PHYSICAL REVIEW B VOLUME 46, NUMBER 8 15 AUGUST 1992-II

Femtosecond relaxation of photoexcited holes in bulk gallium arsenide

A. Chébira, J. Chesnoy,* and G. M. Gale
Laboratoire d'Optique Quantique, Ecole Polytechnique, 91128 Palaiseau, France

(Received 12 March 1992)

The relaxation to the top of the valence band of nonequilibrium photoexcited holes in *n*-type doped bulk gallium arsenide at 77 K is selectively measured by a femtosecond luminescence up-conversion technique. In the low-excitation regime, hole decay times between 560 and 330 fs are observed for fully-ionized-donor concentrations in the range 6×10^{17} to 2.4×10^{18} cm^{-3}. The theoretical treatment of weakly photoexcited *n*-type GaAs displays certain simplifications when compared with earlier work, as both the lattice and the electron bath are in thermodynamic equilibrium, and the results of a simulation invoking hole–LO-phonon and hole-electron interactions give good agreement with experiment.

Picosecond and subpicosecond laser spectroscopy experiments in semiconductors have recently allowed the probing of the ultrafast relaxation dynamics of photogenerated electron-hole plasmas.[1-6] These experiments provide information germane to the temporal evolution of the hot-carrier distributions. This knowledge is important, both for the understanding of the fundamental physics of the relaxation processes involved and for the technology of device development.

It now seems clear that carrier-carrier interactions, free-carrier screening, and phonon emission are important features of the thermalization and relaxation processes of photoexcited carriers. However, experimental observables (for example, time-resolved luminescence) in intrinsic semiconductors contain averaged data concerning the electron and hole distribution functions and it is difficult to estimate the relative contribution of each species to the overall relaxation process. Theoretical descriptions of the electron-hole system are hampered by the absence of a definable carrier temperature and the problems related to a correct description of screening effects. Even partial resolution of these difficulties requires recourse to numerical transient simulations[7,8] which, although extremely useful, do not necessarily provide a great deal of physical insight.

A further complication in semiconductors such as GaAs may be provoked by intervalley transfer,[9] which occurs when the electron energy exceeds the Γ–satellite-valley gap and requires the inclusion of one or two extra bands in the theoretical model, with associated intervalley transition rates.

Many of the above problems are circumvented in our study of the band-edge luminescence of weakly photoexcited *n*-type GaAs, where the number of photogenerated electron-hole pairs is small with respect to the number of ionized donors (electrons). In this case, the time-resolved band-gap luminescence is directly related to the rate of arrival of holes at the top of the valence band and theoretical difficulties are considerably reduced as both the lattice and the electron bath are at thermodynamic equilibrium. This type of experiment allows an unambiguous determination of hole relaxation times in bulk semiconductors and opens up the possibility of direct comparison with model calculations.

As our experimental setup has already been partly described[10] we merely recall the salient features here. A 60-fs duration, 50-MHz repetition rate, 30-mW average power synchronously pumped laser at 620 nm is employed. A backscattering geometry luminescence up-conversion method using a double-Cassegrain telescope matched to a urea nonlinear summing crystal allows time sampling of the luminescence with a time resolution of 90 fs and a band width of more than 100 meV. The uv signal produced by the up-conversion process is detected by a photon counter after spectral selection to eliminate light at 310 nm.

Figure 1 shows the result obtained at 77 K in a sample of GaAs containing 2.4×10^{18} cm^{-3} fully ionized donors. The number density of electron-hole pairs created in the conditions of this experiment at 2.0 eV is estimated as $n_h\approx1\times10^{17}$ cm^{-3} (the band gap of GaAs at 77 K is 1.51 eV). The luminescence signal rises from zero to a plateau level [Fig. 1(a)] with a time constant $\approx$330 fs. The plateau is maintained out to $\approx$50 ps before any decay due to recombination is noticeable. Figures 1(b) and 1(c) show the initial luminescence rise on a linear and logarithmic scale, respectively, and the latter figure indicates that luminescence evolves exponentially, within experimental error.

