

Depletion-Electric-Field-Induced Changes in Second-Harmonic Generation from GaAs

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Experiments reveal that the near surface second-order nonlinear optical susceptibility, $\chi^{(2)}(2\omega, \omega, \omega)$, is significantly affected by band-bending induced-electric fields in the depletion region of GaAs(001). Both *n*- and *p*-type GaAs samples exhibit a reduction of the bulk second-order susceptibility $\chi_{yxz}^{(2)}$ independent of electric field direction. A three band theoretical model was used to qualitatively explain these observations.

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It is well known that an externally applied dc electric field breaks the symmetry of an isotropic medium, and leads to the enhancement of otherwise forbidden second-order nonlinear optical processes. Elegant examples of these phenomena include external-field-induced second-harmonic generation (SHG) in gases [1] and crystals [2]. Static electric fields within the surface depletion region of a doped semiconductor provide a naturally occurring analog of this scenario. In this region the bulk symmetry of the crystal is broken as a result of band bending. The accompanying depletion electric field plays an important role in many semiconductor devices, and is known to affect a variety of optical processes including LO-phonon Raman spectroscopy [3], nonlinear absorption and electroreflectance [4], and far-infrared generation by inverse Franz-Keldysh mechanisms [5,6].

In this Letter we report the effects of depletion electric fields on second-harmonic generation from GaAs(001). Our experiments reveal that the dominant perturbation caused by the depletion electric field is on the *existing* bulk nonlinearity $\chi_{yxz}^{(2)}$. No measurable effects were detected on any other tensor elements. These results are surprising at first glance, since one would expect the most substantial changes to be produced by field-induced perturbations of the *isotropic* semiconductor response. We demonstrate, however, through studies as a function of dopant type and concentration, that the bulk $\chi_{yxz}^{(2)}$ is systematically reduced as a result of the depletion field, and that this diminution depends on the square of the near surface depletion field. We present a simple three band calculation to explain the phenomenon, and we perform photomodulation-second-harmonic generation (PSHG) experiments to demonstrate that $\chi_{yxz}^{(2)}$ in *doped* GaAs can be *enhanced* by carrier excitation in the depletion region [7,8].

The present experiments are the first to elucidate the affect of depletion electric fields on harmonic generation. Our formulation of the problem is conceptually similar to recent models proposed to explain the crystallographic

orientation dependence of far-infrared generation by optical rectification in semiconductors [5]. Our SHG observations, however, can only be explained by invoking three band processes. Finally, besides their intrinsic interest as new phenomena, our measurements illustrate a potentially useful method to probe changes in symmetry and band bending in the near surface region of a semiconductor. This information is often of interest in materials and device applications.

GaAs(001) has a zinc-blende crystal structure and carries a single nonzero bulk second-order susceptibility $\chi_{yxz}^{(2)}$, whose contribution to the output SH radiation is highly anisotropic. In the *p*-in/*s*-out polarization configuration, with the crystalline [100] axis parallel to the plane of incidence [9], the output SHG intensity from $\chi_{yxz}^{(2)}$ is maximized [see Fig. 1(a)]. More importantly, in this polarization configuration the detected SHG intensity is insensitive to the higher order contributions from the bulk magnetic dipole and electric quadrupole transitions [10]. A 10 Hz Nd:YAG pumped dye laser was used as the fundamental light source for SH measurements. The photon energy of the fundamental laser beam was chosen to be near the band gap of GaAs so that the dominant contribution to the second-order susceptibility $\chi_{yxz}^{(2)}$ arose mainly from transitions between the top valence band $|v\rangle$ and the two lowest conduction bands $|c\rangle$, $|c'\rangle$ at Γ point in the Brillouin zone [11] [see Fig. 1(b)].

