RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 8 15 APRIL 1985

Picosecond and nanosecond laser-induced second-harmonic generation from centrosymmetric semiconductors

J. A. Litwin, J. E. Sipe, and H. M. van Driel
Department of Physics and Erindale College, University of Toronto, Toronto, M5S 1A7, Canada
(Received 26 November 1984)

We have studied the anisotropic second-harmonic generation from the centrosymmetric semiconductors Si and Ge with the use of nanosecond and picosecond laser pulses at 1.06 and 0.53 μm. We compare our results with those of similar picosecond experiments performed by Guidotti and Driscoll [Solid State Commun. **46**, 337 (1983)] and nanosecond experiments of Tom, Heinz, and Shen [Phys. Rev. Lett. **51**, 1983 (1983)]. These two groups have reported seemingly different data and have offered totally different explanations for the origin and anisotropy of the effect. The picosecond results were explained by a bulk electric-dipole mechanism permitted through inversion-symmetry breaking by high-density, photoinduced carriers; the nanosecond results were claimed to originate from surface electric dipole and bulk quadrupole effects in the quiescent crystals. Our data reconcile the two earlier sets of results and are shown to be consistent with the surface-dipolar–bulk-quadrupolar model, if dispersion of the nonlinear optical parameters is taken into account.

Within the past year there has been a resurgence of interest in the observation of second-harmonic generation (SHG) in centrosymmetric semiconductors, where electric-dipole bulk contributions are forbidden. The main feature which has attracted attention is that the efficiency of the process depends on crystal cut and orientation of the sample contrary to earlier reports by Bloembergen, Chang, Driscoll, and Gerritsen.[1] Indeed, Guidotti, Driscoll, and Gerritsen,[2] using 10-psec, 1.06- and 0.53-μm pump laser pulses on (111) and (100) crystal faces of Si and Ge at fluence levels near the melting threshold, showed that the efficiency can be highly modulated as the crystal is rotated about its normal. They have explained their results in terms of the loss of inversion symmetry because of the presence of optically generated high-density ($>10^{21}\ \mathrm{cm}^{-3}$) electron-hole pairs which form Frenkel excitons. The angular dependence of the efficiency is claimed to reveal the symmetry of a new, nonequilibrium phase of Si and Ge. More recently, Tom, Heinz, and Shen,[3] using 0.53-μm nanosecond pulses on Si at fluence levels much below the melting threshold, observed what appear to be different results, including different anisotropic behavior, and have offered an explanation in terms of surface electric-dipolar and bulk-quadrupolar contributions[4] from quiescent, centrosymmetric Si. In this Rapid Communication we report experimental and theoretical results for both picosecond and nanosecond induced SHG and show that all the data observed to date are consistent with the surface-dipolar–bulk-quadrupolar model if dispersion of the nonlinear optical parameters are taken into consideration. We also show that the presence of high-density carriers is not intrinsic to the origin of SHG.

In a material possessing inversion symmetry there is no bulk contribution to SHG of electric-dipole symmetry, and the dominant contributions are from terms of electric-quadrupole or magnetic-dipole symmetry. At the surface, where there is of course no inversion symmetry, electric-dipole terms can exist. As have earlier authors,[3] we phenomenologically describe this source by a dipole sheet which we place just above the surface ($z=z_0^+$),

$$P_i(2\mathbf{k},2\omega)=\sum_{jk}\Delta_{ijk}E_j(\mathbf{k},\omega)E_k(\mathbf{k},\omega)\delta(z-z_0^+)\ , \quad (1)$$

where Δ_{ijk} is a third-rank tensor and $E_i(\mathbf{k},\omega)$ is the amplitude of the fundamental field just below the surface and characterized by a wave vector $\mathbf{k}$ parallel to the surface. For Si and Ge, which have bulk O_h symmetry, the bulk nonlinear polarization can be written in the form

$$P_i(\mathbf{r},2\omega)=(\delta-\beta-2\gamma)(\mathbf{E}\cdot\nabla)E_i+\beta E_i(\nabla\cdot\mathbf{E})+\gamma\nabla_i(\mathbf{E}\cdot\mathbf{E})+\xi E_i\nabla_i E_i\ , \quad (2)$$

with respect to the usual crystal axes of the diamond structure, where $E_i=E_i(\mathbf{r},\omega)$. The first three terms are isotropic in nature while the fourth is anisotropic. If the (100) surface is assumed to be characterized by C_{4v} symmetry, the tensor Δ simplifies and the field strength of the s-polarized SH light generated by a single-incident light beam of s, or p polarization, is of the form

