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Energy-gap narrowing and state filling in semiconductors under intense laser irradiation

D. K. Ferry
Colorado State University, Fort Collins, Colorado 80523
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Detailed calculations of the time and energy dependence of the distribution function for optically created electrons in the conduction band of Ge are presented. These indicate that state filling in the conduction and valence bands are strongly controlled by energy-gap narrowing induced by the optically generated interacting electrons and holes.

I. INTRODUCTION

Recently, studies have appeared on the nonlinear, nonequilibrium optical properties of semiconductors, notably germanium.[1-4] These studies probe the optical properties by utilizing intense picosecond laser pulses of sufficient energy to create electron-hole pairs by direct absorption, for example, into the central valley of the conduction band of germanium. The nonlinear optical properties have been probed, not only by the nonlinear absorption of the intense pulse, but also by delayed probe transmission measurements with a second pulse[1,3] and by reflectivity measurements.[4] From this, it is indicated that detailed studies of the photoexcited hot-carrier dynamics can be carried out on a picosecond time scale.[5]

In addition to relaxation processes occurring on a time scale of many tens of picoseconds, Kennedy *et al.*[1] observed an apparent sharp-spike saturation of the absorption of the 1.06-μm laser in probe measurements in Ge, which occurred near zero delay and had a recovery time of the absorption that appeared to be somewhat less than the optical pulse width of 5 psec. Although they initially interpreted this result as a saturation of the direct absorption, Shank and Auston later suggested that this effect was caused by parametric scattering of the intense laser pulse into the probe beam path by the electron-hole plasma.[6] While there is certain to be some of the latter effect occurring, one in general would expect saturation due to state filling also to be a factor. State filling of the conduction and valence bands, as opposed to band filling,[7] arises from monochromatic radiation and results in a δ-function-like spike (in energy) in the distribution function.[8-10] The occurrence of such state filling is dependent upon the generation rate and the length of time that the excitation occurs in a specific energy state. Normally, it is to be expected that such effects will occur under picosecond laser pulses, although one would expect the time width of the resulting saturated absorption to be of the same scale as the laser pulse. In this paper, the results of detailed calculations on the time and energy dependence of the distribution function for the optically created electrons in the central valley of Ge are presented. It is found that the state filling that would normally be expected to occur is restricted by the process of energy-gap narrowing, or band renormalization as it is sometimes called, induced by the electron-hole pairs, but does occur in the region of nonlinear optical absorption for a short period of time, which is dependent upon the incident laser pulse intensity. Moreover, it is found that saturated absorption due to state filling can contribute to results such as those observed by Kennedy *et al.*[1]

As pointed out below, the dominant effect on controlling the time dependence of the state filling is the energy-gap narrowing, a process that apparently has not been previously considered in intense laser excitation studies, other than at very low temperatures for consideration of electron-hole droplets,[11,12] although the role of free electrons and holes on energy-gap narrowing has long been studied for the temperature dependence of the gap,[13] and more recently for the concentration dependence of absorption.[14,15]

II. THEORETICAL APPROACH

A. Iterative integral

To investigate the role of state filling and energy gap narrowing on intense picosecond laser pulse absorption, an iterative integral[16] solution has been utilized to solve the time-dependent Boltzmann equation for the central valley of germanium. This approach has specific advantages in that it allows the full form of the collision integral to be retained. In this way, the detailed energy dependence and time evolution of the distribution function can be ascertained. In short, the Boltzmann transport equation

$$\frac{\partial f}{\partial t} + \vec{V} \cdot \vec{\nabla} f + \frac{e}{\hbar} \vec{F} \cdot \frac{\partial f}{\partial \vec{k}} = \int W(\vec{k}, \vec{k}') f(\vec{k}') \, d\vec{k}' \qquad (1)$$

