

Transverse diffusion of minority carriers confined near the GaAs surface plane

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Spatially separated second-harmonic generating and photocarrier exciting light beams were employed to study transverse diffusion of carriers confined near GaAs(001) surfaces. The measurements utilize the intrinsic sensitivity of second-harmonic generation to surface charge density in order to probe these processes. Carrier transport was found to be diffusive with small effective diffusion coefficients compared to those of carriers in the bulk. Several models are considered to explain these results.

Many years ago an elegant experiment by Haynes and Shockley elucidated the drift of a pulse of minority carriers through a *bulk* semiconductor.¹ The packet of carriers was observed to broaden as a result of diffusive processes, and to attenuate as a result of recombinative processes. In this paper we present analogous measurements of minority carrier diffusion near the *surface* of GaAs. Just as studies of bulk diffusion have proved invaluable for device design over the years,^{2,3} additional knowledge about near-surface charge diffusion may also be of use in the analysis of transport in lower-dimensional devices such as quantum-well heterostructures.⁴ We find that near-surface minority carrier diffusion is quite different from the bulk. These differences are proposed to arise through the effects of charge traps and near-surface charge recombination.

In our experiment we do not use electrical contacts, instead we use spatially separated photocarrier exciting and second-harmonic generating (SHG) light beams to study charge transport (see Fig. 1). The cw laser beam creates surface charge through the photoexcitation and drift of minority carriers in the GaAs depletion field. This *additional* surface charge diminishes the depletion electric field within the excitation beam waist. A second, *spatially separated* SHG beam probes surface charge transport. In particular, we utilize an effect observed recently,⁵ whereby near-surface second-harmonic generation in GaAs is modulated by surface charge-density changes. Because of the substantial band bending near the interface, the minority carriers are constrained to move near (within 10 nm) the surface plane of the sample.⁶ Diffusion takes place primarily in two dimensions, parallel to the GaAs surface plane. Our measurements suggest that surface charge transport is isotropic and diffusive, with small diffusion coefficients relative to the bulk.⁷ Temperature-dependent measurements indicate that charge traps play a prominent role in the diffusion of both holes and electrons.

The present experiments probe lateral, near-surface minority carrier diffusion. In this case the physics of diffusion is dominated by properties of the surface region. Our measurements exploit the intrinsic sensitivity

of SHG to the depletion electric field,⁸⁻¹⁰ and demonstrate a noncontact methodology by which to probe near-surface transport processes. Recently, SHG-based measurements have been used to probe diffusion of *neutral* species such as surface adsorbates through their effects on surface nonlinearities.¹¹ By contrast the present experiments probe the motion of *charge*, utilizing their field-induced perturbation of the bulk second-order nonlinear optical susceptibility.^{5,9} We note that other noncontact

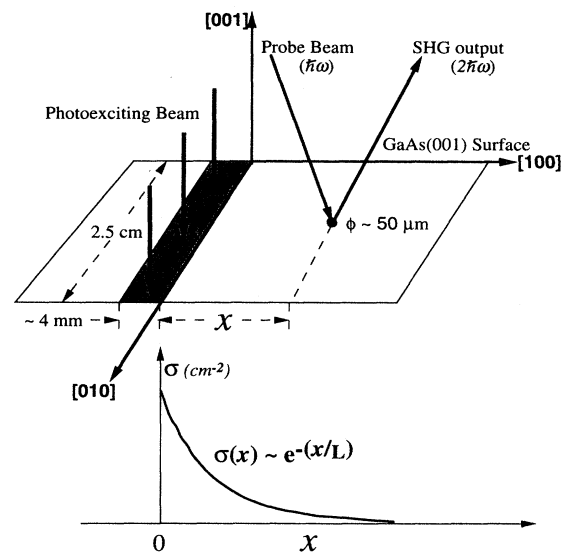


FIG. 1. A 10 Hz Nd:YAG pumped dye laser, with $\sim 50 \mu\text{m}$ sample spot size, was used as the fundamental probe light for the SHG measurements. An Ar^+ ion laser was used as a cw photocarrier excitation beam, and its transverse beam profile on the sample was a narrow rectangle ($\sim 2.5 \text{ cm}$ long, $\sim 4 \text{ mm}$ wide) with sharp ($\leq 50 \mu\text{m}$) edges on all sides. The long edge of the excitation beam was made parallel to the sample [010] axis. The photoexciting beam edge is at $x = 0$, and a schematic drawing of the photoexcited surface minority carrier density with diffusion length L is plotted as a function of the distance x .

methodologies have been employed to study the lateral decay of photoinduced carrier effects.¹² The nonlinear techniques presented here differ from these other methods primarily as a result of their symmetry dependence, and intrinsic interface sensitivity.

