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Large reduction in hot-carrier energy-loss rates in CdSe caused by nonequilibrium optical phonons

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We obtain hot-carrier cooling rates in CdSe using upconversion luminescence with 2.5-psec time resolution. The carrier energy-loss rates are significantly reduced in comparison with those expected in a simple theory of carrier energy transfer to the lattice. The slow cooling can be explained to be caused by hot-phonon effects provided that the lattice dynamical lifetime of optical phonons in CdSe is about 6 ps at 8 K.

Hot-carrier cooling in III-V semiconductors such as GaAs and $In_xGa_{1-x}As$ and their quantum wells has been investigated extensively in the past.[1] In recent years, questions about electron and hole energy-loss rates (ELR's) in confined dimensions as compared to those in three dimensions have attracted much attention.[2] Various issues related to the importance of many-body effects and nonequilibrium phonons in hot-carrier cooling have been topics of intense research activity.[3] The hot carriers, photoexcited by ultrashort pulses in these polar semiconductors, initially lose energy rapidly by emitting longitudinal-optical (LO) phonons in a few hundreds of fsecs via the dominant Fröhlich coupling. Since the LO phonon lifetime in GaAs is long enough[4] (~7 ps), a nonequilibrium population of LO phonons builds up, leading to their reabsorption by the carriers.[5] In effect, the carrier energy-loss rates slow down considerably, being now determined by the less stronger nonpolar-optical (NPO) and acoustic phonon interactions. It appears that the stronger the Fröhlich coupling, the slower the cooling. Also, the cooling rate is then more sensitive to the excitation density (n_0). Thus, for example, the Fröhlich coupling in $In_xGa_{1-x}As$ is 3 times weaker than in GaAs. The ELR's are smaller by a factor of 10 and 100 in $In_xGa_{1-x}As$ and GaAs, respectively, at $n_0 \sim 10^{18}$ cm^{-3}, than expected in a simple theory.[1] Also, the ELR's are less sensitive to n_0 in $In_xGa_{1-x}As$. In addition to the strength of the Fröhlich mechanism, the finite lifetime of the LO phonons is also an important factor in this. Recent increased interest in the applications of II-VI semiconductors and their quantum wells[6] has made such an investigation of hot-carrier energy relaxation dynamics in these materials of much relevance. The Fröhlich coupling of carriers with LO phonons is stronger in CdSe than in GaAs by a factor of 3. On the other hand, the NPO interaction for holes in CdSe is nearly the same as in GaAs. It is therefore expected that the hot-carrier cooling rates are even slower in CdSe, provided that the optical phonon lifetime (τ_{LO}) in CdSe is not much smaller than in GaAs. However, there is no definitive study performed so far as to determine the hot-carrier cooling rate in II-VI materials such as CdSe and no reliable information is available on τ_{LO} in these materials. There have been only a few efforts in the past[7–9] to study hot-carrier cooling in CdS and CdSe. These studies, however, were performed either under the conditions of a large laser pulse width[7,8] (~20–30 ps) or at a very high excitation density[9] (~10^{19} cm^{-3}). In spite of these studies, detailed information on energy relaxation rates in wurtzite II-VI semiconductors, similar to that in III-V semiconductors, is still not available.

In this paper, we present some of the first results on hot-carrier ELR's in CdSe obtained using up-conversion luminescence spectroscopy with a 2.5-ps time resolution. We measure the hot-carrier cooling characteristics and obtain the related energy relaxation rates in CdSe at various carrier excitation densities ($n_0 = 2\times$, $4\times$, and 8×10^{17} cm^{-3}). The cooling rates are found to be very sensitive to change in n_0. We compare these results with theoretical calculations performed with and without the effects of hot-phonon dynamics. While the theory without the hot-phonon effects gives cooling rates much faster than the experimental rates (by about two orders of magnitude), a satisfactory explanation of the data is obtained in the framework of a hot-phonon theory, which leads to a prediction of the lattice dynamical optical phonon lifetime in CdSe (at 8 K) of 6–9 ps, depending upon n_0. We also find that as the carriers cool, the carrier energy loss is in effect dominated by optical phonon emission by holes via the NPO deformation potential interaction, and not by LO emission due to the Fröhlich mechanism.

