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Hot-carrier cooling in GaAs: Quantum wells versus bulk

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Hot-electron cooling dynamics in photoexcited bulk and quantum-well GaAs structures were determined using time-correlated single-photon counting of photoluminescence (PL) decay. Hot-electron cooling curves were generated from analyses of the time-resolved PL spectra. The time constant characterizing the hot-electron energy-loss rate, τ_{avg}, was then determined, taking into account electron degeneracy and the time dependence of the quasi-Fermi-level. This analysis was also applied to earlier data obtained by Pelouch *et al.* with the same samples, but based on PL up-conversion experiments with <80 fs temporal resolution. Both sets of experiments and analyses show that the hot-electron cooling rate can be much slower in GaAs quantum wells compared (at the same photogenerated carrier density) to bulk GaAs when this density is above a critical value. This critical density was found to range from high 10^{17} to low 10^{18} cm^{-3}, depending upon the experimental technique; at the highest carrier densities, values of τ_{avg} for quantum wells were found to be many hundreds of ps.

The cooling of hot carriers following photoexcitation of semiconductor structures with photon energies greater than the semiconductor band gap has been intensively investigated in recent years. Several reviews of this field are available.[1-3]

Despite the publication of many papers on the subject since 1983,[4-24] controversy still exists concerning the important basic question of whether the hot-carrier cooling rate is different for bulk GaAs compared (at the same photogenerated carrier density) to quantum-well structures—i.e., does the cooling rate depend upon dimensionality? One set of research groups[4,5,12,13,18-20] has published work that indicates that at carrier densities above a certain critical value the hot-carrier cooling rate for quantum-well structures is much slower than for bulk material. On the other hand, other workers[1,21-24] have concluded that the cooling rates are independent of quantization.

In this paper, we address this question further with studies on GaAs epilayers and GaAs/Al$_x$Ga$_{1-x}$As quantum wells focusing on high photoexcited carrier densities, where differences in cooling rates become very pronounced. We obtain time-resolved hot photoluminescence (PL) spectra for our samples at 300 K using time-correlated single-photon counting techniques with a time resolution after deconvolution of about 10 ps. Spectra were obtained from about 10 ps out to several ns. In related experiments with these samples reported elsewhere,[20] a luminescence up-conversion technique was used with <80-fs temporal resolution to examine hot-carrier processes at the earliest times (100 fs to 100 ps). We further analyze and discuss the experimental results of both time regimes and address the discrepancies present in the literature.

It is well accepted that a critical parameter affecting hot-carrier cooling for all semiconductor structures is the photogenerated carrier density. In the present and related[20] work, care was taken to compare hot-carrier lifetimes and cooling rates at equivalent carrier densities. These results firmly support the conclusion that the hot-carrier cooling rates in GaAs quantum-well structures are much slower than in bulk GaAs *if the photogenerated carrier density is sufficiently high.* This conclusion is particularly important for applications of quantum-well electrodes in photoelectrochemical cells to promote hot-carrier photoinjection into liquid redox electrolytes.[25-32]

The GaAs/Al$_x$Ga$_{1-x}$As epilayers and quantum-well structures were grown by atmospheric pressure metal-organic chemical-vapor desposition at 725 °C on (100) GaAs substrates. The bulk GaAs samples were double heterojunction (DH) structures that contained capping layers of nondoped Al$_x$Ga$_{1-x}$As ($x=0.48$) on either side of a nondoped 4000-Å GaAs layer. Two multiple-quantum-well (MQW) samples are reported here. MQW sample *A* consisted of 20 periods of 200-Å GaAs wells with 80-Å barriers having an x value of 0.52; MQW sample *B* consisted of 14 periods of 135-Å wells with $L_B=400$ Å and $x=0.48$. The samples were photoexcited with a dye laser operating at 600 nm and a repetition rate of 800 KHz. The laser pulse width was 10 ps; the spectral resolution was 10 Å.

Since the cooling rate for both QW and bulk structures is very sensitive to carrier density,[4-6,18-23] care was taken to ensure that the hot-electron temperatures and cooling rates are compared at equivalent photogenerated carrier densities. We obtained an experimental estimate of the effective average carrier density in a given experiment from an analysis of the line shape of the corresponding PL spectrum. Furthermore, the energy-loss rate for electrons at a given carrier density was calculated as a function of light intensity and time, taking into account the effects of electron degeneracy on the electronic specific heat. From the energy-loss rate, a characteristic time for hot-electron cooling was then determined.

