Initial Thermalization of Photoexcited Carriers in GaAs Studied by Femtosecond Luminescence Spectroscopy

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Relaxation of a nonequilibrium distribution of electrons and holes in GaAs following femtosecond photoexcitation is investigated via spectrally and time-resolved luminescence. A rapid onset of luminescence *over a broad range* shows that both electrons and holes are redistributed over a wide energy range within 100 fs, even at excitation densities as low as 10^{17} cm^{-3}. The data demonstrate carrier-carrier scattering rates higher than predicted by calculations with a statically screened interaction potential. Monte Carlo simulations using dynamical screening account for the experimental results.

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The fastest scattering processes of hot electrons and holes in semiconductors occur on a subpicosecond time scale, and femtosecond optical spectroscopy gives direct insight into the fundamental nonequilibrium properties of carriers.[1-11] Femtosecond excitation of GaAs generates an initial nonequilibrium distribution of electrons and holes, which thermalizes by carrier-carrier and longitudinal-optical- (LO-) phonon scattering to hot Fermi distributions, a process which is still not completely understood. For excitation 20 meV above the band gap, i.e., below the threshold of LO-phonon emission by the carriers,[8,9] the transient absorption spectra exhibit spectral holes. Thermalization times of 50 fs up to 300 fs have been deduced from the data.

For excitation of bulk GaAs at 2 eV, i.e., high above the band gap, the initial electron distribution consists of three narrow peaks created by transitions from the heavy-hole, light-hole, and split-off valence bands with relative electron densities of $\simeq$0.4, 0.4, and 0.2, respectively. The electrons not scattering to the L and X valleys equilibrate in the Γ valley. The transient decrease of absorption observed after femtosecond excitation reveals a spectral hole at 2 eV which disappears in tens of femtoseconds.[2,4] This kinetics is strongly influenced by intervalley scattering and cannot provide direct information about thermalization. The absorption change at energies far below 2 eV showed a rise within the temporal resolution of the experiments, which was interpreted as evidence for relaxation of electrons and holes on a time scale below 50 fs.[4] In contrast to this conclusion, recent Monte Carlo simulations of these experiments predict thermalization times of electrons of up to 300 fs and attribute the signals measured at low energies primarily to the faster equilibrium of holes.[5,6] This discrepancy might be due (1) to the fact that no data were obtained below 1.57 eV, and (2) to the difficulty in interpreting pump-probe experiments, where optical transitions from the heavy-hole, light-hole, and split-off valence bands contribute to the observed transmission changes and the sum of the electron and hole distribution functions, f_e+f_h, is measured. Either electrons or holes can cause bleaching, and carriers in different regions of the valence and conduction bands are monitored simultaneously at a specific probe wavelength. Therefore, unambiguous information on the electron distribution is difficult to extract from *absorption* studies. In contrast, the *luminescence* spectrum at energies below 1.7 eV is dominated by recombination with heavy holes. The emission intensity is proportional to the product $f_e f_h$, i.e., the presence of *both* electrons and heavy holes at the same $\mathbf{k}$ vector is necessary. Thus luminescence spectroscopy gives new information on the distribution of carriers.

In this paper, we present the first luminescence study of carrier thermalization in GaAs with a temporal resolution of $\simeq$100 fs. The temporal and spectral evolution of luminescence within the first picosecond after excitation at 1.93 eV is measured for plasma densities of 1.7×10^{17} and 7×10^{17} cm^{-3} (see below). Luminescence in a wide range of energies from the band gap at 1.42 eV up to 1.7 eV exhibits an instantaneous rise within the first 200 fs. The broad structureless spectra observed at these early delay times give evidence of the fast redistribution of Γ-valley electrons and holes within 10 fs.

The experiments are based on femtosecond luminescence up-conversion.[10] A 0.6-μm-thick GaAs layer clad by Al-Ga-As layers was excited by 120-fs pulses from a dye laser operating at 1.93 eV. The sum frequency of the luminescence and of a second laser pulse was gen-

erated in a 0.5-mm-thick $LiIO_3$ crystal, spectrally analyzed in a double monochromator (resolution 5 meV), and detected by single-photon counting. The time resolution of the experiment is determined by the group-velocity mismatch between the luminescence and the up-conversion pulse in the nonlinear crystal and by the duration of the laser pulses. For the thin crystal used in the present measurements, the latter factor dominates, leading to a time resolution of approximately 100 fs at all luminescence wavelengths investigated.

