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Femtosecond gain dynamics due to initial thermalization of hot carriers injected at 2 eV in GaAs

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The transient absorption changes near the band edge of a thin GaAs film are measured at room temperature with ~100 fs time resolution for various carrier densities photoexcited at 2 eV. For $N \gtrsim 3\times10^{18}$ cm^{-3}, gain is observed on a subpicosecond time scale. By comparing the delay time at which gain is observed at different excitation levels and wavelengths with a simple kinetic model, this ultrafast onset of gain is attributed to (i) nearly instantaneous equilibration of the carrier distributions near the Γ point of the Brillouin zone, together with (ii) a very efficient cooling mechanism for Γ-valley electrons due to preferential scattering of high-energy electrons to the X and L valleys. Evidence for a heated hole distribution on a subpicosecond time scale is presented, which points to the importance of electron-hole interactions.

Although the dynamics of hot carriers in GaAs has been the subject of numerous experimental and theoretical investigations, femtosecond optical measurements continue to reveal interesting facts about ultrafast relaxation processes in this material.[1-10] Anti-Stokes luminescence measurements[4] showed that for carrier densities (N) larger than 10^{18} cm^{-3}, the carriers can reach a thermalized state without any excitation of the lattice. Very recently, time-resolved photoluminescence measurements[10] indicated that both the electron distribution and the (heavy) hole distribution excited by 2-eV photons spread over a wide energy range within 100 fs, even for N as low as 10^{17} cm^{-3}. Other femtosecond pump-probe experiments[3,6] demonstrated similar ultrafast scattering rates out of the initially occupied states. These measurements indicate that at least for $N \gtrsim 10^{18}$ cm^{-3}, a significant portion of the electrons injected at 2 eV reach the band edge in ≤ 100 fs. Although it was not explicitly pointed out, the Monte Carlo simulations reported in Ref. 10 illustrated another important point, discussed qualitatively by Shah *et al.*,[5] and more recently by Kim and Yu,[8,11] that the preferential and rapid scattering of high-energy Γ-valley electrons to the X and L satellite valleys very effectively cools the portion of the electron population that remains in the Γ valley, even on a subpicosecond time scale. Thus, although the effective temperature of the initially excited electrons is ~3000 K, the recent Monte Carlo simulation of the electron distribution near the bottom of the Γ valley exhibits an effective temperature of only ~1200 K, 200 fs after excitation.[10] The simple model of Kim and Yu[8,11] estimates an even faster drop in the Γ-valley electron temperature due solely to this intervalley scattering mechanism.

The nearly instantaneous intra-Γ-valley redistribution, together with the very efficient intervalley cooling mechanism, suggests that it should be possible to observe band-edge gain on subpicosecond time scales even when exciting with 2-eV photons. The purpose of the present paper is to report results of femtosecond pump (2 eV) and probe (near band edge) absorption measurements, which clearly show the buildup of gain near the GaAs band edge on a subpicosecond time scale for $N \gtrsim 3\times10^{18}$ cm^{-3}, with a time to reach gain as short as ~280 fs at 880 nm and the highest N used ($\lesssim 10^{19}$ cm^{-3}). A model similar to that of Kim and Yu[8,11] is shown to be consistent with these gain measurements.

Pump-probe measurements are performed at room temperature on a (0.27 ± 0.02)-μm-thick intrinsic GaAs film attached to a sapphire window using a technique described previously.[9] About 3% of the copper vapor laser amplified CPM pulse of 80–100-fs duration at 620 nm is used as a pump beam. The remainder is focused onto a jet of ethylene glycol and produces a white-light continuum. We obtain a probe pulse of 100–120-fs duration over a wavelength region from 850 nm to 920 nm by using interference filters with a bandwidth of 10 nm. The polarizations of the pump and probe pulses are orthogonal to reduce the coherent artifact. The intensity of the pump pulse is varied over two orders of magnitude, and the carrier density is estimated from the number of photons absorbed by the film, the measured beam spot size, and the sample thickness, provided that each absorbed photon generates one electron-hole pair. Uncertainties in these beam parameters and the efficient surface recombination on unpassivated GaAs samples[12] make the overall uncertainty of the estimated carrier density approximately ±50%.