Detailed studies of hot-electron cooling rates were conducted at two light intensities for both bulk GaAs and a GaAs MQW (sample *B*). At the higher light intensity, the electron densities determined from the fit of the PL spectra for both bulk GaAs and the sample *B* MQW were about $(2-4)\times10^{18}$ cm^{-3}; at the lower intensity, the density values were about $(3-5)\times 10^{17}$ cm^{-3}.

An initial comparison between the bulk GaAs DH structure and a GaAs MQW (sample A) is shown in Fig. 1. Here, we show a three-dimensional plot of the PL intensity as a function of time and photon energy for bulk GaAs [Fig. 1(a)] and the MQW sample [Fig. 1(b)] over the time range of 100 ps to 3.2 ns, and the energy range of 1.42–1.77 eV. The pump power for both samples was 25 mW; their average photogenerated carrier densities were similar and in the range of mid-10^{18} cm^{-3}.

It is clear from these plots that the MQW sample [Fig. 1(b)] exhibits much longer-lived hot luminescence (i.e., luminescence above the lowest $n=1$ electron to heavy-hole transition at 1.565 eV) than bulk GaAs [Fig. 1(a)]. Depending upon the emitted photon energy, the hot PL for the MQW is seen to exist beyond times ranging from hundreds to several thousand ps. On the other hand, the hot PL intensity above the band gap (1.514 eV) for bulk GaAs is negligible over most of the plot; it is only seen at the very earliest times and at relatively low photon energies.

Extensive calculations were performed with the PL intensity versus time and energy data to determine the time dependence of the quasi-Fermi-level, electron temperature, electronic specific heat, and ultimately the dependence of the characteristic hot-electron cooling time on electron temperature. These calculations were done as follows. First, the photoluminescence intensity was modeled as the product of the reduced density of states and the Fermi distribution functions for electrons and holes. The transitions were assumed to obey momentum conservation and a constant optical matrix element was used. Band-gap renormalization was included in the model by a rigid shift of the band gap. The hole distribution was assumed to be in equilibrium with the lattice ($T_h=300$ K) due to the much faster cooling rate of holes.[33] For the bulk sample, nonparabolicity of the conduction band was included in the model through the conduction-band density of states. For the MQW PL, distinct quasi-Fermi-levels for the electron and hole populations were used in the calculation, and the luminescence was summed over allowed transitions. Lifetime broadening[34] of the electron states was included to avoid the abrupt turn on of the calculated PL at low energies.

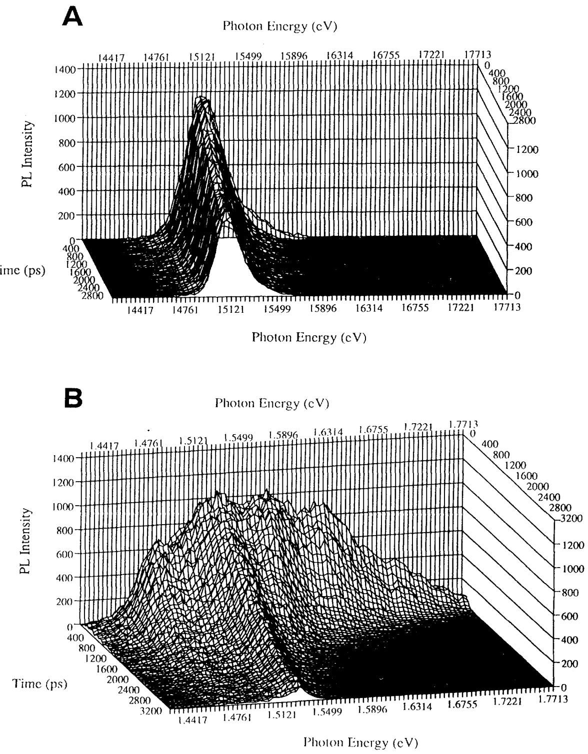

FIG. 1. Three-dimensional plots of PL intensity (in arbitrary units) vs time and photon energy for (a) bulk GaAs and (b) GaAs MQW's (sample A).

The next part of the calculations deals with determining the time constant that characterizes the hot-electron cooling rate of bulk and QW GaAs. The cooling, or energy-loss, rate for hot electrons is determined by LO-phonon emission through electron–LO-phonon interactions. This process can be described by the following expression:[5,35,36]

$$P_e=-\frac{d\bar{E}}{dt}=\frac{\hbar\omega_{\text{LO}}}{\tau_{\text{avg}}}\exp(-\hbar\omega_{\text{LO}}/kT_e)\ , \tag{1}$$

where P_e is the power loss of electrons (i.e., the energy-loss rate), $\hbar\omega_{\text{LO}}$ is the LO-phonon energy (36 meV in GaAs), T_e is the electron temperature, and τ_{avg} is the time constant characterizing the energy-loss rate.

