Intervalley scattering rates in GaAs measured by time-resolved four-wave mixing spectroscopy

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A three-pulse transient grating technique was used to measure the carrier dynamics in photoexcited GaAs. The four-wave mixing signal exhibits a two component relaxation of different magnitudes for various probe energies. The fast relaxation mechanism is due to electrons in the L valleys scattering back to the Γ valley. The effective transfer time for $L \to \Gamma$ was found to be ≈ 8 ps. The slower relaxation arises from carrier recombination.

Transient grating techniques have long been used to study carrier recombination and diffusion in semiconductors.[1-4] The technique consists of exciting the sample with two intense pump pulses whose photon energy is greater than the band gap. The two pump pulses temporally and spatially overlap on the sample at a small angle. If the pump pulses have parallel polarization the resulting interference pattern gives a spatial modulation to the excited carrier population. The spacing of the modulation depends on the pump wavelength and angle of intersection. A third, probe pulse is also focused onto the sample spatially overlapping the pump pulses. The spatial modulation of excited carriers gives a modulation in the refractive index of the sample. This modulation acts as a grating which scatters the probe pulse in the phase matched direction given by

$$\overline{K}_{\text{signal}} = \overline{K}_{\text{probe}} + \overline{K}_{\text{pump1}} - \overline{K}_{\text{pump2}}.$$

The intensity of the signal is measured as the probe pulse is delayed with respect to the pump pulses. The decay of the grating signal is related to the relaxation of the nonlinear polarization and hence to the free-carrier contribution to the real part of the dielectric function. The free-carrier contribution to the real and imaginary parts of the dielectric function is given by[5,6]:

$$\epsilon_1(w) = 1 - \frac{4\pi e^2}{3\hbar^3 w^2} \int \frac{d^3k}{4\pi^3} \sum_n f(E_n) \nabla_k^2 E_n(k) \quad \text{(intraband)}$$
$$+ \frac{\hbar^2 e^2}{\pi^2 m^2} \sum_{nn'} \int \frac{d^3k\,[f(E_n) - f(E_{n'})]}{(E_n - E_{n'})[(\hbar w)^2 - (E_n - E_{n'})^2]} \times |p_{nn'}|^2 \quad \text{(interband)}, \tag{1}$$

$$\epsilon_2(w) = \frac{2\pi e^2 \hbar^2}{m^2 w^2} \sum_{nn'}{}' \int \frac{d^3k}{4\pi^3} [f(E_n) - f(E_{n'})] \times |p_{nn'}|^2 \delta(\hbar w - E_n - E_{n'}). \tag{2}$$

If one is interested in the change in ϵ due to photoexcitation, only the lowest conduction band and highest valence band need be considered. The change in the real part of the dielectric function is

$$\delta\epsilon_1(w) = \frac{-4\pi e^2}{3\hbar^3 w^2} \int \frac{d^3k}{4\pi^3} [f_e(En) \nabla_k^2 (E_n(k)) - f_h(E_{n'}) \nabla_k^2 (E_{n'}(k))] \quad \text{(intraband)}$$
$$+ \frac{\hbar^2}{\pi^2} \frac{e^2}{m^2} \sum_{nn'} \int \frac{d^3k\,[f_e(E_n) + f_h(E_{n'})]}{(E_n - E_{n'})[(\hbar w)^2 - (E_n - E_{n'})^2]} |p_{nn'}|^2 \quad \text{(interband)}, \tag{3}$$

where n and n' are the lowest conduction and the highest valence bands, respectively, $f_e(E_n)$ is the electron distribution function in the conduction band, and the hole distribution in the valence band is $f_h(E_{n'}) = 1 - f_e(E_{n'})$.

The intraband term is a free-electron-like term while the interband term represents transitions between bands. It has been shown that for a direct gap semiconductor with contributions from single parabolic conduction and valence bands, the intraband term reduces to the usual Drüde expression.[6] However, the interband term depends on detailed knowledge of the band structure and carrier distribution functions and is difficult to evaluate. For a probe energy $\hbar w \ll E_g$, the interband term is small compared to the Drüde (intraband) term and of the same sign. In this case, the Drüde term dominates and a transient grating experiment measures the population decay arising from either diffusion of carriers from the peaks to the nodes of the grating or recombination of carriers. For a probe energy $\hbar w > E_g$, the interband component can be comparable to the intraband component and has to be considered. If the probe photon energy is large compared to the typical energy separation of the excited electrons and holes, the interband component is opposite in sign from the intraband component, and when hole population and the electrons (in the Γ valley) are approximately equal, the interband and intraband terms cancel.