At higher excitation levels, approaching 2×10^{18} cm^{-3}, we observe a similar behavior at short times but the luminescence signal continues to increase over times $\approx$20 ps before reaching a plateau. This behavior may be attributed to the slow return of electrons to the Γ valley from the lateral valleys and demonstrates that the number of excited electrons is no longer negligible with respect to the donor concentration and that, as expected at high excitation, the electron dynamics can no longer be neglected.

Comparable results are obtained at an impurity concentration (N_D) of 1.5×10^{18} except that the luminescence risetime is a little slower ($\approx$360 fs). However, at the lowest impurity concentration (6×10^{17}, Fig. 2) it proved impossible to decrease the excitation sufficiently to obtain

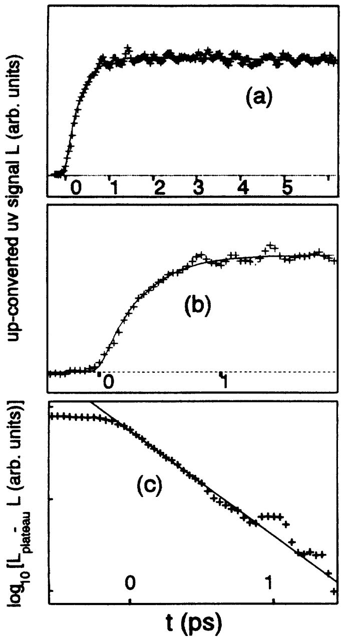

FIG. 1. (a) The measured up-converted luminescence signal in n-doped GaAs at 77 K ($N_D = 2.4\times10^{18}$ cm^{-3}) as a function of sampling-pulse delay in picoseconds, showing plateau formation. The full line is a fit to the signal, yielding a time constant of 330 fs (see text). (b) The initial portion of (a) showing more clearly the luminescence rise. The full line is a fit. (c) Semilogarithmic plot of the luminescence signal as a function of time in picoseconds, illustrating the near-exponential nature of luminescence rise. The straight line represents an exponential with a 330-fs time constant.

a plateau at short times (we note that the signal observed at low excitation is proportional to $n_h N_D$ which, for $n_h = \alpha N_D$ with $\alpha \ll 1$, varies as N_D^2) although, of course, after the return of electrons from the lateral valleys the signal will reach a maximum after some 20 or 30 ps. Hence, in this case, the number of excited electrons can no longer be neglected with respect to the number of ionized donors.

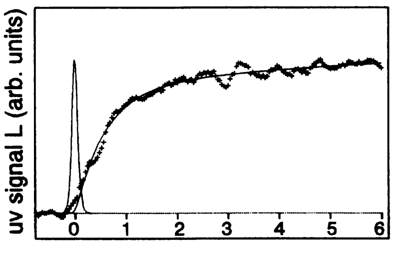

FIG. 2. The measured up-converted luminescence signal in n-type doped GaAs at 77 K ($N_D = 6\times10^{17}$) as a function of sampling-pulse delay in picoseconds. No plateau formation is observed at short times and the data must be fitted (full line) by a more complex expression than for Fig. 1 (see text). Also shown in this figure is the pump–sampling-pulse correlation function (spike) giving the system time response.

We may describe the time evolution of the luminescence $L(t)$ phenomenologically using the expression

$$L(t) = [1 - \exp(-t/\tau_h)][1 - f\exp(-t/\tau_r)] ,$$

where τ_h is the rate of arrival of holes in the detection window (which is determined by the Fermi level of the degenerate electron distribution, see below), f is the ratio of initially excited electrons to the number of ionized donors, and τ_r is the return time of these electrons to the Γ valley from the satellite valleys. The second term in the above equation may thus be set equal to 1 for sufficiently weak excitation. The use of an exponential for the first term above is justified by observation (see Fig. 1) and the form of the second term is determined from long-time (0–60-ps) measurements in intrinsic GaAs.[11] For comparison with experiment, $L(t)$ must be convolved with the 90-fs-width pump-probe correlation function obtained using the urea crystal.

