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Picosecond spectroscopy of hot anti-Stokes luminescence in GaAs

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We use 0.5-psec laser pulses to excite broad-band optical emission up to 0.9 eV above the band gap of GaAs. This emission is characterized by a pump-probe luminescence correlation time of as small as 1.5 psec (full width at half maximum) and allows us to directly study the energy relaxation and thermalization of hot carriers with a temporal resolution of about 1 psec. The variation with carrier density of both the spectral shape and the emission intensity at a given energy show that at densities less than 3×10^{17} cm^{-3}, the carriers can undergo appreciable energy loss via LO phonon emission before attaining a thermal distribution by carrier-carrier scattering.

In a polar semiconductor the process by which nonthermal carriers with a well-characterized initial energy and momentum distribution achieve a hot thermal distribution by carrier-carrier scattering, and come into thermal equilibrium with a host lattice by phonon emission, has been of considerable interest recently.[1] This interest has been stimulated both by the development of subpicosecond optical sources which make possible time-resolved experimental studies of hot carrier relaxation[2-4] and the fabrication of microstructures where nonthermalized electrons can be significant in charged carrier transport.[5,6] (Throughout this Rapid Communication "hot carrier" refers to a carrier far from the relevant band minimum. This term does not, in general, imply a thermal distribution.) We have studied the anti-Stokes nonequilibrium photoluminescence at energies far above the band gap of GaAs and demonstrate in this paper that it can be used to characterize the first picosecond of the relaxation in energy and momentum of optically generated carriers. These results complement previous Raman studies of the nonequilibrium LO phonons generated by the relaxation of hot carriers in GaAs[7] and other time-resolved studies of the nonequilibrium photoluminescence for energies within 0.25 eV of the direct gap and far below the energies at which the carriers are generated.[8,9] We show that the pump-probe luminescence correlation for our anti-Stokes emission can have a temporal width of 1 psec. From this, and the observation that the power dependence of the anti-Stokes photoluminescence can differ from the expected quadratic dependence on the incident power, we demonstrate that at optically injected carrier densities $n_0 < 3\times10^{17}$ cm^{-3}, significant energy transfer from the initially monoenergetic carriers to the lattice can occur before the carriers achieve a hot thermal distribution.

The time evolution of the electron and hole distributions f_n and f_p are defined by the carrier-lattice and carrier-carrier interactions.[10] The carrier-lattice interaction for very hot carriers is dominated in GaAs by the emission of LO phonons. Hot carriers within the direct conduction-band valley can relax via the Fröhlich interaction with a characteristic time $\tau_{e\text{-LO}}\sim150$ fsec,[7,10] independent of carrier concentration n_0 for carrier densities where the plasma frequency is far below the LO phonon frequency. Carrier-carrier scattering, unlike phonon emission, does not alter the average energy of the carriers, merely redistributing the total energy among the carriers, so an initial monoenergetic distribution can evolve into a thermal distribution without transfer of energy to the lattice. The carrier-carrier scattering time τ_c varies with n_0 as $\simeq2\times10^4$ sec cm$^{-3}/n_0$.[10] At low n_0, $\tau_{e\text{-LO}} < \tau_c$, so there can be appreciable energy loss to the lattice before thermalization is reached. At high n_0, $\tau_c < \tau_{e\text{-LO}}$, and a thermalized distribution can be achieved before there is significant energy loss from the hot carriers to the lattice. Given the magnitude of $\tau_{e\text{-LO}}$ in GaAs, differences in the relaxation of the hot carriers due to the competition between carrier-carrier and carrier-lattice scattering will occur primarily during the first 1 to 2 psec. Experimental observation of this competition will therefore require a probe with picosecond resolution, which is beyond the limits of current time-resolved photoluminescence studies.[8,9] On the other hand, the femtosecond measurements of just the carrier dephasing times[3,4,11] cannot fully characterize the thermalization process.

