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SLOWED PICOSECOND KINETICS OF HOT PHOTOGENERATED CARRIERS IN GaAs

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The hot photoluminescent kinetics of GaAs under intense picosecond excitations (10^{28} photons/cm^2 sec) have been measured. A slow risetime of the near bandedge luminescence has been observed arising from a slowed cooling of the electron distribution. The slowed electron kinetics of over 50 fold are attributed to the screening of the electron-phonon interaction. Carrier densities at these excitation intensities are limited by saturation of the absorption. These results are important for understanding and may help clarify the mechanisms of laser annealing.

Over the last decade, there has considerable effort in studying the relaxation of hot photogenerated carriers in semi- conductors[1-6]. Both photoluminescence[1,3,5,6] and absorption[2,4] have been used to examine the relaxation mechanisms at low temperatures. These studies revealed a very rapid loss of most of the initial excess energy of the photogenerated carriers to a effective electron temperature within ~100°K of the lattice temperature. Time-resolved studies have shown that this occurs within 2 ps.[4] Using excite and probe absorption techniques, Shah and co-workers[2] recently observed a moderate decrease in the carrier cooling rate at high intensities. In this letter we are reporting pronounced slowing by over a factor of 50 of the electron kinetics in GaAs at room temperature and very high excitation densities. This is evidenced by a slow risetime of the near bandedge luminescence. The temporal behavior of the hot luminescence far above the bandedge is observed and analyzed. These results are consistent with a saturated absorption coefficient caused by the finite number of absorbing states and depopulation time of these states. This leads to a deeper excited length and lower carrier densities than would be calculated without including this effect. The breakdown in the ability of energetic electrons to transfer energy to the lattice resulting in slowing of carrier relaxation is attributed to screening of the electron-phonon interaction. This is supported by calculation and measurements. Our results are of general interest to the semiconductor community and of particular importance and may help clarify the current controversy on the laser annealing mechanisms[7,8].

The time resolved photoluminescence from the front surface of polished n-type and p-type GaAs crystals were measured at room temperature and at 80K. The crystals were excited by the second harmonic of a single 6 picosecond pulse selected from a mode-locked train of pulses emitted from a Nd-phosphate glass laser with an amplifier[9].The maximum total excitation was $8x10^{16}$ photons/cm^2 (0.035J/cm^2 at the sample in a spot size of ~ 1 mm diameter. The resulting photoluminescence was focused onto the slit of a streak camera (Hamamatsu (C979)). The output of the streak camera was detected and digitized by a SIT camera and Hamamatsu temporal-analyzer. The overall time resolution of the system is 10 ps. A portion of the excitation pulse was directed into the streak camera as a marker pre-pulse. This was correlated to the photoluminescence by measuring the time between the pre-pulse and the scattered excitation light from the crystal surface. This provided an absolute zero time point for the photoluminescence measurements. Filters were placed in the luminescence path to select various spectral regions from the total photoluminescence.

The time resolved emissions at various wavelengths are shown in figure 1. No evidence of stimulated emission was observed[10]. The photoluminescence kinetics follow the temporal profile of the excitation pulse for wavelengths shorter than $\lesssim$8000A. There is an increasing delay

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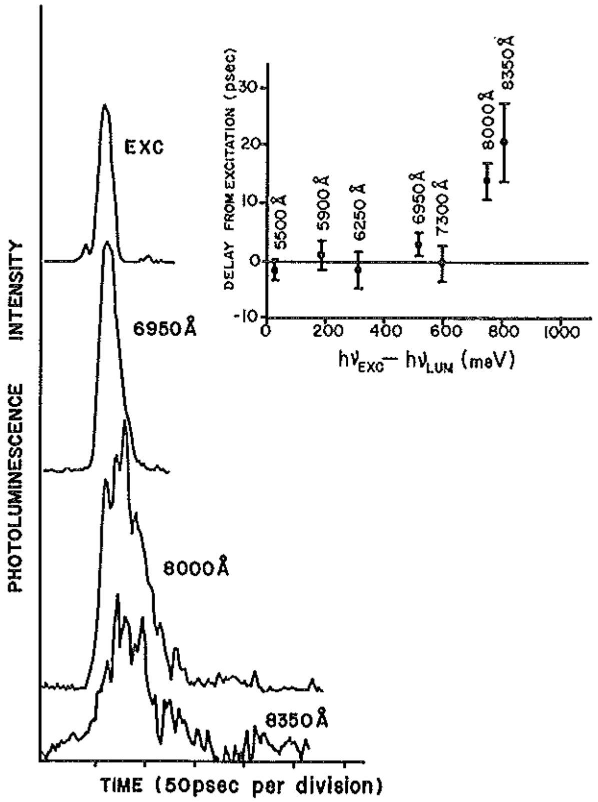