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 in the plane of incidence,¹³ the output SHG intensity from $\chi_{yxz}^{(2)}$ is maximized. More importantly, in this polarization configuration the detected SHG intensity is insensitive to higher-order contributions from the bulk magnetic dipole and electric quadrupole transitions.¹⁴ Our GaAs(001) samples were doped with Si (*n* type) and Be (*p* type) at low density (10^{16} cm^{-3}), and were grown on an undoped GaAs substrate by molecular-beam epitaxy. The sample surfaces were typically As terminated, and exposed to air. Since the As oxides are more volatile, we believe our oxide surfaces are primarily Ga oxides with a thickness of 30–40 Å. The sample surface appeared to remain stable for months as observed by Auger electron spectroscopy. Experiments were performed in air.

A 10 Hz Nd:YAG (yttrium aluminum garnet) pumped dye laser operating at 925 nm, with $\sim 50 \mu\text{m}$ sample spot size, was used as the fundamental light source for the SHG measurements (see Fig. 1). The energy per pulse was $\sim 50 \mu\text{J}$. 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 $|\Gamma_8\rangle$ and the two lowest conduction bands $|\Gamma_7\rangle$, $|\Gamma_6\rangle$ at the Γ point in the Brillouin zone of GaAs.¹⁵ An Ar⁺ ion laser operating at 457 nm, and with intensity at $300 \mu\text{W}/\text{cm}^2$, was used as a cw photocarrier excitation beam. The absorption length of the excitation beam ($\leq 0.1 \mu\text{m}$) was less than the depletion length of GaAs ($\sim 0.4 \mu\text{m}$ for doping density $\sim 10^{16} \text{ cm}^{-3}$).¹⁶ The transverse excitation beam profile on the sample was a narrow rectangle ($\sim 2.5 \text{ cm}$ long, $\sim 4 \text{ mm}$ wide) with sharp ($\leq 50 \mu\text{m}$) edges on all sides. The long edge of the excitation beam was made parallel to the sample [010] axis (see Fig. 1).

Photoexcited carriers can diffuse out of this excitation region parallel to the GaAs surface plane. We assume that charge motion is well approximated by a diffusion equation under these circumstances, so that the surface charge density σ as a function of distance x along the [100] axis ($x = 0$ defines the edge of the photocarrier excitation beam) is given by

$$\sigma(x) = \sigma_0 e^{-\frac{x}{L}} \quad (x > 0). \quad (1)$$

Here the diffusion length $L = \sqrt{D_{\text{eff}}\tau}$ depends on the effective carrier diffusion coefficient D_{eff} and lifetime τ near the surface. σ_0 is the photoexcited minority carrier surface density at the edge of the photoexcitation beam. This surface charge density is approximately 10^{11} – 10^{12} cm^{-2} .¹⁷ In our analysis of the diffusion process, we make the standard electrical neutrality assumption.¹⁸

That is, we neglect the effects of the internal electric field due to the photoexcited minority carriers. Experimentally, we checked this assumption by studying charge diffusion as a function of excitation beam width (which was varied from 2 mm to 5 mm). By changing the beam width, we are effectively changing the transverse electric field due to minority carriers. No variation in diffusion was observed within our experimental error of $\sim 2\%$.

The escape depth of the SHG output photon at 2.68 eV was $\sim 0.1 \mu\text{m}$, less than the depletion width in all of our low doping samples. We approximate the near-surface depletion electric field as a constant over this escape depth. As a result of the minority carrier diffusion, the depletion electric field *along* the [001] direction (normal to sample surface) is perturbed by the minority carriers, i.e.,

$$\delta\mathbf{E}(x) \sim \frac{\sigma(x)}{\epsilon} \quad (x > 0). \quad (2)$$

Here ϵ is the dielectric constant of GaAs and $\delta\mathbf{E}$ represents the change in depletion electric field due to photoexcited carriers. To leading order, we expect the variation of our SHG output intensity $I(2\omega)$ as a function of the distance x from the photoexciting beam edge to be of the form⁵

$$\frac{I_{\text{on}}(2\omega)}{I_{\text{off}}(2\omega)} \sim |1 + \alpha e^{-\frac{x}{L}}|^2 \quad (x > 0). \quad (3)$$