We use band-to-band photoluminescence to investigate the dynamics of hot carrier cooling in GaAs and to demonstrate the competition between carrier-lattice and carrier-carrier scattering during the first picosecond of the excited carrier relaxation. Band-to-band recombination in semiconductors was described theoretically by Mooradian and Fan.[12] In our experiments, we integrate the emission over all time so that $I(\omega_e)$ is given by

$$I(\omega_e)=\int_{-\infty}^{\infty} I(\omega_e,t)\,dt \propto \int_{-\infty}^{\infty}\left[n(t)^2\int |M(\mathbf{k}_n,\mathbf{k}_p)|^2 f_n(\mathbf{k}_n,t) f_p(\mathbf{k}_p,t)\,d^3k\right]dt \ . \tag{1}$$

Here, $f_n(\mathbf{k}_n,t)$ and $f_p(\mathbf{k}_p,t)$ are the probabilities of finding electrons and holes at a particular momentum and time t. M is the matrix element for an optical transition between holes and electrons separated by energy $\hbar\omega_e$ and momentum $\mathbf{k}_n-\mathbf{k}_p=\mathbf{k}_{\text{opt}}$. The photon energy $\hbar\omega_e=E_n+E_p+E_g$, where E_n and E_p are the electron and hole kinetic energies and E_g is the energy gap. The carrier density $n(t)$ can change due to diffusion, recombination, etc. On the time scale of interest in this paper (<2 psec) there will be no appreciable loss of carriers, so $n(t=0)=n_0$.

We are always in the regime of linear absorption where each optical pulse of intensity I_0 generates n_0 electrons and n_0 holes.

Given Eq. (1), if f_n and f_p do not change with excitation density, then $I(\omega_e) \propto n_0^2 \propto I_0^2$. This implies that when $I(\omega_e)$ is normalized against I_0^2, the dependence of the emission on ω_e will be independent of I_0. The complementary result is that a nonquadratic dependence of $I(\omega_e)$ on I_0 or a change in the spectral shape of $I(\omega_e)$ with changing I_0 implies a change with n_0 in the time evolution of the carrier distribution functions. The relative magnitude of the I_0 dependent effects on $I(\omega_e)$ will be determined by the extent to which the emission samples only the time intervals during which the carrier distribution is changing.

We have used 0.5 psec optical pulses at $\hbar\omega_0 = 2.13$ eV to excite the band-to-band photoluminescence. The maximum average power incident on the samples was 20 mW at a repetition rate of 76 MHz, and $n_0 \leq 2\times10^{18}$ cm^{-3}. We estimated n_0 by assuming that photogenerated carriers were uniformly distributed in a cylinder defined by the known absorption depth and the measured $1/e$ radius of the focal spot on the sample. Where results are reported as a function of n_0 only the laser power was changed. Losses due to reflection were included. The emission was analyzed by a triple spectrograph and detected by an F4146M imaging microchannel plate photomultiplier, which allowed multichannel detection[7] of the featureless emission, even at photon energies $\hbar\omega_e > 2.13$ eV where the emission is extremely weak. The photocathode response (MA3) of the photomultiplier extends to 9000 Å. All measurements were made in air at 300 K. The samples were cleaned using organic solvents before every measurement to remove surface contaminants that could generate a spurious signal.[13] The samples studied were as grown epitaxial layers of (100) oriented, nominally undoped GaAs on insulating GaAs substrates.

Using our subpicosecond pulses, we have been able to observe luminescence from GaAs for $\hbar\omega_e \leq 2.45$ eV, i.e., anti-Stokes emission for energies up to 300 meV above the excitation energy. In Fig. 1(a), we show the time integrated emission $I(\omega_e)$ for $1.4 \leq \hbar\omega_e \leq 2.4$ eV. For $\hbar\omega_e > 2.1$ eV, $I(\omega_e)$ is comparable in strength to the Raman scattering from the symmetry-allowed LO phonon of GaAs. $I(\omega_e)$ depends strongly on the peak power of I_0 for the larger values of $\hbar\omega_e$. If 5-psec pulses are used to excite the spectrum, the high-energy emission is about an order of magnitude weaker than when excited by the 0.5-psec pulses using the same average power density. On the other hand, $I(\omega_e)$ near the band edge is comparable for both long and short pulses. This behavior indicates that the carriers responsible for the high-energy emission have a lifetime comparable to 0.5 psec while the cooled carriers which generate the band-edge emission have a lifetime in excess of 5 psec.

Von der Linde, Kuhl, and Rosengart[14] showed that the bimolecular character of the hot luminescence allows the measurement of the luminescence correlation of the emission. The sample is excited by a pump pulse and a delayed probe pulse of comparable magnitude and orthogonal polarization. The time-integrated spectrum is then measured as a function of the delay. The signal consists of two parts.