Our results are obtained by exciting CdSe crystals, maintained at 8 K, with 1.8-ps wide pulses from a Nd-YAG pumped Rhodamine-6G dye laser at a repetition rate of 76 MHz. The photon energy is 2.03 eV. The beam polarization is perpendicular to the c axis of CdSe, causing excitations from both the Γ_9 (A) and Γ_7 (B) valence bands into the Γ_7 conduction band. The up-converted luminescence is measured with an energy resolution of about 2.5 meV and a time resolution of 2.5 ps. The signal is detected in a standard photon counting set up with a cooled GaAs photomultiplier tube. The carrier densities at injection are estimated by taking a sample reflectivity of 0.2 and an absorption depth of 0.2 μm,[10] with the laser beam focused on the sample to a spot of about 50 μm in size. (A possible error in the spot size by 5 μm will change the density estimate by 20%.)

For the moderately large carrier densities used in our experiments, the carrier-carrier interactions are expected to be

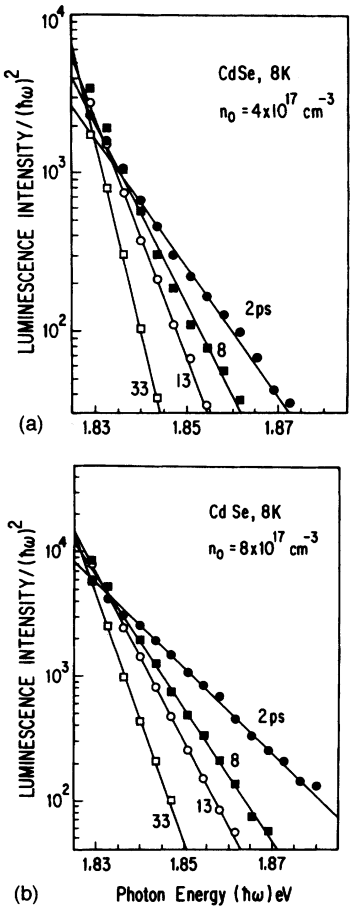

FIG. 1. The $(\hbar\omega)^2\exp(-\hbar\omega/kT_c)$ behavior of the time-resolved luminescence distribution in photon energy $\hbar\omega$ is illustrated for $n_0=4\times10^{17}$ cm^{-3} and $n_0=8\times10^{17}$ cm^{-3} for some of the delay values.

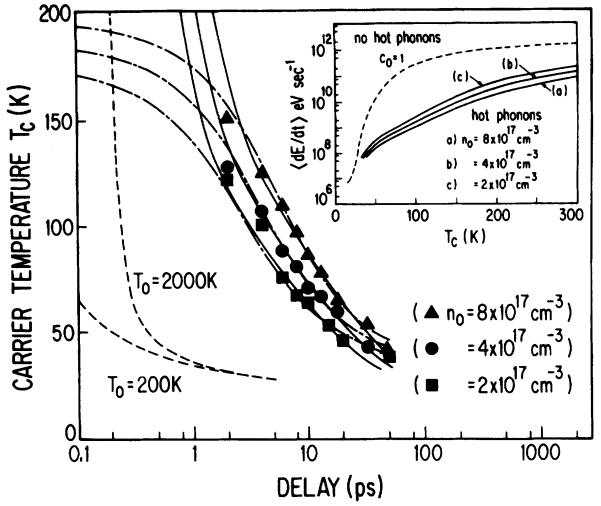

FIG. 2. The time evolution of T_c obtained experimentally is shown for three different carrier excitation densities (discrete points). Cooling rates calculated for $C_0 = 1$ with no hot phonons (dashed curve) are shown for $T_0 = 200$ K (a) and $T_0 = 2000$ K (b). Also shown (dashed-dotted curves) are the same calculations but with reduced C_0 fitting the data (T_0=175, 185, and 195 K for n_0=2×, 4×, and 8×10^{17} cm^{-3}, respectively). Calculations including hot-phonon effects (solid curves) are also seen to fit the data well with $T_0 = 1850$, 1900, and 2000 K for n_0=2×, 4×, and 8×10^{17} cm^{-3}, respectively. The inset shows the corresponding ELR's in the no hot-phonon ($C_0 = 1$) and hot-phonon cases.