$I_{\text{on}}(2\omega)$ [$I_{\text{off}}(2\omega)$] represents the SHG intensity measured when the photoexciting beam is on (off). α is a constant that depends on dipole transition matrix elements and the unperturbed depletion electric field. Because the probe beam spot size is around $50 \mu\text{m}$, much less than the observed minority carrier diffusion length, the surface minority carrier density *within* the probe beam spot was approximately constant. Higher-order field corrections in the [001] direction brought about by the transverse gradient in minority carrier density *outside* the probe beam spot were neglected.¹⁹ In addition, the transverse fields (in plane) resulting from the minority carrier density gradient were too small to affect χ_{yxz} .

The observed variation of the SHG enhancement [$I_{\text{on}}(2\omega)/I_{\text{off}}(2\omega)$] as a function of distance x from the excitation beam edge is plotted in Fig. 2. The solid lines represent our best fits to the data using Eq. (3). In the case of *n*-type (*p*-type) samples, the variation of surface charge density is due to photoexcited holes (electrons). In all cases, the diffusion model appears to account for our observations. The diffusion length of the electrons is larger than that of the holes. From a fit of the data, we determined the hole (electron) diffusion length L_h (L_e) to be $2.83 \pm 0.09 \text{ mm}$ ($7.01 \pm 0.13 \text{ mm}$) at room temperature. Interestingly, the observed surface diffusion lengths are at least one order of magnitude larger than pure bulk carrier diffusion lengths.⁷ We measured these diffusion coefficients as a function of temperature from ~ 250 to 350 K for both *n*- and *p*-type samples. Our temperature-dependent observations will be discussed later in the paper. Further experiments revealed that the photoexcited carrier diffusion processes were isotropic in the surface

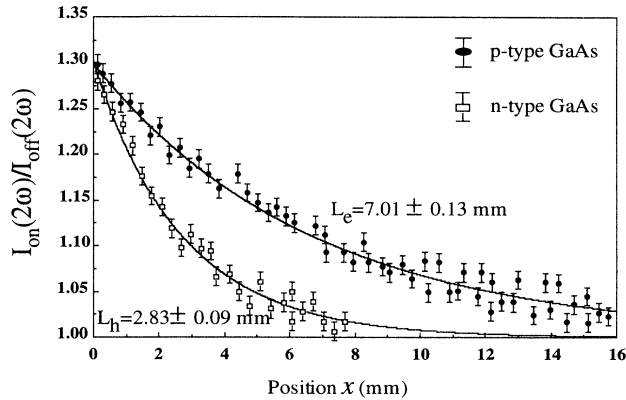


FIG. 2. A typical diagram of the variation of SHG output from n -type (p -type) GaAs plotted as a function of distance x from the photoexciting beam edge, $x = 0$ at room temperature. $I_{\text{on}}(2\omega) [I_{\text{off}}(2\omega)]$ represents the SHG intensity when the photoexciting beam is on (off). The solid lines are our best fits. The error represents the standard deviation of multiple measurements on multiple samples. The hole (electron) diffusion length L_h (L_e) is 2.83 ± 0.09 mm (7.01 ± 0.13 mm).

plane. For example, we rotated the sample through an angle ϕ ($0^\circ \leq \phi \leq 90^\circ$) about the [001] axis. No variation in diffusion was observed under these circumstances. Finally in previous experiments⁵ we have found that minority carriers at the surface live long before recombining. In these experiments the photoexciting beam overlapped the probe beam, and the probe spot was much smaller than photoexciting beam area so that diffusion effects were negligible. Carriers in both n - and p -type samples exhibit approximately the same lifetimes of $\tau \sim 25$ s.

Given these observations, we considered three possible mechanisms for the surface carrier diffusion: (1) free carriers diffusing in near-surface bands; (2) activated free carriers diffusing and trapping between bands and localized states (see Fig 3); and (3) variable-range hopping (VRH) or fixed-range hopping (FRH) of trapped carriers. Several pieces of evidence enable us to rule out *pure* free carrier diffusion. First, the ratio of electron and hole surface diffusion coefficients derived from diffusion length and lifetime measurements, i.e., $\frac{D_e}{D_h} \sim (\frac{L_e}{L_h})^2 \sim 6.1$, is nearly three times smaller than the bulk ratio,⁷ ($\frac{D_e^{\text{bulk}}}{D_h^{\text{bulk}}} \sim 22$). In addition, we observed an *increase* of the diffusion length at higher temperatures. This suggests that the surface carrier diffusion process is not a result of purely free carrier motion in the near-surface bands, but is some sort of thermally activated process. Finally, since the surface acts like a *sink* for free minority carriers, it is unlikely that purely free carriers would exist near the surface over long periods of time.²²