$$E_s^{\mathrm{SH}}=b_{s,p}^{(1)}\xi\sin4\phi\ , \quad (3)$$

where the parameter, $b_{s,p}^{(n)}$, which is proportional to the square of the incident amplitude by a different factor for the different incident polarization, is dependent on the dielectric constant at the fundamental and second-harmonic frequency, the angle of incidence, and the polarization of the fundamental beam. Here ϕ is the angle that the plane of incidence makes with the $\langle 010\rangle$ direction. For p-polarized SHG light the corresponding expression is of the form

$$E_p^{\mathrm{SH}}=b_{s,p}^{(2)}\xi+b_{s,p}^{(3)}\gamma+b_{s,p}^{(4)}f_{s,p}(\Delta_{ijk}^{(100)})+b_{s,p}^{(5)}\xi\cos4\phi\ , \quad (4)$$

where $f_{s,p}$ (and $g_{s,p}$ in the expression below) is a linear function of elements of the surface tensor. For a (111) surface with assumed C_{3v} symmetry the corresponding expressions are

$$E_p^{\mathrm{SH}}=b_{s,p}^{(6)}\xi+b_{s,p}^{(7)}\gamma+b_{s,p}^{(8)}g_{s,p}(\Delta_{ijk}^{(111)})+[b_{s,p}^{(9)}\xi+b_{s,p}^{(10)}\Delta_{111}^{(111)}]\cos3\phi \quad (5)$$

for p-polarized SHG light and

$$E_s^{\mathrm{SH}}=(b_{s,p}^{(11)}\xi+b_{s,p}^{(12)}\Delta_{111}^{(111)})\sin3\phi \quad (6)$$

for s-polarized SHG light, where now ϕ is the angle

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between the plane of incidence and the projection of the ⟨100⟩ vector on the (111) plane. These expressions will be compared with the experimental results below, where the intensity spectra for ν polarized-input light and η polarized SH light is denoted by $I_{\nu\eta}$. Our symmetry assumptions for the surfaces are based on the bulk structure, and are the simplest consistent with it (cf., Ref. 3). Since our samples were exposed to air the surface symmetry is not that of a reconstructed surface but more likely that of a semiconductor/semiconductor-oxide interface. Experimentally, the overall angle dependence observed allows us to distinguish between, e.g., C_{3v} and C_{4v} symmetry [see Eqs. (3)–(6) and the experimental results below], but an unambiguous determination of the surface symmetry [e.g., between C_{3v} or C_{6v} for a (111) face] would require more extensive experiments than those discussed here.

Our experiments were carried out using single-crystal wafers of Ge and Si which were cut to reveal (100) and (111) faces. These were polished with diamond pastes with grit sizes down to 0.25 μm, after which some were chemically etched. Our experimental results were practically independent of surface treatment indicating that surface contributions to SHG are intrinsic in nature and probably due to a native oxide/semiconductor interface. Pump radiation at 1.06- and 0.53-μm radiation was provided by mode-locked or Q-switched Nd-doped yttrium aluminum garnet lasers at pulse widths of 25 psec and 20 nsec, respectively. The laser pulses, at fluence levels at least a factor of 3 below the damage threshold and at a repetition rate of 5 Hz, were incident at an angle of incidence of 45° on the sample face which could be rotated about its normal. The weak SH signal was detected using appropriate blocking filters, a monochromator, and a photomultiplier tube. Glan-Taylor prisms were used to select the polarization of the pump and SH beams.

We were not able to determine any significant differences, in the orientation dependence of the SH signals for the *same* samples of Ge or Si, between our picosecond and nanosecond experiments. For example, Fig. 1 shows the angular rotation pattern of p-polarized SH signal induced by 1.06-μm s-polarized light incident on Ge (111), for both the nanosecond and picosecond excitation sources. To within experimental error the results are identical. Not only is the angular dependence of the data consistent with the symmetry expressed by Eq. (1), but the relative amplitudes of the peaks (which are not determined by symmetry) are essentially the same. Small differences (which are reproducible) in the amplitudes of the peaks were observed on different samples, but these are thought to be due to differences in surface treatment, specifically etching treatment. The maximum fluence in all cases was 50 mJ/cm^2, which is at least a factor of 3 below the melting threshold for both samples and excitation wavelengths. Although the intensities for the picosecond and nanosecond pulses differ by three orders of magnitude, the maximum carrier density was no larger than 5×10^{20} cm^{-3} for the picosecond excitation pulses, and 8×10^{19} cm^{-3} for the nanosecond pulses, as has previously been determined by infrared reflectivity measurements.[5,6] As suggested earlier,[1] these densities are too low to influence the SH signals. They are also far below the densities which are postulated to lead to electronic-mediated phase transitions.[2,7]