We have measured the time resolved differential transmission ($\Delta T/T_0$) and differential reflection ($\Delta R/R_o$) simultaneously on the uncoated sample described above. The unperturbed transmission (T_0) and reflection (R_0) are also carefully measured at each wavelength. In order to explain precisely the transient changes of the optical properties of a thin absorbing film on a thick transparent substrate, we developed a computer algorithm that calculates the absorption coefficient (α) and refractive index (n) from the measured transmission T, reflection R, and the sample thickness. We have checked the validity of this technique by verifying that the calculated transmission spectrum using the well-known optical constants for

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GaAs agrees with the measured unperturbed transmission spectrum within $\pm 15\%$.[13] In this paper we will focus on the dynamics of the absorption. An accurate measurement of R_0 and T_0 is important in order to extract the true value of $\alpha(t)$ near the band edge because gain occurs when α becomes negative. The conservatively estimated uncertainty of $\alpha(t)$ is approximately $\pm 50\%$.

Figure 1 shows $\alpha(t)$ for various carrier densities at a probe wavelength of (a) 880 nm, which is slightly below the original band edge, and (b) 860 nm, which is slightly above the original band edge. A "gain threshold line," below which α becomes negative and stimulated emission (gain) is observed, is also indicated in both figures with its associated error bar. Right after the excitation ($t \sim 0^+$), the data at 880 nm exhibit a short-lived induced absorption, whereas the data at 860 nm show a monotonic decrease of absorption. We attribute this to instantaneous plasma screening and band-gap renormalization caused by hot carriers.[9] The behavior of α at both probe wavelengths is quite similar afterwards, when carriers fall to the perturbed band edge and band filling becomes dominant.

The most interesting aspect of these data is that gain is observed on subpicosecond and picosecond time scales in a range of wavelengths (850–900 nm) for $N \gtrsim 3\times10^{18}$ cm^{-3}. From Figs. 1(a) and 1(b) we find: For $N \sim 3.3\times10^{18}$ cm^{-3}, the time delay to observe gain is $\sim 800 \pm 300$ fs at 880 nm, and $> 3000 \pm 800$ fs at 860 nm. For our highest carrier density ($N \leq 10^{19}$ cm^{-3}), this time is reduced to $\sim 280 \pm 80$ fs at 880 nm, and 450 ± 150 fs at 860 nm. No gain is observed up to 5 ps at probe wavelengths shorter than 840 nm, which is > 55 meV above the unrenormalized band edge.

The observation of subpicosecond gain suggests the presence of a very rapid cooling mechanism for the electrons, which are injected into the Γ valley with an excess kinetic energy corresponding to ~ 3000 K. The obvious mechanism that could provide this rapid cooling is intervalley scattering.[3,8,11] We have developed a model to estimate whether this mechanism is sufficient to explain the subpicosecond gain data. Excitons are assumed to be all ionized due to the high-carrier densities ($> 3\times10^{18}$ cm^{-3}) and temperatures (≥ 300 K). Although the detailed shape of the absorption and gain spectra is undoubtedly influenced by many-body effects in ways that are not yet quantitatively understood,[9,14] so long as the excitons are all ionized, the *threshold* for gain should follow from simple, single-particle considerations,[15] after accounting for the band-gap renormalization. We use the formula of Zimmermann to account for the band-gap renormalization $\Delta E_g(N,T)$:[16,17]

$$\Delta E_g(N,T) = -\frac{4.64(Na_B^3)^{1/2}}{[Na_B^3+(0.107k_BT/R_H)^2]^{1/4}}R_H\,, \qquad (1)$$

where a_B is the excitonic Bohr radius and R_H is the excitonic Rydberg energy. The carrier density N and temperature T are taken to be those of the Γ-valley electrons.[18] At a probe frequency ω, gain should be observed at any given time when the condition