A priori there are several mechanisms that can be invoked to explain our temperature-dependent results. One possible mechanism for near-surface minority carrier diffusion is an active diffusion process which may involve free carriers. In such a model (see Fig. 3), minority carriers excited within the depletion region drift to the sur-

face, and are trapped quickly by interfacial defects in a time τ_c (10^{-6} – 10^{-10} s).²² Before recombining and leaving the surface, however, these carriers can be excited thermally from the traps into free carrier states near the surface. Let τ_e represent the average time a trapped carrier resides in a trap before it is thermally excited into a surface free carrier state. Thermally excited free carriers will *diffuse* along the surface until they become trapped again (usually $\tau_c \ll \tau_e$). The effective diffusion coefficient of the quasifree carriers will depend on the trapping time (τ_c), the excitation time to reexcite thermally out of the trap (τ_e), and the scattering time of the free carrier in the near-surface bands, τ_s (usually $\tau_s \ll \tau_c$). A simple analysis demonstrates that the effective diffusion coefficient $D_{\text{eff}} \sim (v_{\text{free}})^2 \frac{\tau_s \tau_c}{\tau_c + \tau_e}$. Here v_{free} is the free carrier velocity in the near surface bands. v_{free} depends on the effective mass of the near-surface minority carrier. We see that the role of traps is primarily to *reduce* the amount of time an electron or hole spends as a free carrier. Since the SHG signal is only sensitive to the depletion electric field, carriers affect the SHG signal in the same way whether trapped or free. We anticipate that

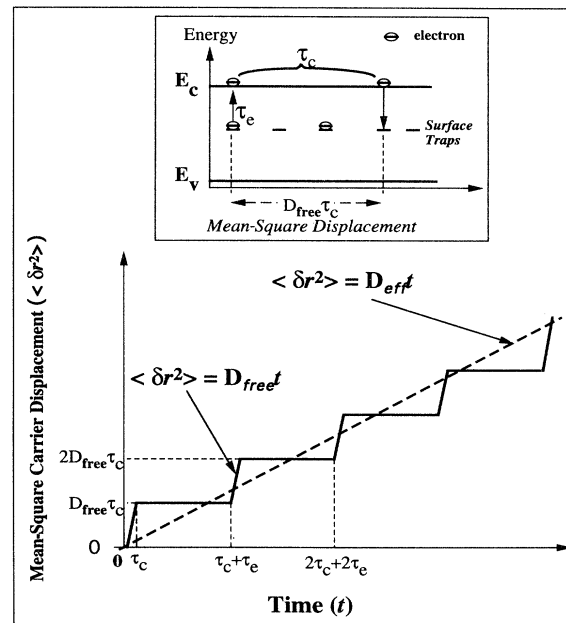


FIG. 3. Schematic of the mean-square displacement $\langle \delta r^2 \rangle$ of the minority carrier as a function of time. The solid line indicates the carrier diffusion process with a free carrier diffusion coefficient D_{free} (large positive slope) and the carrier capture by traps for a time τ_e (flat line). The dashed line (with relatively small positive slope) represents the effective diffusion process (with effective diffusion coefficient D_{eff}) that we observed. Here τ_c is the trapping time for the free carrier, and τ_e is the time required for the carrier to become reexcited out of trap. The inset is a schematic diagram of the energy and position of a minority carrier (p -type sample) that is excited, diffuses, and is then captured again. Figures are intended to convey ideas and are *not* drawn to scale.

a substantial amount of trap excitation and deexcitation occurs during the carrier lifetime τ near the surface. In the case of $\tau_c \ll \tau_e$, we expect $v_{\text{free}} \sim \sqrt{T}$, and $\tau_s \sim T^m$ where m is a constant. The temperature dependence of the effective diffusion coefficient in this model is of the form

$$D_{\text{eff}} = aT^n e^{(-E/kT)}. \quad (4)$$

Here a and n are constants, and k is the Boltzmann constant. E is the energy difference between trap states and the free carrier band (conduction band for p type and valence band for n type). Experimental data and fits for typical n -type GaAs are plotted in Fig. 4. In total we found that $n = -0.1$ (-0.04), and $E = 21$ meV (17 meV) for n -type (p -type) samples. Errors were $\sim 5\%$. This model suggests that shallow trap states just below the conduction band (p -type samples) or above the valence band (n -type samples) affect the carrier diffusion process.