Luminescence spectra recorded at very early delay times are presented in Fig. 1 for carrier densities of approximately 7×10^{17} cm^{-3} (solid lines) and 1.7×10^{17} cm^{-3} (dashed lines). The excitation densities are estimated from the absorption coefficient of GaAs at 1.93 eV, the sample thickness, and the spot size of the excitation beam with an accuracy of $\pm 50\%$. The values quoted are for the center of the Gaussian excitation profile. The average densities are considerably lower.

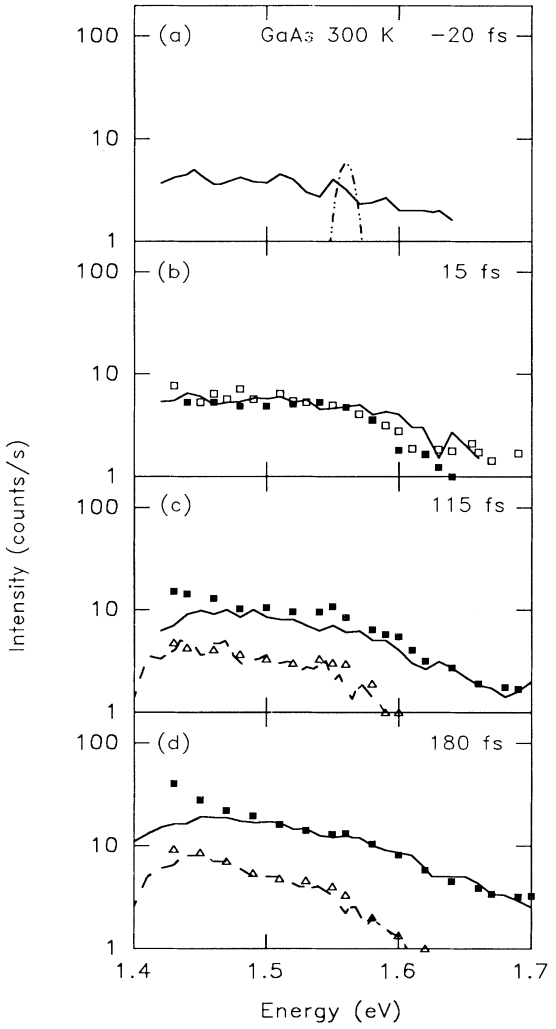

FIG. 1. Luminescence spectra of GaAs after femtosecond excitation at 1.93 eV. The excitation density was 7×10^{17} cm^{-3} (solid lines) and 1.7×10^{17} cm^{-3} (dashed lines). The luminescence intensity is plotted vs energy for delay times of (a) −20 fs, (b) 15 fs, (c) 115 fs, and (d) 180 fs. The solid squares and the triangles represent the spectra calculated from Monte Carlo simulations using static screening. The open squares in (b) are calculated with the molecular-dynamics model.

The well-pronounced temporal evolution of the spectra in Fig. 1 demonstrates the high time resolution of our measurements. At all time delays, luminescence is emitted over a broad range of energies extending from the band gap (1.42 eV) up to 1.7 eV. This interval is much wider than the initial distribution of electrons excited from the split-off band. As indicated in Fig. 1(a) (dash-dotted line), luminescence due to the latter distribution is centered at 1.57 eV with a bandwidth of approximately 15 meV. The spectrally integrated luminescence intensity at a delay time of 180 fs amounts to approximately 15% of the maximum emission intensity that occurs after 10 ps. Broad structureless emission spectra are also observed with the lower carrier density of 1.7×10^{17} cm^{-3}.