fast enough for the carriers to thermalize among themselves and form Fermi energy distributions at a temperature T_c (greater than lattice temperature) as they are generated. The luminescence spectrum due to spontaneous recombination of electrons and holes in the high energy tails of their distributions is expected to have an approximate $(\hbar\omega)^2\exp(-\hbar\omega/kT_c)$ behavior in the photon energy $\hbar\omega$. This is confirmed by our measurements, as illustrated in Fig. 1, which shows the luminescence intensity against the photon energy in a semilogarithmic plot. The carrier temperatures thus obtained are shown in Fig. 2 as a function of various delays following photoexcitation at $t=0$ ps for three carrier excitation densities. The carrier excitation density n_0 appears to have a noticeable influence on the cooling behavior, the ELR's decreasing as n_0 increases. This is similar to the results obtained for GaAs but is in contrast to the insensitivity of the cooling rates to change in n_0 observed in $In_xGa_{1-x}As$ for comparable n_0 values.[1] In CdSe the most dominant energy-loss mechanism is expected to be the LO phonon emission by electrons and holes via the Fröhlich interaction.[11] The hot-carrier ELR may therefore be approximated[12] by $(-\hbar\omega_{LO}/\tau)\exp(-\hbar\omega_{LO}/kT_c)$, where τ is the LO phonon emission time and $\hbar\omega_{LO}$ is the LO phonon energy. This simple picture of cooling, however, leads to an unexpectedly large estimate of 0.44, 0.7, and 1 ps for τ using the data of Fig. 2 for n_0=2×, 4×, and 8×10^{17} cm^{-3}, respectively. A similar conclusion was reached by Masumoto and Sasaki[9] who deduced a value of 1.5 ps for τ at $n_0\sim10^{19}$ cm^{-3} using their excite-probe transmission measurements. This may be compared with the expected time of 40 fs (16 fs) for LO phonon emission by an electron (a hole in the A band) with an energy of $2\hbar\omega_{LO}$ in CdSe based on the bare Fröhlich interaction.[12]

To understand the above experimental results, we consider the physics of carrier energy relaxation in more detail. We take into account contributions of both electrons and holes to the ELR. We assume that the electrons and holes have Fermi energy distributions with a common effective temperature T_c. For the conditions of our experiments, hole occupancies in both the A and B valence bands should be considered. In CdSe, the A and B valence band edges are separated by an energy $\Delta = 25.3$ meV.[13] The average energy per e-h pair can be written as $\langle E\rangle = 3kT_c\times[\gamma_e(T_c) + \gamma_h(T_c)]/2$, where $\gamma_e(T_c)=F_{3/2}(\eta_e)/F_{1/2}(\eta_e)$, $\gamma_h(T_c) = [F_{3/2}(\eta_h)+F_{3/2}(\eta_h-\delta)]/[F_{1/2}(\eta_h)+F_{1/2}(\eta_h-\delta)]$, $\eta_i = \epsilon_{F_i}/kT_c$, $i=e,h$, the Fermi energy ϵ_{F_i} is measured from the conduction band (A valence band) edge for $i=e$ ($i=h$), F's are the Fermi integrals, and $\delta=\Delta/kT_c$. (For nondegenerate distributions with $\eta\ll0$, $\langle E\rangle$ is simply $3kT_c$.) We can now relate the cooling rate dT_c/dt to $[d\langle E\rangle/dt]_{cool}$, the rate of change in $\langle E\rangle$ due to cooling using $[d\langle E\rangle/dt]_{cool} = [d\langle E\rangle/dT_c]\times dT_c/dt$. Also, we expect $[d\langle E\rangle/dt]_{cool} = C_0[\langle dE/dt\rangle]_{ph}$, with $C_0=1$, $[\langle dE/dt\rangle]_{ph}$ being the average ELR per e-h pair due to phonon interactions. As a simplification, we assume that the carriers are thermalized with