The other possible diffusion process involves hopping of carriers from trap to trap. The most common theories considered in this regard are VRH and FRH between localized traps.²⁰ In the case of VRH, the diffusion coefficient D_{eff} is predicted to be temperature dependent and of the form $D_{\text{eff}} \sim e^{-(T_0/T)^s}$. Here T_0 is a positive constant. The exponent s is $1/3$ ($1/4$) in two-dimensional (three-dimensional) systems.²¹ A plot of $\ln(D_{\text{eff}})$ as a function of T^{-s} with $s = 1/3$ for a typical n -type GaAs sample is shown in Fig. 4(a). The solid line is our best fit to the VRH model. In the model of FRH, the diffusion coefficient is of the form $D_{\text{eff}} \sim e^{(-E/kT)}$. A typical plot of $\ln(D_{\text{eff}})$ as a function of T^{-1} for a typical n -type GaAs is shown in Fig. 4(b). In this case, we find the excitation energy E is 19 meV (16 meV) for n -type (p -type) samples. The latter result gives an activation energy quite similar to our first model involving free carrier activation and trapping.

Our temperature-dependent data are insufficient to distinguish between the latter three possible carrier diffusion mechanisms, but clearly demonstrate that *bulk free carrier* mechanisms are unlikely. Recalling the relationship between the diffusion length, the diffusion coefficient, and the carrier recombination time, i.e., $L = \sqrt{D_{\text{eff}}\tau}$, we find that the effective diffusion coefficient is 2×10^{-2} cm²/s (3×10^{-3} cm²/s) for electrons (holes). By comparison, bulk GaAs at the same doping density has the bulk diffusion coefficient, $D^{\text{bulk}} \sim (v_{\text{free}}^{\text{bulk}})^2 \tau_s^{\text{bulk}}$, of 220 cm²/s (10 cm²/s) for electrons (holes).⁷ The bulk diffusion coefficient is three orders of magnitude larger than the effective diffusion coefficients obtained near the surfaces. Furthermore, the ratio of electron and hole diffusion coefficients in the bulk is nearly three times larger than the ratio observed at the surface. Clearly near-surface bands and surface traps may play an important role in the carrier diffusion process. In the model of activated free carrier diffusion, the surface carrier diffusion process can involve extra, trap-related time scales (τ_c , τ_e) relative to bulk free carriers. The diffusion coefficients de-

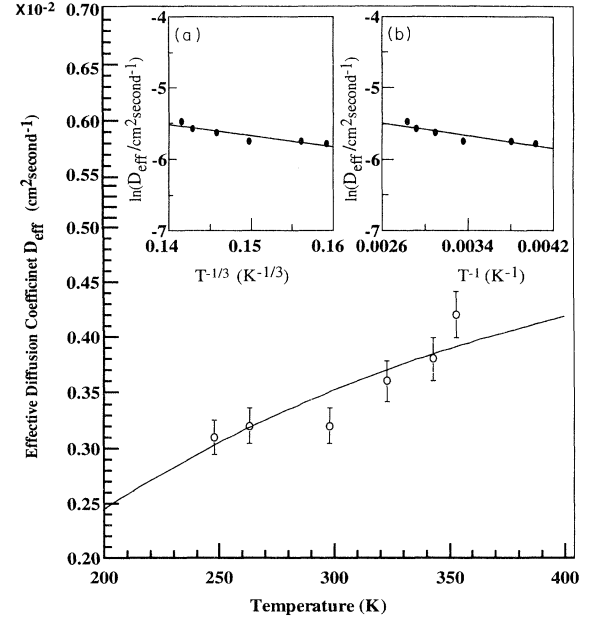


FIG. 4. Diffusion coefficients as a function of temperature for a typical n -type GaAs sample. The solid line is our fitting according to the activated free carrier diffusion model (see Fig. 3.). Inset (a) shows $\ln(D_{\text{eff}})$ as a function of $T^{-1/3}$ for n -type GaAs. The solid line is a linear fit according to the VRH model. Inset (b) shows $\ln(D_{\text{eff}})$ as a function of T^{-1} for n -type GaAs. The solid line is a linear fit according to the FRH model.

crease as a result of the capture of free carriers by traps. On the other hand, either VRH or FRH might also account for the observed diffusion. All models suggest that shallow trap states play an important role in the diffusion process, however, the temperature-dependent data are not of sufficient dynamic range to distinguish these mechanisms.