Guidotti and co-workers have argued that the absence of a SH signal from Si using a 1.06-μm pump (where Si has an

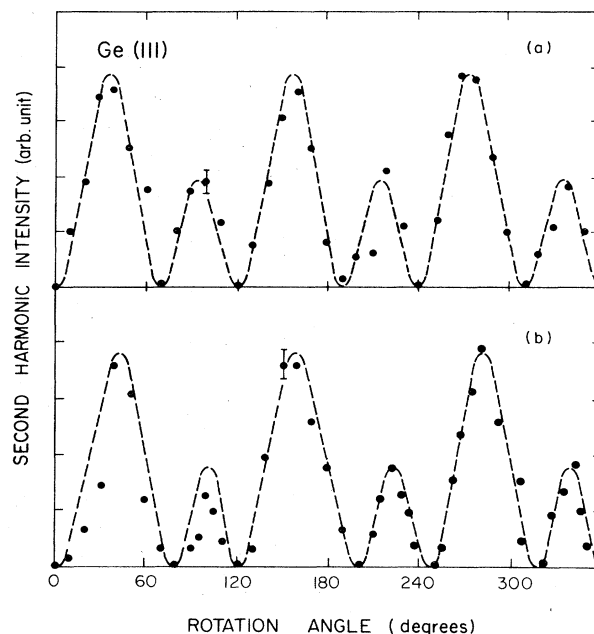

FIG. 1. Angular spectrum of p-polarized second-harmonic generation efficiency from Ge (111) induced by s-polarized 1.06-μm laser light with pulse width (a) 25 psec and (b) 20 nsec. In this and the following figures, the origin of the rotation angle is chosen for convenience of display, and the dotted lines are guides to the eye.

absorption depth of 1 mm) and the presence of SHG for a 0.53-μm pump (corresponding to an absorption depth of 1 μm) suggests that a large carrier density is required for SHG. On the contrary, using 1.06-μm nanosecond pulses we have observed SHG emission from Si, with intensity within an order of magnitude of that from Ge (for which the absorption depth is approximately 1 μm) for the same pump fluence. In the Si case the carrier density is certainly[5] below 10^{19} cm^{-3}. Figure 2 shows typical angular spectra of s- and p-polarized SH emission from Si(111) for s-polarized incident radiation. The spectra are consistent with the field expressions given for quiescent, cubic Si by Eqs. (5) and (6). None of the angular spectra represented by Figs. 1 and 2 changed in form as the pump intensity was varied. The SHG efficiency was also found to vary quadratically with excitation intensity in the usual fashion—a fact which further argues against the need for any induced mechanism such as carrier generation. The data therefore are considered to be representative of the normal quiescent Si.

If the pump fluence exceeds the melting threshold, the angular spectra are similar to those recorded for fluence levels below melting, provided no permanent induced roughness occurred. This can be explained if the SH light emission observed is generated from the solid during the early part of the pulse *before melting occurs,* and the emission from liquid, metallic Si is small. The fact that at these high fluences the SHG intensity varies subquadratically with the incident intensity, is also consistent with a variation of the efficiency during the pulse. Further work is in progress to study the details of the melt threshold region.

In all cases where Guidotti *et al.* have observed angular SH spectra, in which the signal varies as the crystal orienta-

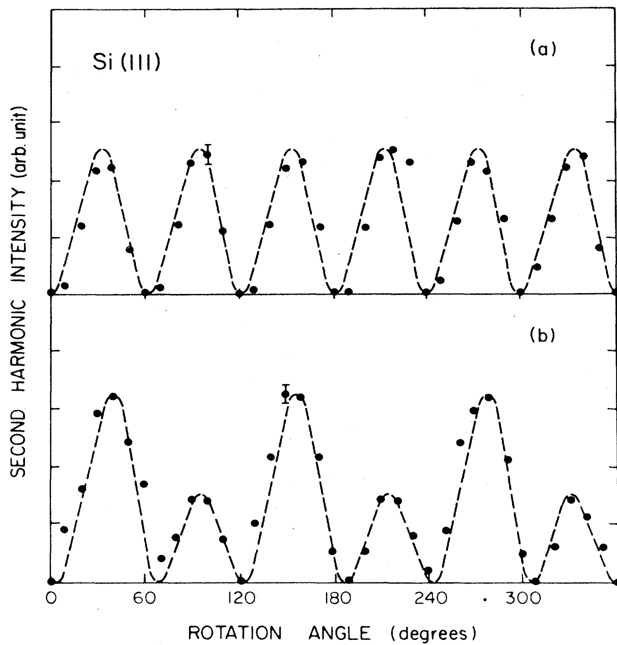

FIG. 2. Angular spectrum of second-harmonic generation efficiency from (111) Si for a 20-nsec, 1.06-μm pump pulse with a *s*-polarized pump beam and (a) *s*-polarized and (b) *p*-polarized emission beams.