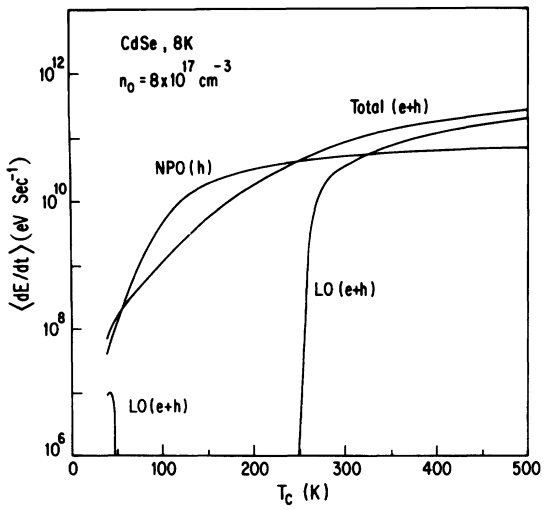

FIG. 3. The dominant contribution to the total ELR is shown for the case $n_0 = 8 \times 10^{17}$ cm^{-3}. Note that the ELR due to LO phonon emission decreases below $T_c \approx$ 350 K (and even becomes negative, feeding energy back to carriers). The effective ELR is then mainly due to NPO interaction of holes.

$T_c = T_0$ at generation at $t = 0$ ps. In our calculations of $[\langle dE/dt \rangle]_{\rm ph}$ we include all the relevant electron and hole energy-loss mechanisms, i.e., phonon interaction via the unscreened Fröhlich, nonpolar optical and acoustic deformation potential, and piezoelectric interactions.[12,14] Possible occupancy of both A and B valence bands is included in calculating the hole Fermi energy. Also the intraband and interband transitions in both the hole bands are taken into account. The basic expressions for $[\langle dE/dt \rangle]_{\rm ph}$ are well known in the literature[12,14] and are not reproduced here. A phenomenological factor of 0.5 is used to account for the reduced hole scattering due to the p-like valence band states.[15] The various parameters for CdSe used in these calculations[16] using the standard symbols of Ref. 12 are $\hbar\omega_{\rm LO} = 26.5$ meV, $\hbar\omega_{\rm TO} = 21.1$ meV, $\epsilon_\infty = 6.25$, $\epsilon_0 = 9.75$, $D_{\rm NPO} = 10 \times 10^8$ eV cm^{-1} (for holes only), $e_{\rm pe}^2 = 0.0144$ C^2 m^{-4} (for LA) and $= 0.0189$ C^2 m^{-4} (for TA), $E_1(dp) = 2.2$ eV (for holes) and 4.2 eV (for electrons), and $m_h^* = 0.8 m_0$, $m_e^* = 0.13 m_0$.

The expressions for the carrier optical phonon scattering rates have terms due to both spontaneous phonon emission and stimulated phonon emission and absorption. We first consider the case in which the stimulated transitions involving the nonequilibrium optical phonons emitted by the carriers are ignored ("no hot phonons"). The carrier temperature T_c is now obtained by integrating $C_0 \times [\langle dE/dt \rangle]_{\rm ph} \times [d\langle E \rangle / dT_c]^{-1}$. Results of these calculations of the cooling behavior for $C_0 = 1$ are shown in Fig. 2 for the assumed $T_0 = 200$ K and 2000 K as an illustration. It is clearly seen that the measured cooling rates are much slower. On the other hand, the theory satisfies the data if the theoretical ELR is reduced by a significantly large factor of 85, 130, and 190 by assuming appropriately reduced values for C_0 for $n_0 = 2\times$, $4\times$, and 8×10^{17} cm^{-3}, respectively, as shown by the dashed-dotted curves in Fig. 2. This may be compared with a corresponding factor[1] of ~ 100 for GaAs and ~ 10 for $In_xGa_{1-x}As$ for $n_0 \sim 10^{18}$ cm^{-3}. The initial temperatures T_0 required for a satisfactory fit to the data are 175, 185, and 195 K, respectively. This small variation in T_0 with n_0 is presumably a result of our ignoring the carrier dynamics during excitation, and screening of the polar interactions by the e-h plasma.