We may fit the results for minimum excitation at donor concentrations of 2.4×10^{18} cm^{-3} and 1.5×10^{18} cm^{-3} with $f=0$ and $\tau_h = 330\pm20$ fs [full lines in Figs. 1(a) and 1(b)] and 360±40 fs, respectively. Using a value of 9 ps for τ_r, obtained in an undoped sample at 77 K, at the lowest donor concentration of 6×10^{17} cm^{-3}, we find $f = 0.3\pm0.05$ and $\tau_h = 560\pm90$ fs (full line in Fig. 2).

We interpret these results by supposing that the photoexcited holes relax primarily by interaction with the electron bath provided by ionized donors and by emission of LO phonons, as the efficiency of all other relaxation mechanisms is at least an order of magnitude smaller.[11,12] In particular, the relaxation of the holes by collision with neutral donors can be excluded, as Hall-effect measurements, between 5 and 300 K, of free-carrier densities in our samples[13] show that the donors are completely ionized at 77 K.

We further suppose that wave-vector conservation (**k** selection, vertical transitions) is obeyed for both absorption and emission processes between the valence and conduction bands, although this hypothesis may not be strictly applicable at high donor concentrations and small wave vectors.

As the "light" holes in gallium arsenide do not contribute significantly to band-edge luminescence due to their small density of states at small **k** and have a dispersion equivalent to that of the heavy holes at moderate **k** (for example, at the excitation wave vector) we consider here that both the light- and heavy-hole bands may be represented by a single isotropic and parabolic band with the mass of the heavy hole. This appears to be a rather drastic simplification, given that approximately equal numbers of light and heavy holes are excited in our experiments, but it has the merit of allowing an extremely simple calculation. One should also note that about 20% of holes are initially excited to the splitoff band. We will reconsider these difficulties later.

Because we are analyzing a situation where the hole number density is small with respect to the electron number density, we neglect hole-hole interactions compared to hole-electron interactions in our calculation (this hypothesis is always justified at sufficiently low relative hole to electron densities). The hole distribution therefore thermalizes uniquely through collision with the cold electron bath. As spatial diffusion of the holes is completely negligible in the times considered here, the only factors affecting hole population are laser excitation and the above-mentioned relaxation processes.

We assume that the holes interact with the electron bath via a static screened potential, which is a good approximation here due to the large hole to electron mass ratio, leading to an interaction Hamiltonian

$$H_{\mathrm{he}} = -\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_0-\mathbf{r}|} e^{-\beta|\mathbf{r}_0-\mathbf{r}|} ,$$

where $\mathbf{r}_0$ and $\mathbf{r}$ are the hole and electron positions, respectively, and β is the Fermi-Dirac screening parameter.

The probability that an electron-hole pair will make a transition from states of wave vector $\mathbf{j}_0$ and $\mathbf{k}_0$, respectively, to $\mathbf{j}$ and $\mathbf{k}$ is given by

$$P_{\mathbf{j}_0,\mathbf{k}_0\to\mathbf{j},\mathbf{k}} = [2\pi/\hbar]|\mathbf{J}_{\mathrm{he}}|^2 f_{\mathbf{j}_0} f_{\mathbf{k}_0}[1-f_{\mathbf{j}}] \times [1-f_{\mathbf{k}}]\delta[E_{\mathbf{j}}+E_{\mathbf{k}}-E_{\mathbf{j}_0}-E_{\mathbf{k}_0}] ,$$

where $\mathbf{J}_{\mathrm{he}}$ is the matrix element of the interaction Hamiltonian and the f are occupation functions. The degenerate electron distribution obeys Fermi-Dirac statistics whereas at *thermal equilibrium* the hole occupation function is given by a Maxwell-Boltzmann distribution.

The transition rate $T_{E(\mathbf{j}_0,\mathbf{j})}$ for a hole of initial energy $E(\mathbf{j}_0)$ to that of final energy $E(\mathbf{j})$ is given by summing the above expression over $\mathbf{k}_0$ and $\mathbf{k}$, taking wave-vector conservation into account ($\mathbf{j}_0+\mathbf{k}_0=\mathbf{j}+\mathbf{k}$) and letting $f_{\mathbf{j}_0}$ equal 1:

$$T_{E(\mathbf{j}_0,\mathbf{j})} = \int d\mathbf{k}_0 \int d\mathbf{k}\, P_{\mathbf{j}_0,\mathbf{k}_0\to\mathbf{j},\mathbf{k}} .$$