Figure 1. Photoluminescence from p-type GaAs at room temperature for several different wavelengths (pre-pulse is not shown). The inset shows the time delay of the photoluminescence peak from the excitation as determined in the text. Error bars indicate one standard deviation.

in the peak of the emission for wavelengths of 8000A and longer. Furthermore, there is significant emission for these wavelengths for times long after the excitation has ended. Figure 2 shows the rise time (10%-90%) of the photoluminescence for wavelengths longer than 8000A as a function of the excitation intensity. At the lowest excitation intensities (2×10^{15} photons/cm^2) the risetime is determined by the pulse width of the excitation. However, as the excitation intensity is increased the rise time becomes longer reaching a value of 35 ps for our highest intensities (8×10^{16} photons/cm^2). The ratio of the photoluminescence at 8000A to that at 8350A as a function of time is shown in figure 3. These values were obtained by taking two decay profiles of the photoluminescence at the appropriate wavelengths and same excitation intensity. The lines on the graph are values of the luminescent ratio calculated using the two models which will be discussed later.

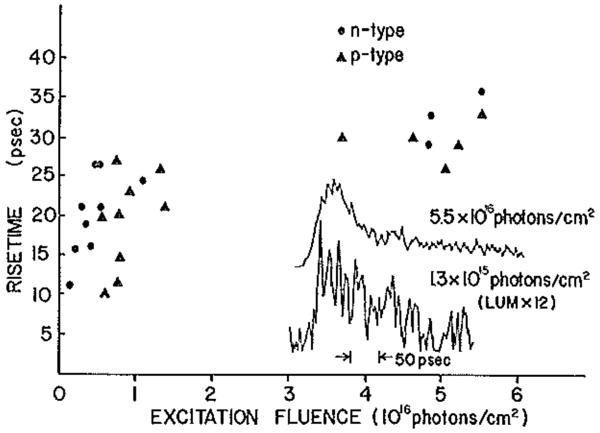

Figure 2. Risetime (10% to 90%) of the photoluminescence of GaAs at room temperature for wavelengths of 8000A and longer vs total excitation fluence (photons/cm^2). Inset shows typical photoluminescence curves for high and low excitations.

The above results can be interpreted using the following model. As the excitation photons are absorbed, electrons are excited from the light and heavy hole bands as well as the split-off band into the conduction band with an average excess energy of 800 meV . These electrons thermalize amongst themselves in a time short compared to the pulsewidth via electron-electron collisions.[11] They also lose energy to the lattice via optical phonon emission. Since the phonon energy is 36 meV and the phonon emission time is 0.1 ps,[4] we expect the carriers to relax to the lattice temperature in 2 to 3 ps. This is consistent with our data at low excitation densities (2×10^{15}photons/cm^3) where the pulse risetime is comparable to the excitation pulsewidth.

At high excitation intensities the process starts similarly and it is the rapid thermalization of the carriers that leads to the photoluminescence at wavelengths $<$ 8000A following the temporal profile of the excitation pulse. For wavelengths 8000A and longer the kinetics are different due to the high carrier densities. The optical phonon emission is inhibited and the slower cooling causes the near bandedge electron density (and hence the near bandedge photoluminescence intensity) to increase slowly. This results in the long risetimes shown in figures 1 and 2. There are two possible mechanisms that have been suggested for this to occur. The first is a screening of the electron-phonon interaction[12]. The second is that the phonon temperature becomes heated and equilibrates with the hot carriers[13](phonon bottleneck). The carrier energy loss will be determined by

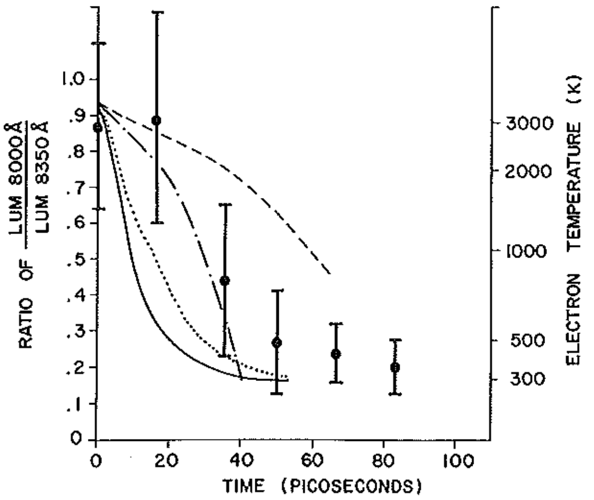

Figure 3. Ratio of the photoluminescence at 8000A to 8350A of n-type GaAs at room temperature as a function of time after the excitation ($3\text{-}4\times10^{16}$photons/cm^2 or 0.015 J/cm^2). The right hand ordinate is the electron temperature corresponding to that ratio of the luminescence. The error bars represent one standard deviation. The lines are calculated values from the two mechanisms as follows: the solid line and dotted line are the phonon build-up mechanism at excitation densities of 5×10^{18} cm^3 and ...1×10^{19}cm^3. The dashed line and dot-dash line are calculated values for a reduction of the phonon emission rate of -.-x50, ---x100.

the phonon depopulation losses, which is the phonon decay time. Recent measurements[14] of the phonon decay time in GaAs at low excitation levels ($\sim 10^4$ lower than our maximum) and 77K gave a phonon decay time of 7 ps.