Our GaAs(001) samples were doped with Si (*n* type) and Be (*p* type), and were grown on an undoped GaAs substrate by molecular-beam epitaxy. As is usually the case, surface defect electronic states (traps) pin the material Fermi level leading to near surface band bending [see Fig. 1(c)]. A strong electric field is thus produced along the crystalline [001] direction. The depletion length of our samples was between 0.1 and 3.0 μm depending on the doping levels. With the exception of the most highly doped samples, the SHG penetration depth of $\sim 0.1 \mu\text{m}$ was substantially less than the sample depletion length. Since the Fermi level pinning can depend on surface treat-

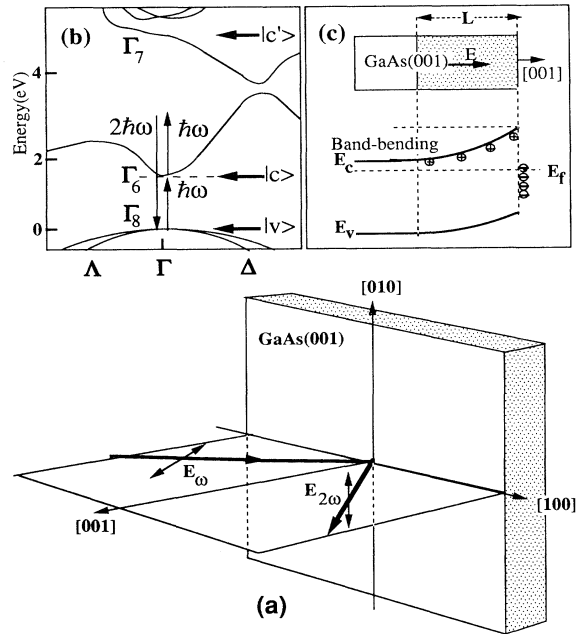


FIG. 1. (a) Schematic of the SHG experiment in *p*-in/*s*-out polarization configuration with crystalline [100] direction in the plane of incidence. The output SHG intensity is dominated by the contributions from $\chi_{yxz}^{(2)}$. To eliminate the generation of carriers in the sample by the fundamental laser beam, the photon energy of the dye laser was tuned just below the band gap of GaAs. (b) When the photon energy of SHG fundamental beam is just below the direct gap of GaAs, the second-order susceptibility $\chi_{yxz}^{(2)}$ arises mainly from transitions between the top valence band $|v\rangle$ and the two lowest conduction bands $|c\rangle$, $|c'\rangle$ at the Γ point of the Brillouin zone. Notice that the virtual transitions from $|c\rangle$ to $|c'\rangle$ and $|c'\rangle$ to $|v\rangle$ are nonresonant. (c) Schematic of the energy-band profile as a function of the depth for *n*-type GaAs(001) system. The band bending is caused by the pinning of Fermi level at the surface. L is the length of the depletion region; E_c and E_v represent the conduction and valence bands.

ments, all samples were grown in the same way to ensure that the primary variation from sample to sample was the near surface depletion electric field, E , which scaled with doping density ρ (i.e., $E \sim \sqrt{\rho}$) [12]. We assume here, consistent with previous work [13], that the *n*-type (*p*-type) samples have built-in potential of ~ 0.75 V (~ 0.5 V).

Before discussing our results we consider briefly the microscopic changes induced by the static depletion field. The most obvious change is that the bulk symmetry in the depletion region is reduced from $\bar{4}3m$ towards $mm2$. In principle all elements of $\chi^{(2)}$ will be modified. We focus first on the changes in the existing bulk nonlinearity $\chi_{yxz}^{(2)}$.