Since the hole density is small, we may neglect $f_{\mathbf{j}}$ with respect to 1. Because of the low effective electron mass, at the doping concentrations considered here, the electron distribution is always degenerate and the corresponding occupation functions are given by the Fermi-Dirac distribution. In these conditions the above double-vector integral may be replaced by a double scalar integral of an analytic function. Similarly, the transition rate involving LO-phonons, $T_{E(\mathbf{j}_0),[E(\mathbf{j}_0)-E_{\mathrm{LO}}]}$ and its converse, may be reduced to a single scalar integral.[11]

This simplification of the calculation of time-independent hole transition rates to a semianalytic form allows calculation of a total 120×120 T_E transition matrix, with 1-meV energy steps, in a few minutes of microcomputer time. The evolution of an arbitrary hole distribution may then be rapidly evaluated in a time-dependent simulation.

The initial energy distribution of the holes is centered 72 meV below the bottom of the valence band [see Fig. 3(a)] and we choose a full width at half height of 10 meV for the distribution to account for band warping and asymmetry. It is to be noted, however, that the time evolution of the calculated band-edge luminescence depends only very weakly on the initial width of the hole distribution. The simulation is initiated 200 fs before the peak ($t=0$) of a 60-fs, 2.0-eV, sech^2-shape laser excitation pulse. Additional hole distributions are evaluated using the appropriate T_E matrix at 2- or 5-fs time intervals out to at least 2 ps.

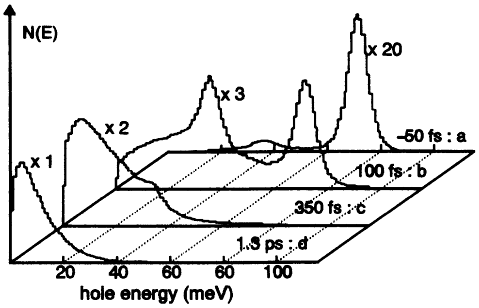

FIG. 3. Calculated hole energy distributions with 1-meV steps in n-type doped GaAs at 77 K ($N_D=10^{18}$ cm^{-3}). The center of the 60-fs laser excitation pulse defines $t=0$. Distributions are shown at (a) -50 fs, (b) 100 fs, (c) 350 fs, and (d) 1.3 ps.

Figure 3 shows some of the results of a simulation at a donor concentration of 10^{18} cm^{-3} and a temperature of 77 K. A strong LO-phonon peak 36 meV (the LO phonon energy) below the initial maximum is noticeable shortly after excitation [Fig. 3(b)], but for times above ≈ 300 fs [Fig. 3(c)] the hole population may be quite well approximated by a Maxwell-Boltzmann distribution with a temperature T_{MB} superior to the lattice and electron temperatures (for example, at 350 fs, $T_{\mathrm{MB}}\approx 140$ K). After $t\approx 1300$ fs, in this simulation, the hole distribution is fully thermalized at the electron temperature of 77 K [Fig. 3(d)].

We have simulated hole-distribution-time evolutions in the donor concentration range 2×10^{17} to 2.6×10^{18} cm^{-3}. Apart from minor changes in the detailed distributions, this time evolution is essentially independent of donor concentration in the cited range. We attribute this insensitivity to increasing donor concentration to compensation of the augmentation of hole-electron collisions by the parallel elevation of screening of the electron-hole interaction. This compensation occurs when the electrons obey Fermi-Dirac statistics because the number of electrons that interact with holes increases more slowly than electron density, due to the small average energy loss of the holes and the degeneracy of the electron distribution, which means that only electrons near the surface of the Fermi sea can accept hole energy.

The results of the calculation are also quite insensitive to LO-phonon screening by the electrons. Although we employ the full static screening parameter (β) for phonons in the data presented here, the overall evolution rate only increases by a few percent when β is reduced by 30%. In contrast, the hole-electron-bath energy-loss rate varies as $\approx\beta^2$ near the static screening value. We note that LO phonons alone cannot bring the hole system to thermal equilibrium and that hole–LO-phonon relaxation rates are smaller than hole-electron bath rates. This means that LO phonons play a secondary role in our model.