The electron energy-loss rate is related to the electron temperature decay rate through the electronic specific heat. Since in our experiments at high light intensity the electron distribution is degenerate, the classical specific heat is no longer valid. Hence, we calculated the temperature and density-dependent specific heat for both the quantum well and bulk samples as a function of time in each experiment; τ_{avg} could then be determined.

The results of these calculations are presented in Fig. 2, where τ_{avg} is plotted versus electron temperature for bulk and MQW GaAs (sample B) at the high and low carrier densities. These results clearly show that at the high carrier density [$n\sim(2-4)\times 10^{18}$ cm^{-3}], the τ_{avg} values for the MQW are much higher ($\tau_{\text{avg}}=350-550$ ps for T_e between 440 and 400 K) compared to bulk GaAs ($\tau_{\text{avg}}=10-15$ ps over the same T_e interval). On the other hand, at the low carrier density [$n\sim(3-5)\times 10^{17}$ cm^{-3}] the differences between the τ_{avg} values for bulk and MQW

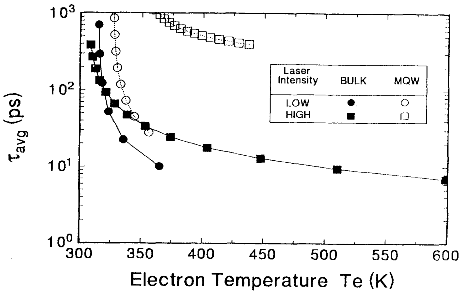

FIG. 2. Time constant for hot-electron cooling (τ_{avg}) vs electron temperature for bulk GaAs and GaAs MQW's (sample B) at the high and low excitation intensities.

GaAs are much smaller. Thus, we see from Fig. 3 that at n values of about $(3-5)\times10^{17}$ cm^{-3}, τ_{avg} values for MQW GaAs range from 30 to 60 ps for T_e between 340 and 365 K, while for bulk GaAs, τ_{avg} ranges from 8 to 15 ps over the same electron temperature interval.

The present experimental results using time-correlated single-photon counting can now be compared with earlier work[20] that used up-conversion techniques to explore the time region of 100 fs to 100 ps; the same bulk and MQW GaAs samples were used in both studies. The time-resolved PL spectra from 100 fs to 100 ps for two bulk GaAs samples (DH structures with 2000- and 4000-Å GaAs epilayers) and a MQW GaAs sample (sample B) at three carrier densities (viz., light intensities) are given in Figs. 1 and 2 of Ref. 20. The three light intensities were 5, 12.5, and 25 mW, and correspond to photogenerated carrier densities of 2×10^{18}, 5×10^{18}, and 10^{19} cm^{-3}, respectively. Following the same analysis described above, τ_{avg} values were determined for these up-conversion experiments and they are plotted versus T_e in Fig. 3.

We again see clearly in Fig. 3 that at high carrier densities the time constant characterizing hot-electron cooling in MQW GaAs is much longer than for bulk GaAs. Thus, for example, at the highest n (10^{19} cm^{-3}), τ_{avg} for the MQW varies from 200 to 500 ps for T_e between 650 and 400 K, while for bulk GaAs, τ_{avg} varies from 2 to 10 ps over the same T_e interval. However, with n at 2×10^{18} cm^{-3}, the τ_{avg} values for bulk and MQW GaAs are quite similar (e.g., 2 ps for bulk GaAs and 4 ps for MQW GaAs at $T_e=500$ K). It is clearly evident from Fig. 3 that above an apparent critical carrier density of $\sim2\times10^{18}$ cm^{-3}, the difference in hot-electron cooling rates between bulk and MQW GaAs becomes dramatically different. Although τ_{avg} for both bulk and MQW GaAs increases with increasing n, τ_{avg} for the MQW increases suddenly and dramatically above 2×10^{18} cm^{-3} to become greater than that for the bulk by up to two orders of magnitude.

It is also apparent in Figs. 2 and 3 that the values of τ_{avg} for both bulk and MQW GaAs increase sharply as the electron temperature approaches the lattice temperature; this occurs below about 350 K. This is because τ_{avg} is essentially a parameter which describes the energy-loss rate of the electron distribution in terms of an effective emission time constant for LO phonons. As the carrier distribution approaches thermal equilibrium with the lattice, its energy-loss rate naturally decreases; the fraction of the electron population having sufficient kinetic energy to efficiently emit LO phonons is diminished. Hence, a large increase in τ_{avg} occurs at lower temperatures for both bulk and MQW samples.