Since our detected SHG signal is dominated by the contribution from the three level transition process at the Γ point depicted in Fig. 1(b), we calculated the per-

turbation to $\chi_{yxz}^{(2)}$ by considering the effect of the depletion field on the states $|\Gamma_6\rangle$, $|\Gamma_7\rangle$, and $|\Gamma_8\rangle$. A detailed calculation of such a modification requires a full group theoretical analysis [14]. We have applied these techniques to determine the manner in which these states are mixed. We find that, to lowest order, the modification of the states is linear in the depletion field E . For example, $|\Gamma_{+\frac{1}{2}}^6\rangle \longrightarrow |\Gamma_{+\frac{1}{2}}^6\rangle + \alpha|\Gamma_{+\frac{1}{2}}^7\rangle + \gamma|\Gamma_{+\frac{1}{2}}^8\rangle$, here α and γ are proportional to the matrix elements of perturbation Hamiltonian and therefore depend *linearly* on depletion field E [15]. We computed the change in second-order susceptibility by substituting these perturbed states into the microscopic expression for $\chi_{yxz}^{(2)}$, which contains products of matrix elements of the form $\chi_{yxz}^{(2)} \sim \langle v|y|c'\rangle \langle c'|x|c\rangle \langle c|z|v\rangle$. This leads to a change in $\chi_{yxz}^{(2)}$ that is *second order* in E , i.e.,

$$\chi_{yxz}^{\text{new}} = \chi_{yxz}^{\text{old}} + \delta\chi_{yxz} \quad (1)$$

with

$$\delta\chi_{yxz} = \beta E^2.$$

Here we have assumed the near surface depletion electric field E is constant [16]. β is a complex number proportional to a product of electric dipole transition matrix elements. When the bulk symmetry of the depletion region is lowered towards $mm2$, we expect the in-phase component of the polarization generated through $\delta\chi_{yxz}^{(2)}$, to add destructively with the unperturbed nonlinear polarization produced by χ_{yxz}^{old} [17]. The bulk second-order susceptibility χ_{yxz} in the depletion region is *reduced* by the built-in electric field, and therefore the detected bulk SHG signal will *decrease* as a function of *increasing doping density*. Notice also that the perturbation is independent of the depletion field direction.

The output SHG intensity is modified by an interference between the initial bulk second-order susceptibility χ_{yxz}^{old} and the small perturbation $\delta\chi_{yxz}$, i.e.,

$$\frac{I^{2\omega}(E)}{(I^\omega)^2} \sim |\chi_{yxz}^{\text{old}}|^2 + 2 \text{Re}(\chi_{yxz}^{\text{old}} \delta\chi_{yxz}) + |\delta\chi_{yxz}|^2. \quad (2)$$

Here I^ω is the fundamental laser beam intensity, and $I^{2\omega}(E)$ is the E -dependent SHG intensity. The lowest order change in SHG will depend linearly on the perturbation $\delta\chi_{yxz}$ and hence quadratically on E . We also examined corrections to other tensor elements of $\chi^{(2)}$ which are initially zero in the electric dipole approximation. In many cases the corrections, $\delta\chi^{(2)}$ (such as $\delta\chi_{zzz}^{(2)}$), are proportional to E . However, because there is no interference term these changes are much more difficult to detect. For example, we carried out SHG experiments in the *p*-in/*p*-out polarization configuration, with the crystalline [100] parallel to the plane of incidence in order to suppress the χ_{yxz} signal by $> 10^5$, and thereby greatly enhance our sensitivity to the contribution from $\chi_{zzz}^{(2)}$. However, the contribution from $\delta\chi_{zzz}^{(2)}$ was still below our

detection limit, as observed in earlier work [18].