Despite the invariance of the hole distribution time-evolution with donor concentration, the observed luminescence time dependence can change due to the modification of the *intrinsic* detection window by donor concentration. This effect is explained schematically in Fig. 4, where it can be seen that holes with a wave vector exceeding a maximum value $\mathbf{k}_{\max}$, defined by the Fermi level of the electrons in the conduction band cannot recombine with electrons and hence do not produce luminescence via vertical transitions. Higher donor concentrations raise the Fermi level in the conduction band and enlarge the detection window leading to faster luminescence risetimes. The energy width of the window is given approximately by $kTE_F(m_h/m_e)\approx E_F\times 1$ meV at 77 K (for example, about 9 meV at $N_D=10^{18}$ cm^{-1}), although it is to be noted that the total luminescence bandwidth is $\approx kT[1+(m_h/m_e)]E_F$ meV.

In the present work the luminescence is calculated using the exact Fermi distribution for the electrons and the hole distribution obtained from the simulation. After an initial period of about 50 fs the computed luminescence signal can be very well represented by an expression of the form $[1-\exp(-t/t_c)]$ over at least 1.5 ps.

Figure 5 shows a comparison between the experimentally observed luminescence risetimes t_r (open rectangles) and the computed times t_c (full line). Agreement is excellent, especially considering that the calculation contains no adjustable parameters. Nevertheless, we would like to make some comments on the various approximations made in our calculation. The neglect of hole-hole interactions, which tend to thermalize the hole energy distribution, is not as important as it might first appear to be, given that in our experiment the hole-hole coupling is screened by the high-density electron bath and that hole densities are small, and hence we expect pure hole-hole thermalization times to be significantly longer than those obtained in Ref. 6. Also, the hole-electron-bath interaction in itself efficiently thermalizes hole energy, leading to a notable redistribution of holes in the first 100 fs of our simulation (Fig. 3).

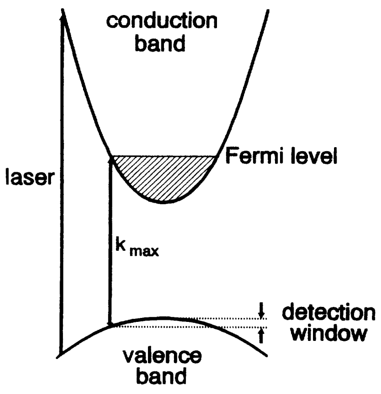

FIG. 4. Simplified schema of the energy vs wave-vector dependence in GaAs showing the effect of the Fermi level for electrons in the conduction band on the detection window for holes arriving at the top of the valence band.

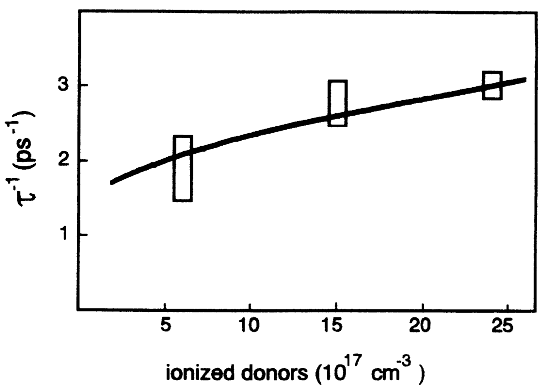

FIG. 5. The inverse measured luminescence risetime, τ^{-1} in ps^{-1}, in *n*-type doped GaAs at 77 K for three donor concentrations: 6×10^{17}, 1.5×10^{18}, and 2.4×10^{18} cm^{-1} (open rectangles). The full line is calculated (see text).

The replacement of the heavy- and light-holes bands by a single band is an approximation which is difficult to justify quantitatively. In the limiting case where we suppose that the light- and heavy-hole bands do not communicate except near $k=0$, due to the similar dispersion of these bands except at small k, the time evolution of both populations is expected to be similar. In the opposite hypothesis, where the light holes relax rapidly into the heavy-hole band, the initial heavy-hole distribution will be somewhat changed but the overall time evolution should not be dramatically modified.