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is transformed via a path integral formalism into the integral formulation[17]

$$f(\vec{k},t)=\int_0^\infty ds\int d\vec{k}'\,f(\vec{k}',t-s)W_i\left(\vec{k}',\vec{k}-\frac{e\vec{F}s}{\hbar}\right)\times\exp\left[-\int_{-s}^{0}\lambda\left(\vec{k}-\frac{e\vec{F}y}{\hbar}\right)dy\right], \quad (2)$$

where $W(\vec{k}',\vec{k})$ has been split into the out-scattering W_0 and in-scattering W_i portions, and

$$\lambda=\int d\vec{k}'\,W_0(\vec{k}',\vec{k}). \quad (3)$$

In particular, the in-scattering and out-scattering rates can include terms representing the generation and recombination of carriers,[18] and a normal continuity equation provides normalization constraints on $f(\vec{k},t)$. An iterative procedure for solving (2) has been detailed by Rees[16] that depends upon the stability of the steady state for its convergence properties, although a Monte Carlo technique can also be used for obtaining the solution.[18] In the iterative approach, each step iteration represents a time step in the solution, and the iterative evolution of $f(\vec{k},t)$ is a surrogate for the time evolution of the distribution function. In the present treatment, we specifically do not treat diffusion (a process deferred to later work), and we neglect the role of the ac electric field, other than in generation processes. This latter assumption is questionable, but it is felt that such processes as field-induced modifications of the scattering rates[19,20] and drift effects will be of second-order to those considered here. Under these assumptions, the iterative integral in (2) greatly simplifies, and a relatively rapid solution can be obtained.

Direct absorption and recombination, intervalley scattering to the dominant L valleys, and scattering within the central valley are all incorporated into the solution. Scattering rates for the intervalley and intravalley acoustical phonons are well known, and values for the coupling constants were taken from Paige.[21] Decay of the electrons from the excitation state via emission of intravalley optical phonons is hindered in Ge, since this is a forbidden process and occurs through a weaker first-order interaction.[22]

Direct recombination is characterized by a lifetime of about 10^{-9} sec at low light intensities. However, at high intensities, the band population increases drastically and a shorter lifetime is expected. Because the distribution is non-Maxwellian, it is actually questionable whether a lifetime description is viable. In the present treatment, we use the direct recombination treatment introduced by Mooradian and Fan.[23] An energy-dependent capture cross section is utilized, and an effective recombination lifetime determined from it. This is normalized to give the proper value at low light levels, but also reflects the details of the distribution function. The direct recombination emission intensity is[23]

$$I(h\nu)\sim\nu^2\langle M\rangle^2 f_e(\nu)f_h(h\nu-E_G)\rho(h\nu), \quad (4)$$

and the integral of this can be related to a recombination time. In (4), f_e and f_h are the electron and hole distribution functions and ρ is the density of states.

B. Band renormalization

Energy-gap narrowing at high concentrations of electrons and holes arises primarily from two principal mechanisms: self-energy, or exchange energy, contributions to the band-gap[24] and the free-carrier induced shifts of the phonon frequencies.[25] The narrowing of the energy gap due to the interacting nature of the free carriers has been considered by Inkson, using a dynamically screened potential.[24] The introduction of free carriers alters the quasi-Fermi level so that the exchange integral, as well as its contribution to the exchange energy throughtout the band, must change. He has estimated that at low temperature the gap closure is given by

$$\Delta E_g=(2e^2/\pi\epsilon_0)\{k_F+a[\tfrac{1}{2}\pi-\tan^{-1}(k_F/a)]\}, \quad (5)$$

where $a=\lambda/\epsilon_0^{1/2}$ and λ is the screening wave vector. Now, (5) is a zero-temperature approximation and its validity at higher temperatures is restricted. However, k_F reflects primarily an estimate of the number of interacting carriers within the conduction band (or valence band). An estimate of this effect can be found by deriving k_F from the Fermi energy, given by

$$E_F-E_C=k_BT_e\ln(n/N_c), \quad (6)$$

where

$$N_c=\tfrac{1}{4}(2m_ek_BT_e/\pi\hbar^2)^{3/2} \quad (7)$$

is the effective density of states in the conduction band and T_e is the electron temperature.