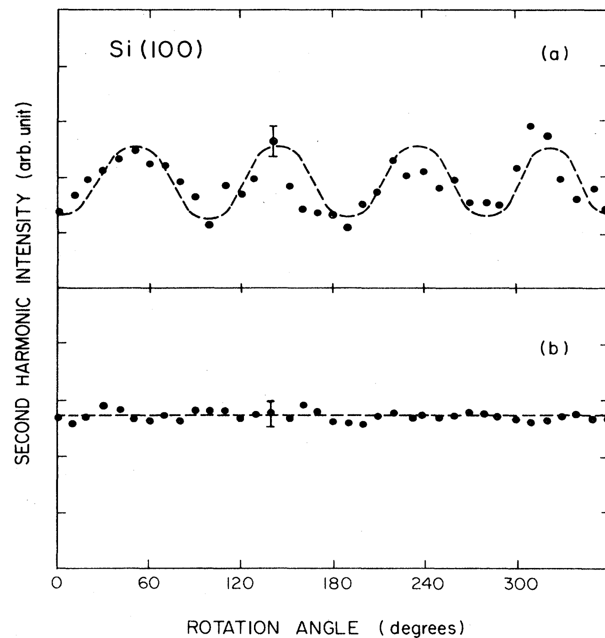

FIG. 3. Angular spectrum of *p*-polarized second-harmonic generation efficiency from (100) Si for a 20 nsec *s*-polarized pump pulse of wavelength (a) 1.06 μm and (b) 0.53 μm.

tion is changed, we have obtained similar results. For (100) Si and Ge, however, our results differ. Guidotti *et al.* have noted the apparent selection rules that $I_{ss} = I_{ps} = 0$ with I_{pp} and I_{sp} being angle independent. In Fig. 3 we show the angular spectra for I_{sp} from Si using nanosecond 1.06- and 0.53-μm pump beams. Similar results are obtained for I_{pp}. All these results are consistent with the expressions in Eq. (4). For the 0.53-μm case, the nonzero modulation, also observed by Tom *et al.*, is due entirely to a nonzero value for the bulk-anisotropic-quadrupolar SH emission. Note that the modulation amplitude is comparable to the size of the error bars claimed by Guidotti *et al.* The absence of modulation noted by ourselves and Guidotti *et al.* at 1.06 μm can be interpreted as a reduction of the bulk-anisotropic effects relative to bulk or surface isotropic effects. Our results, therefore, are indicative of a dispersion effect in the nonlinear coefficients. We have also searched for *s*-polarized emission from (100) Si or Ge. Although we have observed nonzero signals, the signal to noise ratio is near unity, making it difficult to obtain detailed angular spectra as Heinz, Tom, Zhu, and Shen[8] have also found. From Eq. (3) the I_{ss} signal would be due entirely to bulk-anisotropic effects. From the modulation induced by the bulk term for the I_{sp} spectra we would conservatively estimate that the I_{ss} signal would be weaker by nearly two orders of magnitude.

In summary, we have examined the origin of SH emission induced in the centrosymmetric semiconductors Si and Ge. We have found that all the data are consistent with a model based on surface-dipolar and bulk-quadrupolar effects in quiescent, cubic crystals. We have determined that induced carrier densities play an insignificant role in both the picosecond and nanosecond experiments. The data of Guidotti *et al.*, which are generally in agreement with ours and those of Tom *et al.*, differ only in those cases where they are apparently limited by their detection system and signal-to-noise ratio.

Finally, it is worth commenting on the role that SH emission can play in yielding information about crystal symmetry and structural-phase transformations in centrosymmetric cubic crystals as Shank, Yen, and Hirlimann have suggested.[9] These authors, by time resolving the I_{pp} signal from (111) Si on a femtosecond time scale, have found that the angular spectrum changes character from anisotropic to isotropic at high-pump intensities and have interpreted this in terms of bulk melting. From Eqs. (3)–(6) it is seen that anisotropic angular spectra may in general be expected for both (111) and (100) surfaces for all polarizations of the pump and SH beams. In particular for the (111) surface, anisotropic effects are due to surface and bulk effects and the disappearance of anisotropy in the SH signal cannot be uniquely interpreted in terms of an alteration of the bulk or surface contributions. Only for the case of *s*-polarized emission from (100) surfaces does one have a probe of only bulk effects, but in this case the signals observed are very small.

We gratefully acknowledge financial support of this work from the Natural Sciences and Engineering Research Council of Canada.

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