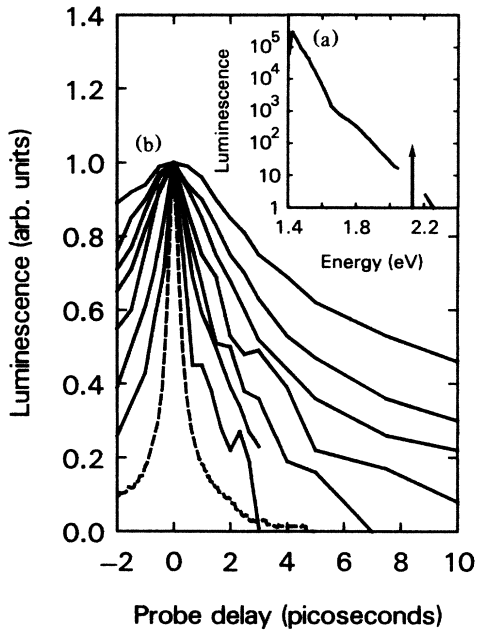

FIG. 1. (a) The photoluminescence spectrum of GaAs excited by single 0.5-psec pulses injecting about 10^{18} carriers cm^{-3} per pulse at 2.13 eV. The spectrum has been normalized against the instrumental response. (b) The variation with delay between pump and probe of the intensity of the time-correlated photoluminescence from GaAs under 0.5-psec optical excitation. Pump and probe beams each inject about 5×10^{17} cm^{-3} per pulse. The emission energy, $\hbar\omega_e$, at which each curve is obtained is, going from the narrowest curve to the broadest curve, 2.45, 2.22, 2.03, 1.99, 1.94, 1.80, and 1.65 eV. The broken line is the autocorrelation of the laser pulse. All these curves have been normalized to a scale from 0 to 1; the time-correlated photoluminescence rides on a background.

The first is a background which is the emission when pump and probe are very far apart in time. The second term depends on the delay and arises from holes excited by the pump pulse combining with electrons excited by the probe, and vice versa. This second term is the luminescence correlation or time-correlated photoluminescence. In Ref. 14, it was demonstrated that for $\hbar\omega_e \simeq 1.8$ eV and $\hbar\omega_0 = 2.15$ eV, correlation times as short as 8 psec full width at half maximum (FWHM) could be measured. Significantly longer correlation times were obtained for $1.5 < \hbar\omega_e < 1.8$ eV. In Fig. 1(b), we show the dependence on the delay time between the pump and the probe of the intensity of the time-correlated photoluminescence for GaAs pumped by 0.5 psec pulses. With our shorter pulses and more sensitive detector, we are able to extend the earlier results of von der Linde up to $\hbar\omega_e = 2.4$ eV. At this energy, the FWHM of the luminescence correlation is 1.5 psec. Given the nature of the correlation process and the finite laser pulse width, a luminescence decay time of less than 1 psec is implied. The correlation time increases rapidly with decreasing $\hbar\omega_e$. A correlation time of 9 psec (FWHM) has been measured for emission energies near 1.8 eV, similar to the previous results. Our correlation

measurements show that the highly excited carriers responsible for the luminescence which we observe at $\hbar\omega_e \gg \hbar\omega_0 = 2.12$ eV persist for only about 1 psec.

For the values of n_0 in Fig. 1, $\tau_c \ll 10^{-13}$ sec. The hot carriers will be thermalized almost instantly and the carrier distribution functions will vary as $\exp(-E_c/k_B T_c)$ where E_c and T_c are the carrier energy and temperature. For $\hbar\omega_e > k_B T_c$, and if (a) T_c has a time constant of the order of 1 psec and (b) $n(t)$ decays in less than 1 nsec, then $I(\omega_e)$ will be dominated by the highest-temperature contributions to Eq. (1). The rapid decrease in the intensity of the time-correlated emission at high energies reflects the cooling of the thermalized carriers. If all of the optically injected kinetic energy (0.7 eV per electron-hole pair) can become thermal energy in the free-carrier system (4200 K), then the 1-psec lifetime in Fig. 1 implies the emission of about 5 LO phonons in 1 psec or $\tau_{e-\mathrm{LO}} \sim 200$ fsec as expected.[7,10]