The shift in the phonon frequencies, induced by the free carriers, also causes a gap narrowing. Brooks[26] relates the energy-gap variation to the change in the lattice vibration frequencies from ω_i to ω_i' when an electron-hole pair is excited across any particular gap. The gap change arises from a change in chemical potential,[27] and can be expressed as[26]

$$\Delta E_g=\sum_i[f(\omega_i',n)-f(\omega_i,0)], \quad (8)$$

where $f(\omega,n)$ is the standard formula for the free

energy of an oscillator of frequency ω, which itself is a function of n (or p). The variation of the energy gap at high densities (high temperatures) for Si was shown by Heine and Van Vechten[25] to be dominated by the anharmonicity in the TA phonons. The TA modes depend critically upon the covalent nature of the bonding in the diamond structure. Without this bonding, the TA modes go unstable and the diamond structure itself becomes unstable.[28] The generation of electron-hole pairs removes bond charge, thus destabilizing and softening the TA mode. It is significant that estimates of the peak electron density in picosecond laser experiments at the damage threshold[2] is within a factor of 5–8 of that necessary to completely destabilize the TA mode. Heine and Van Vechten have shown that the density dependence of the anharmonic TA mode may be expressed as

$$\omega_{TA}' = \omega_{TA}\,[1 - f_{cv} n \epsilon_0 \epsilon_0^* / 4(\epsilon_0^* - \epsilon_0) N_A]\,, \qquad (9)$$

where $f_{cv} = 0.85 \pm 1$ is the bond-charge shift per electron-hole pair, $\epsilon_0^* = 24$ is the dielectric constant of the competing β-tin phase, and N_A is the atomic density.

III. RESULTS

Using the above theoretical basis, detailed calculations on the time and energy dependence of the distribution function for the optically created electrons in the central valley of Ge have been carried out. The carriers are introduced into the conduction band by optical absorption at a defect energy $h\nu - E_G$ above the band minima. They then relax within the band via scattering processes and/or scatter to the primary L valleys and/or recombine. The results of these calculations indicate that energy-gap narrowing and state filling should be significant processes in nonlinear optical absorption in semiconductors. First, at low values of the laser intensity, band-gap narrowing restricts state filling, since as the gap narrows and the excitation energy is swept to higher band energies, the generation rate is too low to create sufficient carriers during the dwell time of the excitation on a particular state, particularly as the thermalization time is found to be less than 0.25 psec. As the excitation intensity is increased, state filling begins to occur over a narrow time spike near the peak of the laser pulse. This begins to occur at an excitation intensity closely corresponding to that experimentally observed for the onset of the enhanced transmission.[1,3] During this time spike, the appropriate state is filled to near-saturation value. Further intensity increases lead to broadening of the time spike, until saturated absorption is significant throughout the laser pulse for levels

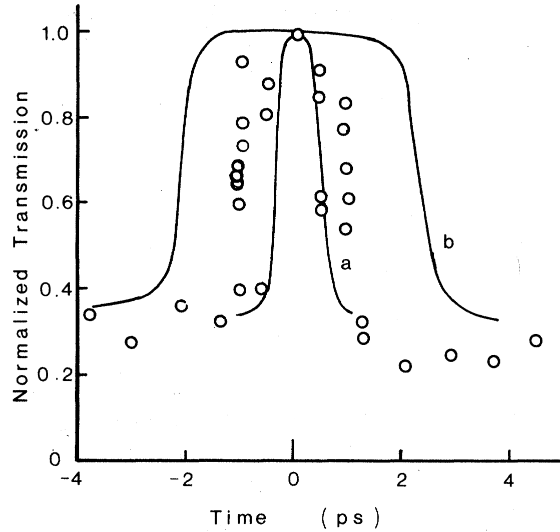

FIG. 1. Enhanced transmission through a thin slab of Ge due to state filling during the intense laser pulse. A Gaussian pulse of 8.3 psec FWHM was used. A peak intensity of 2×10^8 W/cm^2 for curve a and 4×10^8 W/cm^2 for curve b is assumed. The data points are taken from Ref. 1.

close to those experimentally observed for saturation of the enhanced transmission. A result for an excitation level within the nonlinear optical absorption region is shown in Fig. 1 with the experimental results for comparison.