$$\hbar\omega < \mu_{\rm eff} + E_g \qquad (2)$$

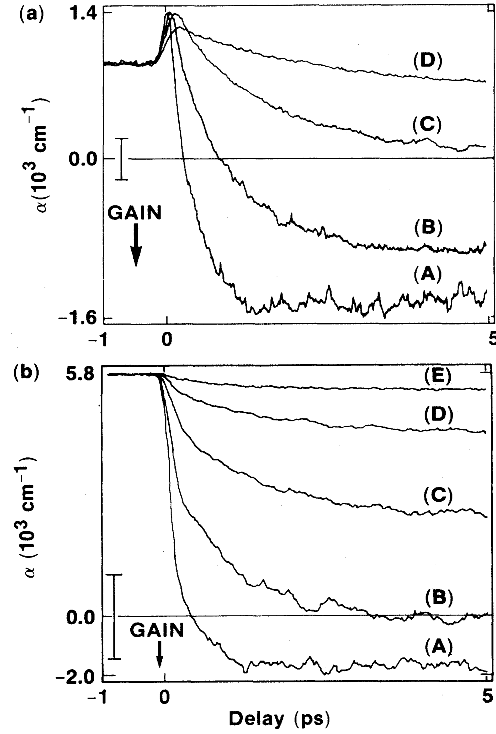

FIG. 1. Measured temporal evolution of the absorption coefficient $[\alpha(t)]$ at (a) 880 nm and (b) 860 nm for different nominal carrier densities where N is approximately (A) 9.0×10^{18} cm^{-3}, (B) 3.3×10^{18} cm^{-3}, (C) 1.0×10^{18} cm^{-3}, (D) 3.3×10^{17} cm^{-3}, and (E) 1.0×10^{17} cm^{-3}. The uncertainty on N is $\pm 50\%$. The error bar associated with the uncertainty of the measured absolute values of α is indicated.

with

$$\mu_{\rm eff} = \frac{m_e+m_h}{\beta_e m_h + \beta_h m_e}(\beta_e\mu_e + \beta_h\mu_h) \qquad (3)$$

$$\beta_{e\,(h)} = \frac{1}{k_B T_{e\,(h)}} \qquad (4)$$

is satisfied.[19] Here $\mu_{e\,(h)}$ is the quasichemical potential of the Γ-valley electrons (holes) with respect to the conduction (valence) band edge, and E_g is the renormalized band gap.

The calculation of $\mu_{\rm eff}$ involves solving a set of kinetic equations similar to those described by Kim and Yu[8,11] for the temporally evolving density and kinetic energy of Γ-valley electrons and holes. A sech^2 profile laser pulse with a full width at half maximum (FWHM) of 100 fs is the source of excitation. The electrons are injected into the Γ valley with an initial average kinetic energy ~ 0.415 eV. All the electrons in the Γ valley and all the holes are assumed to equilibrate instantaneously and independently. This assumption is supported by numerous femtosecond measurements at $N \gtrsim 10^{18}$ cm^{-3} (Refs. 4–6) and particularly by recent time-resolved photoluminescence studies.[10]

As pointed out previously, energetically allowed scattering of electrons from the Γ valley to the X and L valleys will preferentially remove the high energy portion of the distribution, thus acting as a heat sink for the remaining

electrons. Since the return time to the Γ valley is ~2.5 ps,[5] once scattered, these electrons are effectively out of the picture on a subpicosecond time scale. Scattering to the X and L valley is, therefore, incorporated into the kinetic model as an energy-dependent sink for the high-energy Γ-valley electrons, including zone-edge phonon emission and absorption and using the deformation potential parameters recently summarized by Zollner, Gopalan, and Cardona.[20] This is the only mechanism included for cooling of Γ-valley electron distribution. A small amount of energy will be lost via zone-center LO-phonon (intravalley) emission, but this will be comparatively negligible on these time scales when screening is included.[21] On the other hand, the interaction of the holes with optical phonons is via a deformation potential mechanism, which is relatively strong and weakly screened, thus it has often been assumed that the holes which have an initial temperature of ~600 K thermalize to the lattice temperature instantly.[5,8] However, recent Monte Carlo simulations[10] indicate a heated Maxwellian distribution of holes on 100-fs time scales. A heated hole distribution indicates that Coulomb-mediated electron-hole scattering cannot be completely neglected on this time scale. Estimates of the cooling rate associated with electron-hole scattering based on static screening calculations,[21] suggest that this is a more efficient cooling mechanism for electrons than via screened Fröhlich interaction, and that the energy-loss rate of hot electrons could be in excess of 60 meV/ps. Our static screening calculation indicates a rate of 165 meV/ps under the condition of $T_e = 2000$ K, $T_h = 600$ K, $N_e^\Gamma = 4\times10^{18}$ cm^{-3}, and $N_h = 5\times10^{18}$ cm^{-3} and by including contributions from inter- and intra-valence band scattering processes.[22] This rate would likely be even larger if full-dynamic screening was included in the calculation.[23] Rather than attempting to microscopically model these complex hole kinetics using numerous simplifying (and poorly justified) assumptions, we have chosen instead to treat the hole temperature as a parameter.