In Fig. 2, we show $I(\omega_e)$ excited by a single laser pulse for 2.1 eV $< \hbar\omega_e <$ 2.4 eV and several different values of n_0. At the higher values of n_0, $I(\omega_e) \propto n_0^2$ and the spectral shape is independent of I_0. However, for $n_0 < 3\times10^{17}$ cm^{-3}, we observe changes in the shape of the anti-Stokes spectrum. The emission at higher energies decreases more rapidly with decreasing n_0 than the emission at lower energies. In Fig. 3 we show the variation of $I(\omega_e)$ for several different values of ω_e as a function of I_0. The emission above 2.2 eV shows a superquadratic dependence on I_0 at the lower excitation levels and approaches a quadratic dependence only at the higher-excitation levels.

A quadratic dependence of $I(\omega_e)$ on I_0 can occur for $n_0 > 10^{18}$ cm^{-3} when a thermalized state can be reached without any excitation of the lattice. Once the carriers are thermalized, the polar optic phonon-carrier interaction determines the rate at which T_c decreases. Theoretically, the cooling rate can depend on n_0. However, the slowing of the cooling rate due to the presence of nonequilibrium LO phonons[15] should not be significant during the first 1–2 psec since it takes more than 2 psec for the nonequilibrium phonon population to develop and the carriers to approach 300 K. When $n_0 > 10^{18}$ cm^{-3}, the screening of the long-range Fröhlich interaction can also produce a slowing of the cooling process. However, Kim, Das, and Senturia[16] showed that when the high-energy coupled mode frequency of the LO phonon plasmon is significantly greater than the LO phonon frequency, there is an "antiscreening" of the carrier-coupled mode scattering strength. As a result, there can be an increase in the strength of the carrier scattering by the collective modes of the system. Finally, diffusion of carriers[17] from the surface can reduce the density of carriers available for recombination. However, for realistic carrier velocities ($< 10^7$ cm sec^{-1}) and our opti-

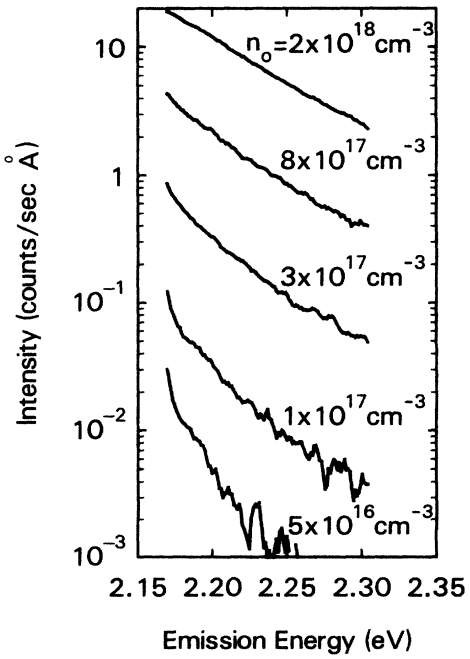

FIG. 2. The anti-Stokes luminescence spectrum of GaAs excited by 2.13-eV pulses with a temporal width of 0.5 psec for various injected carrier densities n_0.