Two other results of these studies are significant. First, direct recombination during the laser pulse is a significant process. Although the direct lifetime is of the order of a few nanoseconds at low illumination levels, the transition probability

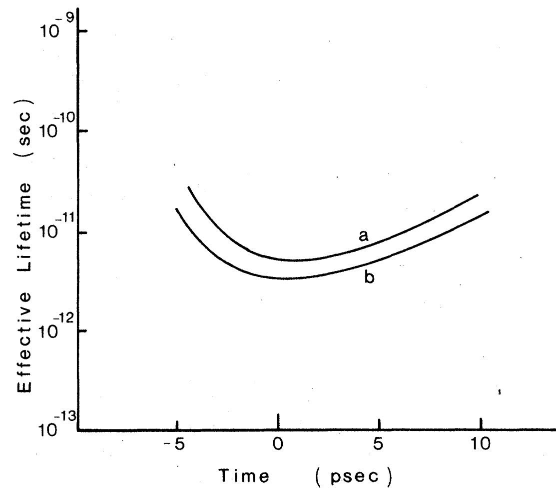

FIG. 2. Variation of the effective direct recombination lifetime during the pulse. The two curves correspond to the peak intensities of Fig. 1. Time is measured from the peak of the laser pulse.

is energy and distribution function dependent. In these calculations, direct recombination rates are calculated directly as scattering integrals. Under intense laser illumination, the direct recombination rate is enhanced and the effective lifetimes are found to be as short at 1–2 psec over much of the region of nonlinear optical absorption. This is shown in Fig. 2. Secondly, it is found that a short time after the laser pulse, the carriers are distributed between the Γ and L valleys in such a manner that it is reasonable to treat them with a single quasi-Fermi level and hot-electron Fermi-Dirac distribution, as has been attempted recently.[5] The distribution of carriers in the two valleys are shown in Fig. 3.

IV. DISCUSSION

Over most of the range of laser intensities for the observed nonlinear optical absorption, the energy-gap narrowing is dominated by the contribution from the exchange energy. The amount of narrowing, approximately 32 meV for 2×10^{19} cm^{-3} in the central valley, agrees well with the values inferred from absorption edge shift with doping in Ge.[24,29] At high laser intensities, however, such that the total free-electron concentration exceeds 10^{21} cm^{-3}, the contribution from softening of the TA phonon mode begins to dominate the effect. From the estimate of the damage threshold 0.5 J/cm^2,[2] the estimated carrier density found at damage is only a factor of 5–8 below the density required to drive ω_{TA} to zero. As a consequence, it is possible that lattice strain arising from TA mode softening may be a contributive factor to the crystal damage.

As to the optical absorption, it is found that the state filling that would normally be expected to occur is restricted by the energy-gap narrowing, but does occur in the region of nonlinear optical absorption for a short period of time, which is dependent upon the incident laser pulse intensity. Moreover, it is found that saturated absorption due to state filling can contribute to results such as those observed by Kennedy *et al.*[1] Also, the occurrence of this affect in the region of nonlinear optical absorption may signal that it is this state-filling effect that is responsible for the details of the absorption versus intensity curve.

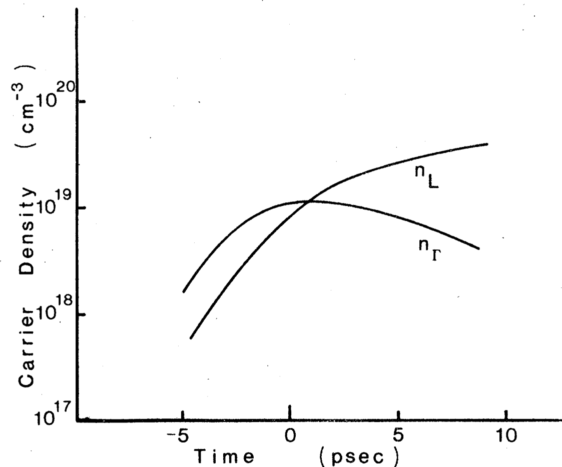

FIG. 3. Variation of the carrier densities in the Γ and L valleys during the laser pulse. A peak power of 4×10^8 W/cm^2 is assumed.

ACKNOWLEDGMENT

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