As a possible origin of the considerably reduced carrier cooling rates noted above, we next consider the so-called hot-phonon effects. Here, the amplification of nonequilibrium optical phonons via both the Fröhlich and NPO couplings leads to significant phonon reabsorption by the hot carriers if the lattice dynamical LO and transverse optical (TO) phonon lifetimes ($\tau_{\rm LO}, \tau_{\rm TO}$) are large enough.[5] This effectively delays the energy transfer to the lattice due to optical phonon emission. The carrier cooling rates therefore reduce. One may expect that dynamic screening of the polar interactions due to the carriers would also be important for slowing down the cooling. However, detailed investigations in the past for GaAs have established that screening is only of secondary importance.[5] We therefore do not include this in our calculations. Also, the computation is simplified by replacing the two valence bands by one effective band (A) for ELR calculations but accounting for the two bands in the hole Fermi level determination as in Ref. 8. We once again obtain the cooling behavior using all the phonon interactions considered earlier, this time also including the stimulated optical phonon emission and reabsorption. For this, we solve the coupled time-dependent equations for T_c and the LO and TO phonon occupancies, taking $\tau_{\rm LO} (= \tau_{\rm TO})$ as a parameter. It is seen in Fig. 2 that the results of such a calculation agree with the experiments if the values of 6, 7.5, and 9 ps are chosen for the lattice dynamical optical phonon lifetime ($\tau_{\rm LO}$) for $n_0 = 2\times$, $4\times$, and 8×10^{17} cm^{-3}, respectively. This may be compared with $\tau_{\rm LO} = 7$ ps for GaAs determined using Raman measurements.[4] A direct measurement of this lifetime in CdSe is yet to be performed. A value of about 1 ps at 300 K was deduced previously[17] from a fit to the dielectric function obtained in Ref. 18 using infrared reflectivity measurements on CdSe.

Understanding the weak dependence of $\tau_{\rm LO}$ on n_0 obtained above requires further investigation. This may be related to the effects of acoustic phonon bottleneck,[17] screening, phonon renormalization,[19] etc. In addition to these effects, not considered here, an improved calculation should also include band gap renormalization and plasma expansion and recombination. For the dashed-dotted curves of Fig. 2 fitting the data in the case of "no hot phonons," reduced ELR's are used for all times. On the other hand, the ELR's in the hot-phonon case do not attain the required reduced values until the optical phonon occupancies fully build up. This results in larger cooling rates initially. Much larger values of T_0 are therefore needed in this case than in the case of no hot phonons for a satisfactory fit (see Fig. 2). When phonon interactions of hot holes in the B valence band are also included, we obtain an even larger initial ELR (by about 70%). However, this also leads to a quicker generation of hot phonons. These two have opposite effects. We find that this, together with static screening of the Fröhlich interaction, in effect leads to a larger T_0 (by 12%), but does not change our final results on $\tau_{\rm LO}$ significantly.

The inset in Fig. 2 shows the total ELR's obtained in both the no hot-phonon ($C_0 = 1$) and hot-phonon cases corre-

sponding to the dashed and solid curves of Fig. 2. Figure 3 shows the main contributions to the total ELR calculated in the hot-phonon case. It is seen that as the carriers cool to $T_c < 350$ K the primary mode of energy loss by the hot carriers to the lattice is TO phonon emission by holes via the NPO interaction, and not LO phonon emission via the Fröhlich mechanism. This is so because the LO phonon emission by electrons and holes is suppressed due to the hot-phonon effects much more than the TO phonon emission. A similar conclusion was reached in the case of GaAs previously.[5]

In summary, we have reported a definitive study of hot-carrier cooling rates in CdSe using picosecond up-conversion luminescence spectroscopy: The rates are significantly less than expected in a simple theory. This is due to the hot-phonon effects provided that the lattice dynamical lifetime τ_{LO} of optical phonons is 6–9 ps, depending upon the excited carrier density n_0. It would be interesting to have a direct experimental determination of τ_{LO} in CdSe.

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