In a semiconductor with a multivalley conduction band, such as GaAs, electrons can scatter into the L and X valleys which affects the electron contribution to the dielectric function. Kahen and Leburton[7] have calculated the imaginary part of $\epsilon(w)$ and the real part of $\epsilon(0)$. They have determined

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that the dielectric constant for GaAs depends 90–95% on the L and X valleys and only 5–10% on the Γ valley. Kash *et al.*[8] have studied the free-carrier contribution to third-order optical nonlinearities in GaAs using nanosecond pulses from a CO_2 laser. They found a temperature dependence for the four-wave mixing signal that was due to the distribution of electrons in the Γ and L valleys.

Consider the intraband term in Eq. (3). Assuming parabolic bands, $\nabla_k^2(E) \rightarrow 3\hbar^2/m^*$, and the intraband term reduces to the usual Drüde expression:

$$\delta\epsilon_1(w) = -4\pi e^2 n/w^2 m_r^* \text{ (intraband)}, \tag{4}$$

where n and m_r^* is the density of excited carriers and the reduced effective mass, respectively.

Consider the interband term in Eq. (3). Only the heavy hole valence band is considered because of its much larger density of states and its stronger optical absorption than the light hole or split-off bands. The bands are treated as parabolic and the interband term in the central valley is numerically integrated using the value of $|p_{nn'}|^2 = \hbar w_g m^2/4m^*$ from $k\cdot p$ perturbation theory.[6,9] The L-valley contribution is approximated by assuming all the electrons are at the L minima which is reasonable considering its large density of states. The electrons which scatter into the L valley lose 0.286 eV of kinetic energy when they scatter over and additionally they rapidly lose energy to the lattice by optical polar phonon emission since they are not screened even at our high intensity of excitation.[10] The hole population optically coupled to the L valley is taken to be zero and the reduced effective mass at the zone edge is taken to be the electron effective mass. The L-valley contribution to $\delta\epsilon_1$ is small reducing to

$$\delta\epsilon_1(w) = \frac{\pi e^2 \hbar w_g n_L}{m_L^* E_L w^2(\hbar^2 w^2 - E_L^2)}, \tag{5}$$

where E_L is the energy separation of the L-valley minima and the heavy hole band (3.1 eV) and n_L is the electron population in the L valley. Figure 1 shows $|\delta\epsilon_1|^2$ as a function of the ratio of electrons in the Γ valley to the L valleys

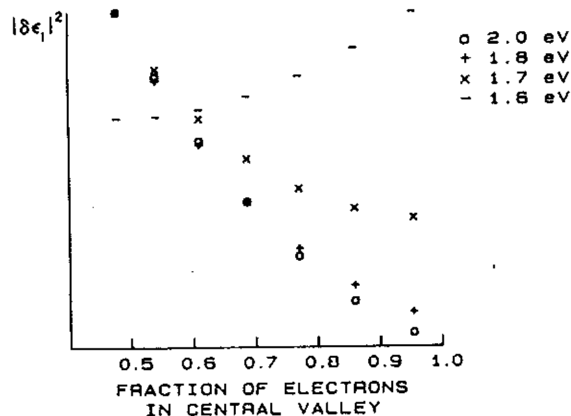

FIG. 1. $|\delta\epsilon_1|^2$ plotted as a function of the fraction of electrons in the central valley. The total number of electrons and holes was taken equal ($10^{19}/cm^3$). The carrier temperature was taken to be 1100 K. A better quantitative fit to the data would be achieved by including the light hole and split-off bands as well as band nonparabolicity. The actual carrier temperature, measured by pump and probe absorption, is not a constant over our measured relaxation time.

for different probe energies. For these calculations the carrier density was taken to be $1\times10^{19}/cm^3$ and carrier temperature = 1100 K. The carrier density was estimated based on pump and probe absorption measurements to be published elsewhere. Our calculations show that for probe energies near or below band gap, $\delta\epsilon_1$ does not depend strongly on the ratio of electrons in the Γ to L valleys, and $\delta\epsilon_1$ relaxes by carrier recombination. For probe energies high above gap, the interband and intraband terms cancel when most of the electrons are in the Γ valley and consequently the four-wave mixing signal is very weak. When a significant percentage of electrons are in the L valleys the interband term is small and the four-wave mixing signal is large. By measuring the relaxation of the four-wave mixing signal probe at frequencies high above the band gap, we measure the rate at which electrons return from the L valleys to the Γ valley.

The laser system used was a CPM rhodamine 6G dye laser with a four-stage amplifier system pumped by a Q-switched Nd:YAG laser operating at 20 Hz. The output laser pulses of this system have a width of 500 fs, at 620 nm and an energy of 250 mJ. The laser pulse was divided into two pump pulses and a probe pulse and focused onto the sample at a small angle. The angle between the pulses was not equal to separate the two-pulse signal from the three-pulse signal. The initial distribution of pulse energy was 47% to each pump and 6% to the probe. A motor-driven variable delay line was inserted in each beam path. To ensure temporal and spatial overlap of the three pulses, the sample was replaced with a KDP crystal. The second-harmonic signal produced by the two pump pulses was maximized to ensure temporal and spatial overlap. The probe pulse was then aligned to maximize the second harmonic produced by it and one of the pump pulses. It was then verified that this alignment also maximized the second harmonic produced by the probe and the second pump pulse. The KDP was replaced by the GaAs sample. Under these conditions, we were able to visually observe, in addition to the three transmitted pulses, nine diffracted pulses corresponding to all combinations of $K_i + K_j - K_k$. Initially, data were taken with the pumps and probe degenerate but eventually a cell of CCl_4 was inserted in the probe pulse to produce a broadband continuum probe. Apertures were used to select the correct scattered pulse.