In conclusion, we have used spatially separated photoexciting and second-harmonic generating light beams to study near-surface carrier diffusion processes. We find the diffusion is isotropic with a small effective diffusion coefficient relative to pure bulk. A possible mechanism for this motion is through an activated diffusion process which involves surface traps and may involve free carriers. Future work will include studies of the properties of interface states utilizing these ideas, and more careful studies of diffusion using time-dependent methods in more well-characterized systems.

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- ¹ J. R. Haynes and W. Shockley, *Phys. Rev.* **81**, 835 (1951).
- ² A. Castaldini, A. Cavallini, E. Gombia, R. Mosca, and L. Tarricone, *Appl. Surf. Sci.* **50**, 485 (1991).
- ³ R. Hakimzadeh, H. J. Möller, and A. G. Bailey, *J. Appl. Phys.* **72**, 2919 (1992).
- ⁴ P. L. Gourley, R. M. Bifeld, T. E. Zipperian, and J. J. Wiczer, *Appl. Phys. Lett.* **44**, 983 (1984).
- ⁵ J. Qi, M. S. Yeganeh, I. Koltover, A. G. Yodh, and W. M. Theis, *Phys. Rev. Lett.* **71**, 633 (1993).
- ⁶ J. L. Shay, *Phys. Rev. B* **2**, 803 (1970); here the term *near surface* corresponds approximately to the spatial extent normal to the surface of carrier wave functions confined by the depletion field.
- ⁷ S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
- ⁸ M. S. Yeganeh, J. Qi, A. G. Yodh, and M. C. Tamargo, *Phys. Rev. Lett.* **69**, 3579 (1992).
- ⁹ S. L. Chuang, S. Schmitt-Rink, B. I. Greene, P. N. Saeta, and A. F. J. Levi, *Phys. Rev. Lett.* **68**, 102 (1992).
- ¹⁰ E. Burstein, G. Pajer, and A. Pinczuk, in *Proceedings of the 18th International Conferences on the Physics of Semiconductors, Stockholm, 1986*, edited by O. Engstrom (World Scientific, Singapore, 1987), Vol. 2, p. 1691.
- ¹¹ X. D. Zhu, Th. Rasing, and Y. R. Shen, *Phys. Rev. Lett.* **61**, 2883 (1988); G. A. Reider, U. Hofer, and T. F. Heinz, *Phys. Rev. Lett.* **66**, 1994 (1991).
- ¹² A. E. Willner, O. J. Glembocki, D. V. Podlesnik, E. D. Palik, and R. M. Osgood, *Proc. SPIE* **946**, 48 (1988); M. Sydor, J. R. Engholm, M. O. Manasreh, K. R. Evans, C. E. Stutz, and W. C. Mitchel, *Phys. Rev. B* **45**, 13 796 (1992).
- ¹³ M. S. Yeganeh, J. Qi, J. P. Culver, A. G. Yodh, and M. C. Tamargo, *Phys. Rev. B* **46**, 1603 (1993).
- ¹⁴ R. W. Boyd, *Nonlinear Optics* (Academic Press, San Diego, 1992).
- ¹⁵ C. Y. Fong and Y. R. Shen, *Phys. Rev. B* **12**, 2325 (1975).
- ¹⁶ 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).
- ¹⁷ H. Shen, M. Dutta, L. Fotiadis, P. G. Newman, R. P. Mørkirk, W. H. Chang, and R. N. Sacks, *Appl. Phys. Lett.* **57**, 2118 (1990).
- ¹⁸ J. P. Mckelvey, *Solid State and Semiconductor Physics* (Harper & Row, New York, 1966).
- ¹⁹ The escape depth of the SHG output photons is $\sim 0.1 \mu\text{m}$, much less than the fundamental probe beam diameter $\sim 50 \mu\text{m}$. The near-surface electrical field produced by the photoexcited minority carrier transverse gradient is nearly normal to the [001] direction, i.e., parallel to the surface plane. As a result, the electric field *along the [001] direction* due to the transverse carrier gradient outside the probing beam spot can be neglected.
- ²⁰ M. Pollak and B. Shklovskii, *Hopping Transport in Solids* (North-Holland, New York, 1990).
- ²¹ M. R. A. Shegelski and R. Barrie, *Phys. Rev. B* **36**, 7549 (1987).
- ²² D. E. Aspnes, *Surf. Sci.* **132**, 406 (1983).