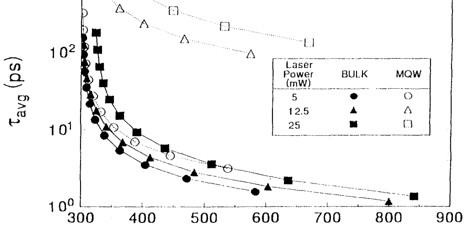

FIG. 3. Time constant for hot-electron cooling (τ_{avg}) vs electron temperature for bulk GaAs and GaAs MQW's (sample B) at three excitation intensities (based on data from Ref. 20).

Both sets of experiments discussed here, covering vastly different time regimes and time-resolved techniques, show that above a critical region of photogenerated density the hot-electron cooling rate for MQW's is dramatically slowed compared to bulk GaAs. We emphasize that the hot-electron cooling rates for MQW's and bulk GaAs both decrease with photogenerated carrier density, but that above a certain density the cooling rate for the MQW's suddenly becomes much slower relative to that for bulk material. The two experiments do yield differences in the absolute value of the critical carrier density. The up-conversion experiments suggest the critical carrier density is about 2×10^{18} cm^{-3}, while the time-correlated single-photon counting PL experiments indicate that the critical density is above $(3-5)\times10^{17}$ cm^{-3} but below $(2-4)\times10^{18}$ cm^{-3}. One possible reason for this discrepancy is that the former experiments, covering much earlier times, reflect higher carrier densities than the latter experiments because nonradiative decay processes may have depleted the original photogenerated carrier population produced at time zero. Other reasons may be related to the differences in the experimental techniques and laboratory calibration factors.

Previous experiments[21–24] that compared the rate of hot-electron cooling in QW and bulk GaAs were conducted at carrier densities estimated to be less than 10^{18} cm^{-3}. Under these conditions these experiments led the authors to conclude that hot-electron cooling rates are independent of dimensionality, being the same for GaAs QW's and bulk GaAs. However, the maximum carrier densities produced in these prior experiments[21–24] were just at or below the critical carrier density which we find is necessary to produce a large decrease in hot-electron cooling rates in QW's compared to bulk GaAs. Thus, the present experiments do not contradict the previous experiments[21–24] in that both sets of experiments agree that at sufficiently low photogenerated carrier density (< mid-10^{17} cm^{-3}) the hot-carrier cooling rates are the same for QW's and bulk GaAs. Rather, we find that the general conclusion of the prior work[1,21–24] that there is no difference in cooling rates between bulk and QW GaAs at *any and all* carrier densities is not valid. As shown above, and in prior work,[4,20] we find that above a critical carrier density region (ranging from mid-10^{17} to low-10^{18} cm^{-3}) a difference in cooling rates does develop and that this difference increases dramatically with increasing carrier density.

In general, theories that treat the dynamics of hot-carrier relaxation in quantum wells and bulk semiconductors invoke nonequilibrium or "hot" phonons to explain slowed cooling with increasing photoexcited carrier densities;[37–41] these theories have not considered the very high carrier density regimes above 10^{18} cm^{-3}. However, a recent treatment of hot-electron cooling in quantum wires[38] does show a very sharp increase in τ_{avg} above about 5×10^{17} cm^{-3} for a 100-Å quantum wire when confined phonon modes are considered. It was further concluded[38] that the hot-phonon-bottleneck effect is the single most important mechanism that produces slowed hot-carrier cooling in these semiconductor structures. It thus appears from our results that at very high photogenerated carrier densities, hot-phonon-bottleneck effects are greatly enhanced in quantum wells compared to bulk GaAs.

Another possible mechanism for slowed hot-electron cooling is the screening of the electron-phonon interaction by the high density of photogenerated electrons. Previously reported work at lower carrier densities discounted the importance of screening.[1,6,21] However, at the higher carrier densities in the present work, screening may play a more important role in reducing the hot-electron cooling rate in the quantum-well samples. Further work is required to establish this possibility.

In conclusion, we have estimated the time constant (τ_{avg}) characterizing hot-electron cooling in bulk GaAs and GaAs QW's as a function of photogenerated carrier density using time-resolved single-photon counting of hot luminescence decay over the time regime of tens of ps to several ns. We have also reanalyzed prior experimental data[20] on hot-carrier cooling in the same GaAs samples, but covering the time regime of 100 fs to 100 ps using luminescence up-conversion techniques. Our results show that below a critical photogenerated density the hot-electron cooling rates for QW's and bulk GaAs are equivalent, while above this critical value the hot-electron cooling rate for QW's become much slower (by one to two orders of magnitude) than in bulk GaAs. This critical density is estimated to be in the range of high-10^{17} to low-10^{18} cm^{-3}. These results are attributed to an enhanced hot-phonon-bottleneck effect in QW's at high photogenerated carrier densities.

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