The samples consisted of a thin layer of GaAs (either 0.25 or 0.75 μm) with an AlGaAs cover layer, whose band gap was larger than the laser photon energy. We estimate the photogenerated carrier density to be $\approx 10^{19}/cm^3$.

The diffracted signals are displayed in Fig. 2 for various probe energies. The signal at 2.0 eV displayed in Fig. 3 was fitted by a single exponential decay with a 4.0 ps decay time which corresponds to an 8 ps relaxation. The grating curve was calculated using a 500 fs Gaussian laser pulse and an 8 ps relaxation time using the expression for the diffracted energy given by Wherrett *et al.*[11] The relaxation time of the grating was found to be independent of pump intensity or the angle between the pump pulses. This should eliminate spatial diffusion as the relaxation mechanism. As the probe wavelength was tuned closer to the band edge of the GaAs, a long component began to be evident whose intensity relative to

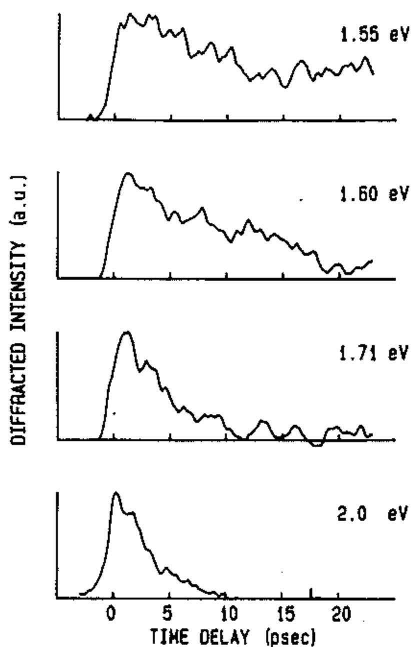

FIG. 2. Diffracted signal at different probe energies.

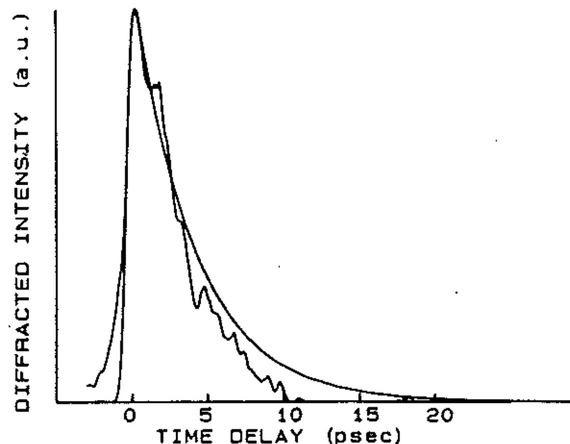

FIG. 3. Typical grating decay curve for both pumps and probe = 2 eV as well as the calculated signal for an 8 ps decay convoluted with a 500 fs Gaussian pulse.

the short component increased (see Fig. 2). A short component of 8 ps exists in all curves. For a 2.0 eV probe only the short component is present. The long component is too weak to be observed. For a 1.71 eV probe the long component is barely evident. For the 1.6 and 1.55 eV probes the long component begins to dominate although the short component is still clearly evident. The long component decay was much longer than our maximum optical delay and is due to carrier recombination and/or diffusion. The relative strength of the long (population) component increases as the probe wavelength is tuned to energies closer to the band edge. This is to be expected from Eq. (3) which predicts that the intraband and interband terms will cancel at large probe energies when all the excited electrons are in the Γ valley. When a significant fraction of electrons are in the L valleys, then the carriers do not contribute to the interband term and the cancellation of the intraband and interband terms is not complete and the four-wave mixing signal is greater.

Our measured effective scattering time from the L to the Γ valley of 8 ps is in close agreement with the recent results of Shah *et al.*,[12] who report a 10 ps rise time in the luminescence intensity of GaAs due to electrons scattering back from the L to the Γ valley. This is an effective scattering time since we measured the net time for electrons to return from the L valleys. At high carrier density and temperature, electrons can undergo multiple scattering back and forth between valleys. The $L \rightarrow \Gamma$ time of ≈ 2.7 ps is estimated by assuming three $\Gamma \Leftrightarrow L$.[13] To get the exact scattering rate from our effective scattering time requires either Monte Carlo calculations[13] or detailed knowledge of the carrier distribution function.

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