The electron temperatures can be calculated from the ratio of the photoluminescence intensity at two wavelengths if we know the carrier distribution functions (Fermi functions), the density of states, and matrix elements. It is also necessary to know the spatial distribution of carriers within the sample since reabsorption will strongly influence the ratio. The heavy hole band to conduction band transition which dominates the absorption at 2.34 eV yields electrons with an energy distribution of 50 meV[15]. The effective density of absorbing states is 10^{17}/cm^3. The occupied states can be depopulated by electron-electron scattering, plasmon emission, optical phonon emission, and intervalley scattering. The dominate mechanism for GaAs at high carrier densities is electron-electron scattering[11]. This rate is $2\text{-}4\times10^{-14}$ sec. at our carrier concentrations. Using this rate and the relevant equations describing absorption including the occupancy of the absorbing states, yields a maximum absorption rate of $\sim 10^{25}$ photons/cm^2 sec. Since our maximum excitation intensity is 10^{28} photons/cm^2 sec, we have very deep penetration of the excitation. We should like to emphasize that only those states which are directly populated during the absorption are saturated. The model used to describe the excited electron distribution is quasi-thermalized with a highly peaked spike in the absorbing region. This spike relaxes rapidly ($\sim$ 1 psec) through electron-electron interaction after the pulse ends (see ref. 15). As the direct absorption is saturated the indirect absorption and free carrier absorption become important. We have concluded that the transfer from the indirect heavy-electron valleys to direct valley cannot be responsible for the slow risetime because the calculated rates are too fast even for the smallest deformation potentials assumed[11]. Furthermore, screening is relatively ineffective in these valleys[12], particularily for phonons with large $\vec{q}$.

To determine electron temperatures from our measured ratio of the luminescence or the ratio of the luminescence for a given electron temperature, we have calculated the ratio of the luminescence at 8000A to that at 8350A for various depths of penetration of the excitation into the sample using density of states, fermi functions and bandgap renormalization[16]. The calculations assumed that the electrons were in thermal equilibrium with themselves[17] due to the high rate of electron-electron scattering. We have calculated the electron temperatures for the two mechanisms that were discussed previously. The resulting luminescence ratios are plotted in figure 3 with our experimental data. On the right hand ordinate is the calculated electron temperature corresponding to that ratio of luminescence. The solid line is the calculated luminescence ratios for temporal evolution of the electron temperatures including the phonon build-up for an electron-hole density of 5×10^{18} cm^{-3}. The dotted line is for the same mechanism with an electron-hole density of 1×10^{19} cm^{-3}. Neither density is able to account for the observed electron temperatures cooling rates. Also plotted in figure 3 are the calculated luminescent ratios assuming the phonon emission rate has been reduced due to the screening of the electron-phonon interaction. We have shown these ratios for a reduction of the phonon emission rate of a factor of 50 and 100.

These emission rates correspond to 7.2 and 3.6 mev/ps energy loss rates, respectively. This is the range of values calculated by Yoffa[12] for electron densities of $5 \times 10^{18} cm^{-3}$. The uncertainty is due to uncertainty in the strength of the deformation potential scattering which reduces the effect the screening has on the overall phonon emission rate. The experimental data fits within this range of phonon emission rates. We therefore assign the slowing mechanism to screening of the electron-phonon interaction.

Additional evidence for the assignment of the slowing mechanism to the screening phenomena is the risetime data presented in figure 2. This data shows that the slowing occurs at lower excitation densities in n-type material than in p-type material. This is as expected for the screening mechanism since background electronsin the central conduction band valley effectively contribute to the screening while the background holes in p-type material do not contribute to the screening.[12] The conductivity type of the crystal would have no influence on the phonon build-up and thus one would expect the slowing to begin at the same excitation level in p- and n-type crystals.

We have demonstrated the very strong slowing (greater than a factor of 50) which occurs in the kinetics of electron energy relaxation in GaAs during intense photoexcitation of GaAs. This slowing of the kinetics can alter the energy deposition and diffusion during such intense excitation as laser annealing. These effects in the pulsed laser annealing regime should be even stronger since the obtained carrier densities are much higher due to the longer pulse width and total energy fluences at least by an order of magnitude larger. These results provide important new evidence in the attempt to understand the role of hot electrons on the transient optical transmission in semiconductors[19].

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