We have compared the experimental results with the model calculation as follows. First, if all intervalley scattering is "turned off," there is no gain on a subpicosecond time scale up to the maximum carrier density achieved in the experiments (~10^{19} cm^{-3}), even if the holes are assumed to thermalize to 300 K, instantly. Second, there is no gain if all the electrons excited above the threshold for intervalley scattering are assumed to scatter before they thermalize within the Γ valley. Thus, efficient intervalley cooling and very rapid Γ-valley equilibration are *both* required to explain the subpicosecond gain dynamics.

Figure 2 summarizes our efforts to fit the experimental gain-delay times at the highest two excitation levels in Fig. 1, given the latitude provided by the uncertainities in both the experimental parameters and the model parameters. Specifically, the delay time for gain to be observed at 880 and 860 nm is compared with the calculated $\mu_{\rm eff}+E_g$ from Eqs. (1)–(4). The high-excitation case ($\lesssim 10^{19}$ cm^{-3}), for which gain is observed in less than 500 fs at both 880 and 860 nm, is least sensitive to the uncertainties involved in the model calculation, since $\mu_{\rm eff}+E_g$ is changing rapidly with time, and intervalley scattering should definitely be the dominant cooling mechanism at these short-time scales. The two gain-delay times, 280±80 fs at 880 nm and 450±150 fs at 860 nm, observed for this highest level of excitation, can be best fit to our model using N close to the high limit indicated by the experimental uncertainty, together with a heated hole distribution. Figure 2(a) shows a plot of $\mu_{\rm eff}+E_g$ versus time for $N = 1\times10^{19}$ cm^{-3} with the hole temperature T_h as a parameter. Given the conservative error bars, both curve C ($T_h = 800$ K) and curve D ($T_h = 900$ K) intersect the two experimental "points." However, it appears that a better fit would be obtained if T_h was allowed to cool from ~900 K after 200–300 fs to ~750 K after ~450 fs. In order to test the validity of this heated-hole model, we also run the same calculation at the lower limit of T_h (300 K).

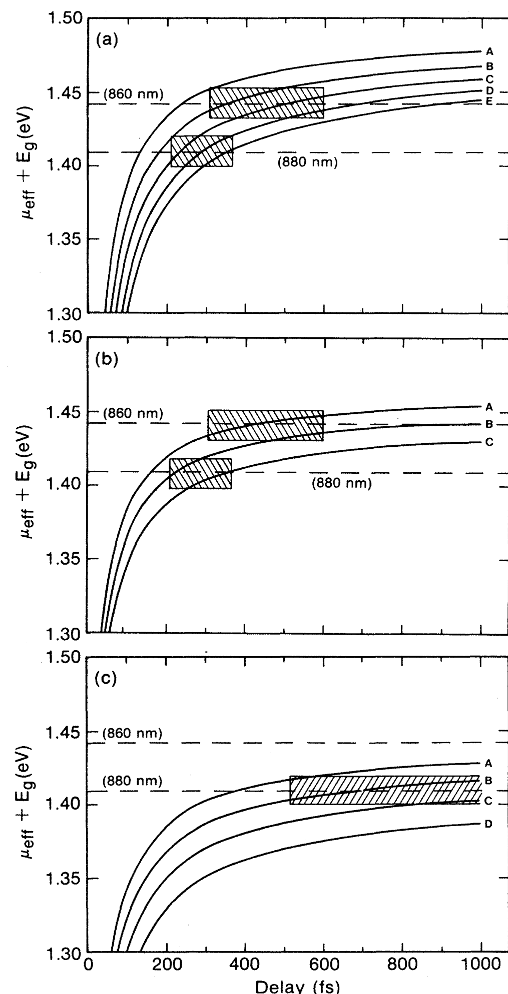

FIG. 2. Calculated time-dependent $\mu_{\rm eff}+E_g$ at different T_h and for different N: (a) $N = 1\times10^{19}$ cm^{-3}, T_h equals (A) 600 K, (B) 700 K, (C) 800 K, (D) 900 K, and (E) 1000 K; (b) $T_h = 300$ K, N equals (A) 6.3×10^{18} cm^{-3}, (B) 5.7×10^{18} cm^{-3}, and (C) 5.1×10^{18} cm^{-3}; (c) $T_h = 300$ K, N equals (A) 5.0×10^{18} cm^{-3}, (B) 4.5×10^{18} cm^{-3}, (C) 4.0×10^{18} cm^{-3}, (D) 3.5×10^{18} cm^{-3}. The hatched area is the measured gain-delay times at 880 and 860 nm with associated experimental uncertainties.