Some 20% of the total hole population is excited into the splitoff band. If these holes relax rapidly by phonon emission into the heavy- or light-hole bands at relatively high energy, they could significantly increase hole temperature and slow down hole relaxation by as much as 50% according to our estimate. However, the splitoff holes could also relax to lower energy by interaction with the dense electron bath in the doped crystal. Because of the small splitoff mass and the large energy exchange, this mechanism should only be weakly screened and all of the electron Fermi sea can participate in the interaction. As most of the splitoff hole energy is absorbed by the electrons, this second process is much less perturbative.

In conclusion, it has been shown that the relaxation to thermal equilibrium of holes excited by 2.0-eV photons in *n*-type doped gallium arsenide at 77 K can be characterized by a relaxation constant ≈350 fs, essentially independent of doping concentration in the range 6×10^{17}–2.4×10^{18} cm^{-3}. The quasi-invariance of the hole relaxation time appears to result from the near-perfect compensation of the increase of hole-electron collisions, as donor concentration increases, by the reduction of the hole-electron Coulomb interaction in the static screening regime applicable here. The fairly weak variation of the luminescence risetime with donor concentration can be attributed to the intrinsic change of the detection-window width with the electron Fermi level.

The study of photoexcited doped semiconductors can allow, in certain circumstances, the isolation of the time evolution of a single carrier species. This experimental simplification should enable more direct comparison with theory and in restricted cases with model calculations which, although lacking rigor, may permit the underlying physical mechanisms to be better elucidated.

The authors wish to acknowledge useful discussions with Dr. Fabrice Vallée (Optique Quantique), Dr. Jacques Collet from INSA, Toulouse, France, and Dr. Eugenio Fazio from the University of Rome (La Sapienza), Italy. Laboratoire d'Optique Quantique is Unité Propre du Centre National de la Recherche Scientifique.

---

[*] Present address: Alcatel Alsthom Recherche, Route de Nozay, 91460 Marcoussis, France.

[1] J. Shah, B. Deveaud, T. L. Damen, W. W. T. Tsung, A. C. Gossard, and P. Lugli, Phys. Rev. Lett. **59**, 2222 (1987).

[2] P. C. Becker, H. L. Fraguito, C. H. Brito-Cruz, J. Shah, R. L. Fork, J. E. Cunningham, J. E. Henry, and C. V. Shank, Appl. Phys. Lett. **53**, 2089 (1988).

[3] W. Z. Lin, R. W. Schoenlein, J. G. Fujimoto, and E. Ippen, J. Quantum Electron **QE-24**, 267 (1988).

[4] R. A. Höpfel, J. Shah, and A. C. Gossard, Phys. Rev. Lett. **56**, 765 (1986).

[5] J. A. Kash, J. C. Tsang, and J. M. Hvam, Phys. Rev. Lett. **54**, 2151 (1985).

[6] T. Elsaesser, J. Shah, L. Rota, and P. Lugli, Phys. Rev. Lett. **66**, 1757 (1991).

[7] C. J. Stanton, D. W. Bailey, and K. Hess, Phys. Rev. Lett. **65**, 231 (1990).

[8] M. A. Osman and D. K. Ferry, Phys. Rev. B **36**, 6018 (1987).

[9] J. B. Gunn, Solid State Commun. **1**, 88 (1963).

[10] A. Mokhtari, A. Chébira, and J. Chesnoy, J. Opt. Soc. Am. B **7**, 1551 (1990).

[11] A. Chébira, Ph.D. thesis, Université de Paris (Sud), Orsay, France.

[12] A wide range of hole–TO-phonon coupling parameters may be found in the literature. Subsequent to the completion of this work, it has come to our attention that a similar study at room temperature in *n*-type doped GaAs has been effectuated [X. Q. Zhou and H. Kurz, in *Proceedings of the VIIth International Symposium on Ultrafast Proceedings in Sepctroscopy*, edited by A. Laubereau (Institute of Physics, London, 1992)]. In the latter work it appears that predominance is given to hole–TO-phonon coupling. A consideration of the temperture dependence of both mechanisms could yield additional information on this subject.

[13] Measurements made at Philips Electronics Laboratory (LEP).