The variation of SH intensity at 2.68 eV as a function of doping density is displayed in Fig. 2. At this energy, the escape depth of a SHG photon is less than or comparable to the depletion width in all of our samples. Therefore, we can safely assume that the detected SHG signal was generated within the depletion region. Our data clearly exhibit that the SHG intensity of both *n*- and *p*-type samples decreases as a function of increasing doping densities. This picture is in agreement with our theoretical expectations. Since the depletion electric field E is proportional to the square root of the doping density, the perturbed second-order susceptibility $\delta\chi_{yxz}$ is linearly proportional to the doping density (i.e., $\delta\chi_{yxz} \sim \beta E^2 \sim \beta\rho$). The relation between the SHG intensity $I^{2\omega}(E)$ and the doping density can be deduced from Eq. (2) and will have a form $I_0^{2\omega} - I^{2\omega}(E) \sim 2|\text{Re}(\chi_{yxz}^{\text{old}}\beta\rho)| = C\rho$. Here $I_0^{2\omega}$ is the SHG intensity in the limit of small ρ (i.e., $I_0^{2\omega} \sim |\chi_{yxz}^{\text{old}}|^2 |I^\omega|^2$), and C is a constant. The solid lines in Fig. 2 represent the best fits to our experimental results using this model with $I_0^{2\omega}, C$ as free parameters [19]. In the inset of Fig. 2(b), we demonstrate the linear (quadratic) relationship between the SHG intensity and dopant density (electric field) at low dopant concentration. The deviations between our theoretical model and experimental results at high dopant density result from

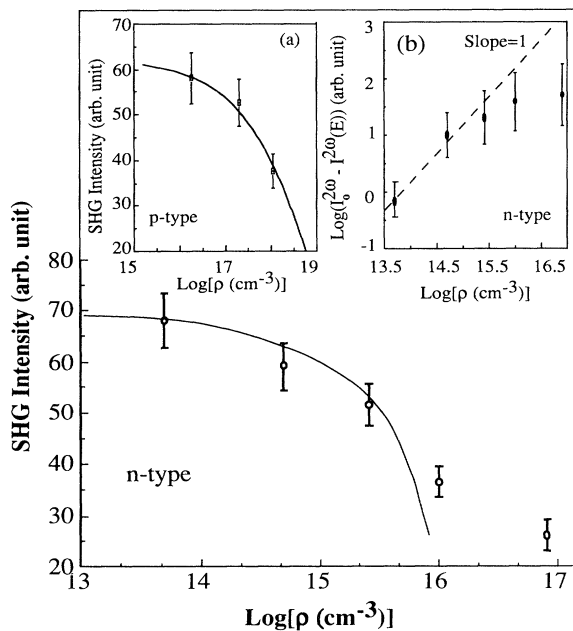


FIG. 2. The variation of SH intensity at 2.68 eV as a function of doping density. Both *n*- and *p*-type [see inset (a)] samples exhibit a reduction in SHG intensity as a function of increasing doping density. The solid lines are our theoretical fit to the data. Inset (b): The plot of $\ln[I_0^{2\omega} - I^{2\omega}(E)]$ as a function of $\ln(\rho)$. It clearly can be seen that the relationship between the SHG intensity and dopant density (electric field) is linear (quadratic) at the low dopant densities.

the fact that SHG penetration depth is comparable to the depletion length, and thus the position dependence of the electric field must be considered. In addition, it is possible that the density of majority carriers in highly doped samples could exceed the maximum number density of surface states. In this case the electric field at the surface reaches a maximum value, independent of dopant density. Both possibilities will produce a saturation of the SHG reduction at high doping levels.

The sensitivity of the near surface bulk second-order susceptibility to the depletion electric field has also been checked by a PSHG technique [7,8]. In such PSHG experiments (see Fig. 3), light from a tungsten-lamp monochromator illuminates the sample to modulate the band bending in the depletion region while the SHG experiment is in progress. The photon energy of the photo-modulation light was set at 2.72 eV where the absorption length ($\sim 0.1 \mu\text{m}$) is within the depletion region [20]. Experimentally, an *enhancement* of the second-harmonic intensity has been observed for both *n*- and *p*-type samples as a result of light illumination. The microscopic mechanism of enhancements in the PSHG experiments can be described as follows. The linear photoexcitation creates electrons and holes in the depletion region. These carriers are separated by the built-in field and, as a result, partly neutralize the surface charge. This in turn decreases the depletion electric field and the band bending. Thus $|\delta\chi_{yxz}|$ becomes smaller, and an enhancement of the SHG signal is observed. Here the experimental observations again confirm our theoretical model. The saturation of enhancements with respect to photoexcitation intensity has been found for all of the samples. Qualitatively the saturation of enhancements is expected to be related to the density of the surface states (traps), their lifetimes, and the charge transport in the depletion region. More details about these phenomena will be published elsewhere.