In Fig. 2(b) the $\mu_{\rm eff}+E_g$ curves are shown at $T_h=300$ K and for three different (lower) N. Here only curve B ($N=5.7\times10^{18}$ cm^{-3}, much below the nominal carrier density) intersects both experimental points just within the error bars. Thus the fit is much poorer than that shown in Fig. 2(a).

The gain delay observed experimentally at the lower nominal density of $N\sim3.3\times10^{18}$ cm^{-3} is 800 ± 300 fs. At these long delays T_h should be close to 300 K, because heating of the holes is less efficient when the electrons are cooler and because of the relatively strong coupling between the holes and the lattice. Thus, Fig. 2(c) shows $\mu_{\rm eff}+E_g$ for $T_h=300$ K and four different N from 3.5 to 5.0×10^{18} cm^{-3}. The best agreement with the experimental results is obtained for $N\sim4.2$–4.5×10^{18} cm^{-3}, again within, but towards the high-density limit allowed by the experimental uncertainty.

Finally, in Fig. 3 we show the calculated evolution of the Γ-valley-electron population and temperature for $N=4\times10^{18}$ cm^{-3}. This explicitly shows the dramatic cooling provided by the intervalley scattering process,[5,8,11] which also results in approximately 60% of the electrons being transferred to the satellite X and L valleys. The degree to which the incorporation of a nonparabolic conduction band affects the results is also illustrated.

Given the inherent uncertainties involved in femtosecond experiments on semiconductors, and given the relative simplicity of the model, care must be taken in extracting quantitative information from a comparison of the data with the model. However, from this work it appears clear that (i) at $N\gtrsim3\times10^{18}$ cm^{-3} injected at 2 eV, rapid intervalley scattering, together with a nearly instantaneous equilibration of the electron population within the Γ valley, cool the Γ-valley electron distribution to <1000 K within 200 fs, and thus lead to gain near the band edge on a subpicosecond time scale, and (ii) the hole distribution appears to be slightly heated to $\sim$800–900 K within 300 fs, but cools rapidly to the lattice temperature within $\lesssim1$ ps. We expect that the proper inclusion of electron-hole, and hole-phonon interactions, together with a more complete treatment of the band structure[24] would improve the model calculation and yield even more reliable estimates of the system parameters.

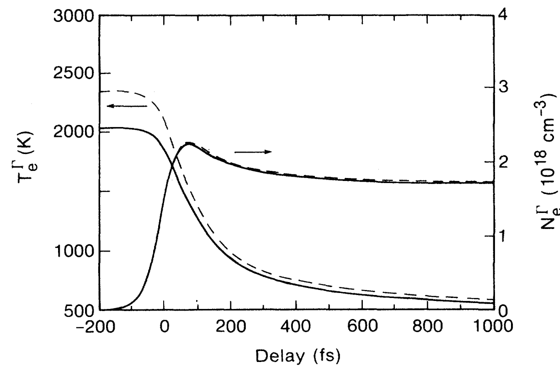

FIG. 3. Calculated time-dependent temperature (T_e^Γ) and population (N_e^Γ) of Γ-valley electrons at $N=4\times10^{18}$ cm^{-3} using a nonparabolic conduction band (solid lines) and a parabolic conduction band (dashed lines).

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[18]This calculation slightly underestimates ΔE_g because the hole temperature is lower than that for the electron, and hole density is larger than that for Γ-valley electrons.
[19]When electrons and holes are not in equilibrium ($T_e\neq T_h$), the condition to obtain gain can be simply derived from $1-f_v<f_c$ where f_v and f_c are Fermi-Dirac distribution functions in the conduction band and valence band, respectively. This leads to Eq. (2) with $\mu_{\rm eff}$ defined as Eq. (3) instead of $\mu_e+\mu_h$ at $T_e=T_h$.
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[24]In this simple model, a non-negligible amount of energy gets transferred to the X and L valleys from the Γ-valley electrons with kinetic energy up to $\sim$1 eV. This indicates that when equilibration is allowed to take place at short time, a better (beyond simple nonparabolic corrections) treatment of the conduction-band structure is required.