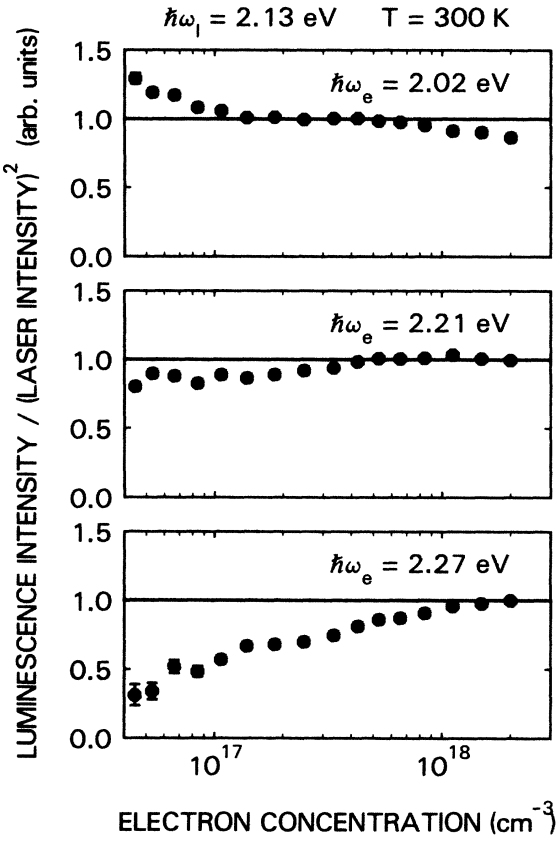

FIG. 3. The dependence of the anti-Stokes emission intensity on I_0 for three different values of $\hbar\omega_e$ and GaAs excited by 0.5-psec pulses at 2.13 eV. Since $I(\omega_e)$ should be proportional to I_0^2, the data are plotted normalized against I_0^2. As a result, a quadratic dependence on I_0 appears as a horizontal line, a subquadratic dependence as a negative slope, and a superquadratic dependence as a positive slope. Error bars, where present, indicate the shot noise error limits. If error bars are smaller than the symbols, they are not shown.

cal penetration depth (200 nm), this effect should only be important at longer times (>2 psec). Significant carrier diffusion effects at short times are also not consistent with the observation of long correlation times at lower photon energies. We conclude that the high-density corrections to the normal quadratic dependence of the emission intensity on pump power should be small, which is consistent with our observations for $n_0 > 5\times10^{17}$ cm^{-3}.

The variation in the slope of $I(\omega_e)$ and the superquadratic change of the emission intensity at fixed anti-Stokes emission energy with respect to changing I_0 for I_0 small, shown in Figs. 2 and 3, are inconsistent with a simple model in which f_n and f_p are independent of I_0. It was noted earlier that the strength and slope of the high-energy emission is determined by the highest temperatures achieved by the carriers when they thermalize. As n_0 decreases, τ_c increases, and the peak temperature will decrease, the magnitude of the decrease depending on the amount of energy lost to the lattice before a thermalized distribution is achieved. A decrease in n_0 will result in a decrease in the high-temperature contribution of the thermalized distribution to the hot luminescence. This produces the superquadratic variation of the intensity of the high-energy anti-Stokes emission for small I_0 and an effective cooling of the shape of the anti-Stokes emission.

Our results suggest that the nonthermalized carriers do not contribute significantly to anti-Stokes emission which we observe at high energies. This is reasonable since it is the carrier-carrier scattering which generates a thermal population where some carriers will have considerably more kinetic energy than the average value, unlike the initially generated distribution which is monoenergetic. In the absence of carrier-carrier scattering which conserves the total energy in the carrier system, the nonthermalized carriers only lose energy to the lattice, making it unlikely that they could contribute significantly to the anti-Stokes emission. The superquadratic behavior seen in Fig. 3 at low injection densities simply reflects the fact that the carriers are instantly thermalized at high densities but lose considerable energy before thermalization at lower densities. It should be noted that for $n_0 < 5\times10^{16}$ cm^{-3}, the hot carriers can lose much of their energy to the lattice before becoming thermalized. We observe no detectable anti-Stokes emission at these carrier densities. However, as von der Linde[14] showed, bimolecular Stokes emission can be readily observed. In Fig. 3, we show that deviations from the quadratic dependence of the emission intensity on I_0 can also be observed in the Stokes emission. However, the considerably longer correlation times associated with the Stokes emission below 2.0 eV, the complexity of the band structure of GaAs with its indirect minima, possible contributions to the emission from extrinsic sources[13] and other factors make any interpretation of these deviations problematical.

We have used subpicosecond optical pulses to excite above band-gap photoluminescence in GaAs. We demonstrate that the anti-Stokes emission can be used to study the dynamics of the hot carriers on the picosecond time scale. By working with optical pulse widths smaller than the times required for the optically injected carriers to lose their excess energy to the lattice, we have been able to study the competition between carrier-carrier and carrier-lattice scattering in the thermalization of the hot carriers. Variations in both emission efficiency and luminescence correlation with excitation power measure changes in the distribution of the optically injected carriers. These changes result from the varying relative importance of electron-electron and electron-phonon scattering during the first few picoseconds of the relaxation process.

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