We have performed time-dependent measurements to follow the *decrease* of the SHG intensity after the photo-modulation light is turned off. This is a direct measurement of the surface state (trap) *discharging* time [21]. Here *discharging* refers to the removal of charge from the the surface traps. The measurements were carried out by illuminating the sample for at least 2 min, turning off the lamp, and monitoring the SH signal as the function of time. A typical time-dependent SHG intensity of a *p*-doped $10^{16}/\text{cm}^3$ sample for the discharging case is plotted as a function of time in the inset of Fig. 3. The solid line is our best fit to the experimental results based on a simple carrier recombination and generation model which was described in Ref. [21]. Although samples with different doping densities have much different depletion widths, all of our samples exhibit approximately the same discharging time (~ 25 s). Since the characteristic time for the carrier trapping on the surface states is much longer than the time it takes a carrier to pass through the depletion region, this suggests that the surface re-

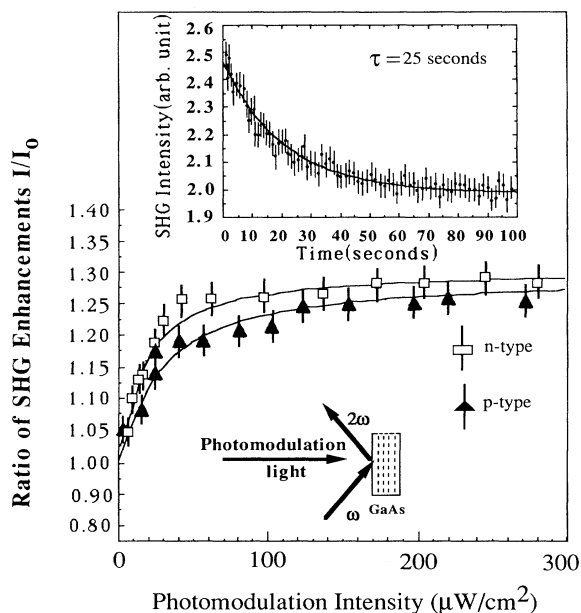


FIG. 3. The enhancement of normalized SH intensity at 2.68 eV for two typical n -type ($n = 10^{16}/\text{cm}^3$) and p -type ($p = 10^{16}/\text{cm}^3$) samples as a function of the photoexcitation intensity. The solid lines are the theoretical fit to the data. The inset shows SH intensity from a typical p -type ($p = 10^{16}/\text{cm}^3$) sample as a function of time after photomodulation light was turned off. From our theoretical fitting (solid line), the discharging time, τ , of the surface traps is found to be ~ 25 s. All samples give about the same discharging time.

combination process is the slowest step in discharging of the traps on the surface. Thus the rate limiting step for discharging arises primarily from the surface trap lifetime. Our experimental results suggest that the surface trap lifetime is similar in all samples.

In conclusion, we have shown that bulk second-order susceptibility of GaAs has been significantly reduced by the depletion electric field. According to our simple three band model, the depletion electric field causes a quadratic field-dependent perturbation of the second-order bulk susceptibility $\chi_{yxz}^{(2)}$. Such built-in depletion field effects have been observed in our SHG experiment as a function of doping density and type, and have been confirmed by our PSHG experiments. The time-dependent PSHG measurements indicate that the traps discharge at about the same rate, independent of band bending in all samples. Future work is underway to measure the properties of Schottky barrier samples and quantum-well structures using these ideas.

