in good agreement with the calculations.

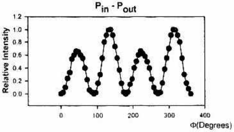


Fig.3:
The rotation -angle dependence of the surface SH intensity in the (P_{in}- P_{out}) case.
The incident angle is 45° and the wavelength of the fundamental beam is 1064 nm.

4. Conclusion

The theoretical and experimental observations of the rotational symmetry are very useful, in particular for the case of noncentrosymmetric materials. These help us to simplify our experiments when studying the surface-reflection SHG. The surface contribution to SHG is small but it is magnified by interference with the strong bulk contribution. Further studies on rotational symmetry of surface SHG for different faces of ZnSe crystal will be done to give more information about the properties of the surfaces.

References

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