The onset of luminescence was measured for a number of fixed photon energies. In Figs. 2(a)–2(c), examples are shown for different photon energies (solid lines). The luminescence at 1.575 eV originates from conduc-

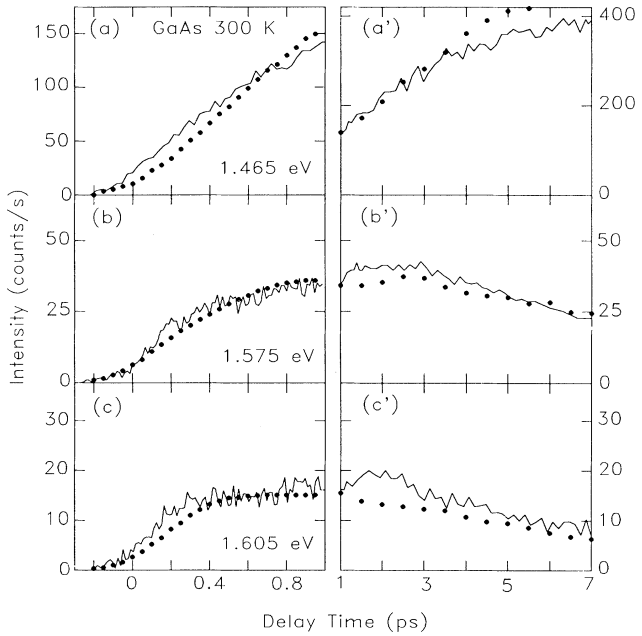

FIG. 2. Femtosecond (left-hand side) and picosecond (right-hand side) time evolution of the luminescence intensity at photon energies of (a),(a') 1.465 eV, (b),(b') 1.575 eV, and (c),(c') 1.605 eV (solid lines, excitation density 7×10^{17} cm^{-3}). The points are the result of Monte Carlo simulations using static screening.

tion-band states directly populated by excitation from the split-off band and rises instantaneously with excitation. The luminescence kinetics in Fig. 2(b), which is proportional to the time integral over the excitation pulse convoluted with the probe pulse, serves for a calibration of delay zero. The emission at all other photon energies from 1.42 to 1.7 eV exhibits the same instantaneous onset between -200 and $+200$ fs. These femtosecond transients, giving information on the fastest carrier relaxation processes, are followed by a slower picosecond increase of intensity, which is due to the backscattering of electrons from the L and X to the Γ valley and to carrier cooling.[3] The relative amplitudes of the fast and the slow rise strongly depend on the specific spectral position. Close to the band gap [Fig. 2(a)], the femtosecond component makes up approximately 10% of the intensity found after 7 ps, whereas the fast contribution dominates at higher energies [Figs. 2(b) and 2(c)]. The luminescence at 1.465 eV reaches its maximum after $\simeq 10$ ps and then decays with the lifetime of the electron-hole plasma.

Recombination with heavy holes dominates the luminescence in the observed spectral region because of the larger density of states and larger occupation of the heavy-hole band. At early times (<200 fs), the electrons in the Γ valley come from two sources: (1) electrons excited from the split-off band and (2) a small fraction of electrons excited from the heavy- and light-hole bands that have not transferred to the subsidiary valleys. These electrons and holes are created with narrow ($\simeq 15$ meV) distributions and thermalize by interacting with other carriers. In addition, they also emit and—to a lesser extent—absorb optical phonons. *The large spectral width, the absence of any narrow structures in the spectra (Fig. 1), and the rapid initial rise of luminescence at all energies (Fig. 2) demonstrate that, for excitation densities of 1.7×10^{17} and 7×10^{17} cm^{-3}, the electrons in the Γ valley as well as the holes in the heavy-hole band equilibrate within the time resolution of our experiments of $\simeq 100$ fs.* The absence of any structure with optical-phonon spacing shows that inelastic carrier-carrier scattering is the main mechanism of thermalization, much faster than the LO-phonon emission time of $\simeq 150$ fs. The integrated intensity of luminescence at 180 fs is 15% of the maximum intensity (at about 10 ps). This finding gives evidence that (1) most of the electrons are in the subsidiary valleys at these early times,[3] and (2) practically all electrons in the Γ valley are redistributed over a broad energy range.

Thermalization of a nonequilibrium distribution generated by optical excitation at 2 eV has been simulated by Monte Carlo (MC) calculations with carrier densities between 10^{17} and 10^{18} cm^{-3}.[3,5,6,12-15] Assuming a statically screened carrier-carrier interaction, the holes were found to thermalize within the first 100 fs, whereas the electrons equilibrate much slower. *Such electron relaxation would result in structured luminescence spectra at early times and can be ruled out from our luminescence data*, which unambiguously show the rapid population of electronic states over a wide energy interval.