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- [1] R. S. Finn and J. F. Ward, Phys. Rev. Lett. **6**, 285 (1971); P. Sitz and R. Yaris, J. Chem. Phys. **49**, 3546 (1968).
- [2] C. H. Lee, R. K. Chang, and N. Bloembergen, Phys. Rev. Lett. **5**, 167 (1967); R. W. Terhune, P. D. Maker, and C. M. Savage, *ibid.* **8**, 404 (1962).
- [3] F. Schäffler and G. Abstreiter, Phys. Rev. B **34**, 4017 (1986).
- [4] N. M. Jokerst and E. Garmire, Appl. Phys. Lett. **53**, 897 (1988); M. Sydor, J. R. Engholm, M. O. Manasreh, C. E. Stutz, L. Liou, and K. R. Evans, *ibid.* **56**, 1769 (1990).
- [5] S. L. Chuang, S. Schmitt-Rink, B. I. Greene, P. N. Saeta, and A. F. J. Levi, Phys. Rev. Lett. **68**, 102 (1992).
- [6] X. C. Zhang, B. B. Hu, J. T. Darrow, and D. H. Auston, Appl. Phys. Lett. **56**, 1011 (1990); X. C. Zhang, J. T. Darrow, B. B. Hu, D. H. Auston, M. T. Schmidt, P. Tham, and E. S. Yang, *ibid.* **56**, 2228 (1990).
- [7] M. S. Yeganeh, J. Qi, A. G. Yodh, and M. C. Tamargo, Phys. Rev. Lett. **68**, 3761 (1992).
- [8] M. S. Yeganeh, J. Qi, A. G. Yodh, and M. C. Tamargo, Phys. Rev. Lett. **69**, 3579 (1992).
- [9] M. S. Yeganeh, J. Qi, J. P. Culver, A. G. Yodh, and M. C. Tamargo, Phys. Rev. B **46**, 1603 (1992).
- [10] R. W. Boyd, *Nonlinear Optics* (Academic Press, San Diego, 1992).
- [11] C. Y. Fong and Y. R. Shen, Phys. Rev. B **12**, 2325 (1975).
- [12] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
- [13] W. E. Spicer, I. Lindau, P. Skeath, and C. Y. Su, J. Vac. Sci. Technol. **17**, 1019 (1980).
- [14] S. Rodriguez, P. Fisher, and F. Barra, Phys. Rev. B **5**, 2219 (1972).
- [15] For example, $\alpha \sim \langle \Gamma_{+\frac{1}{2}}^7 | H' | \Gamma_{+\frac{1}{2}}^6 \rangle / \Delta\epsilon$, here $H' \sim \mathbf{z} \cdot \mathbf{E}$ is the perturbation Hamiltonian and $\Delta\epsilon$ is the energy difference between states of $|\Gamma_{+\frac{1}{2}}^6\rangle$ and $|\Gamma_{+\frac{1}{2}}^7\rangle$.
- [16] With constant surface band bending (ϕ), the electric field in the depletion region can be written $E = 4\pi N_t/\epsilon - 4\pi\rho z/\epsilon$, where the z is the depth measured from the surface, ϵ is the dielectric constant of GaAs, and $N_t = \sqrt{(2\pi)^{-1}\epsilon\phi\rho}$ is the surface charge density. Since our SHG photon probes regions close to the surface, the first term in $E(z)$ is dominant. Therefore the constant E -field approximation is reasonable, particularly at low doping levels.
- [17] Note, if the system exhibited purely $mm2$ symmetry, then χ_{yxz} would be zero.
- [18] J. H. McFee, Appl. Phys. Lett. **11**, 228 (1967).
- [19] The constant electric field assumption breaks down for very high dopant density ($n > 10^{17}/\text{cm}^3$). Because of this fact the data point for $n \approx 10^{17}/\text{cm}^3$ was not considered in our fitting routine.
- [20] S. D. Offsey, J. M. Woodall, A. C. Warren, P. D. Kirchner, T. I. Chappell, and G. D. Pettit, Appl. Phys. Lett. **48**, 475 (1986).
- [21] M. S. Yeganeh, J. Qi, A. G. Yodh, and M. C. Tamargo, J. Opt. Soc. Am. B (to be published).