We performed a Monte Carlo simulation of the dynamics of the photoexcited plasma using a three-valley Γ,L,X model for the electrons, with the parameters given in Ref. 3. The holes are treated within a three-band scheme.[13] Carrier-carrier scattering is accounted for via a *time-dependent* static screening formulation,[16] where the screening length is updated every 50 fs to follow the evolution of the carrier distribution functions. Degeneracy and nonequilibrium phonons are included in the simulation.[17]

The MC luminescence spectra and time evolution obtained under the same conditions as the experiments are shown in Fig. 1 (solid squares and triangles) and Fig. 2 (points), respectively.[18] Good agreement between theory and experiment is found for delay times longer than 200 fs.[19] The MC results do *not* reproduce the data at shorter times. In particular, during the laser pulse the MC spectra [Fig. 1(b)] drop sharply above 1.57 eV indicating an insufficient energy exchange between electrons excited from the split-off band and those at higher energies. We ascribe this difference to the intrinsic failure of the static screening approach that underestimates the carrier-carrier interaction at the earliest times.

This conclusion has been verified by simulating the interaction among electrons via a molecular-dynamics scheme that has been shown to include all the features of

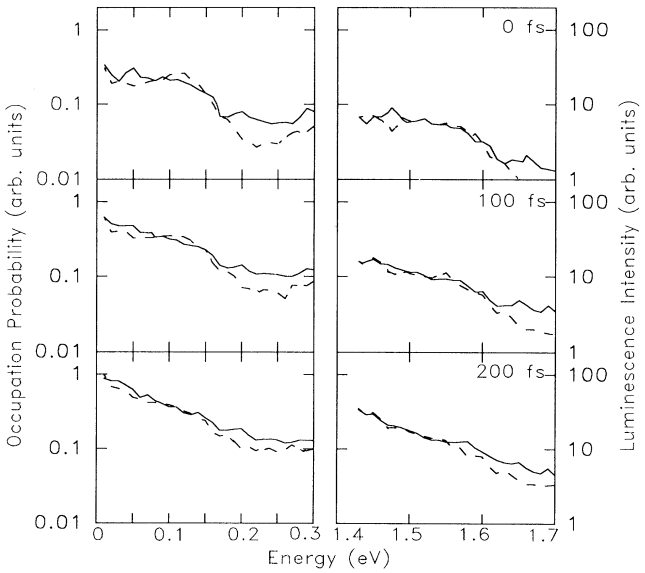

FIG. 3. Electron distribution function in the Γ valley (left-hand side) and luminescence spectra (right-hand side) as calculated from the Monte Carlo simulation using a static screening (dashed lines) and a molecular-dynamics approach (solid lines). The carrier density is 7×10^{17} cm^{-3}.

dynamical screening.[20] Such an approach also incorporates the collective components of a Coulombic plasma,[15] reproducing experimental situations where plasmon losses are important.[21] A comparison of the static screening and the molecular-dynamics model is shown in Fig. 3. The latter approach does enhance the scattering between the different electron populations, leading to smoother distribution functions and to a much better agreement with the experimental spectra at early delay times [Fig. 1(b), open squares].[22]

We now compare our results to other investigations of subpicosecond relaxation of carriers photoexcited at 2 eV. Femtosecond nonlinear absorption studied between 1.57 and 2.15 eV (Refs. 2 and 4) could not provide unambiguous information on carrier thermalization as discussed earlier. Dephasing of a coherent polarization by carrier-carrier scattering has been investigated in photon-echo experiments with pulses of a duration of 6 fs.[23] The dephasing times of 12–45 fs reported for carrier densities between 7×10^{18} and 1.5×10^{17} cm^{-3} are not in contradiction with our results since coherence can be broken by purely elastic collisions which do not lead to thermalization. Also, the thermalization time of 180 fs obtained for a hot low-density (2×10^{15} cm^{-3}) electron gas in the presence of a cold electron-hole plasma of high density ($\simeq8\times10^{16}$ cm^{-3}) (Ref. 21) cannot be directly compared with our faster thermalization times because of different experimental conditions.

In conclusion, the results presented here give the first direct insight into the initial relaxation of Γ-valley electrons at energies close to the band gap of GaAs. Femtosecond luminescence spectroscopy reveals the redistribution of electrons and holes over a wide energy range within the first 100 fs after excitation. Our data show inelastic carrier-carrier scattering rates higher than calculated from a statically screened carrier-carrier interaction. In contrast, dynamical screening accounts well for the experimental results.

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