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Ultrafast carrier recombination and plasma expansion via stimulated emission in II-VI semiconductors

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Time-resolved beam deflection and four-wave mixing techniques have been used to investigate the spatial and temporal evolution of degenerate electron-hole plasmas in CdS, $CdS_{0.75}Se_{0.25}$, and ZnSe following two-photon absorption of 120 fs, 620 nm pulses at temperatures between 80 and 295 K. The decay times for carrier densities larger than 10^{19} cm^{-3} are found to be less than 10 ps, and are independent of the local density gradient. We suggest that stimulated emission recombination and reabsorption occur until the entire plasma becomes nondegenerate. This fast carrier transfer process may account for other reports in the literature of rapid expansion in degenerate ambipolar plasmas.

Although many microscopic processes which govern the evolution of spatially homogeneous, low density carriers in semiconductors following ultrashort pulse excitation are reasonably well understood,[1] the evolution, particularly the spatial evolution, of high density (degenerate) spatially inhomogeneous carrier distributions is less clear.[2-6] Ambipolar diffusion coefficients as large[2] as 10^6 $cm^2\,s^{-1}$ have been used to explain observations of rapid plasma expansion, particularly in II-VI semiconductors. Such high diffusion rates have been discussed in terms of screened carrier-phonon or carrier-impurity scattering[4,6] or attributed to Fermi pressure in degenerate plasmas.[7] Here we report the use of beam deflection and four-wave mixing techniques to monitor the decay of carrier density gradients of degenerate plasmas in the II-VI semiconductors CdS, $CdS_{0.75}Se_{0.25}$, and ZnSe. The decay times for high density plasmas are found to be less than 10 ps, and are found to be independent of the magnitude of the local plasma density gradient (i.e., the decay is not governed by a simple diffusion process). We attribute this to an ultrafast "explosion" of the plasma through stimulated emission recombination of carriers followed by reabsorption of the emitted radiation in regions of lower density. This process can lead to an ultrafast spatial redistribution of carriers on a picosecond time scale and may account for some of the reports in the literature of the rapid expansion of degenerate plasmas.

The concept of radiative transfer through *spontaneous emission* is well known in applications ranging from the transport of radiation in stellar atmospheres[8] to charge transport in semiconductors.[9,10] In the latter case Dumke[9] concluded that for low density plasmas the effective diffusion coefficient is small compared to that of conventional diffusion, although others[10] have suggested that for densities approaching 10^{18} cm^{-3} the two may become comparable. Here we show that the stimulated emission in the plane of the sample can accelerate the charge-transfer process. Stimulated emission has, of course, been considered in the context of rapid recombination of carriers in semiconductors[11,12] and in semiconductor lasers,[13,14] but we are not aware of any work in which reabsorption has also been considered leading to a rapid plasma expansion.

Recently we reported[15] time-resolved measurements of the deflection of a probe beam in 100-μm-thick single crystals of CdS, $CdS_{0.75}Se_{0.25}$ (band gaps of 2.42 and 2.125 eV, respectively, at 295 K) following two-photon absorption (2PA) of 620 nm (2 eV) 120 fs pulses. The probe beam was focused to a <15 μm spot size with its center located close to the e^{-2} radius (40 ± 15 μm) of the pump beam. Figure 1 shows the time-resolved deflection in $CdS_{0.75}Se_{0.25}$ for five discrete excitation levels (the excitation levels are described by I_{loc}, the temporal peak irradiance of the pump pulse evaluated at the location of the probe pulse). The beam deflection is consistent[15] with a band filling refractive index change and hence is proportional to the *radial* gradient in the local carrier density. The increasing deflection in the first 2 ps is consistent with cooling of the initially hot photoexcited carriers to the band edge.[16] For I_{loc} above a threshold value of 25 $GW\,cm^{-2}$ (for which the peak irradiance at the center of the pump spot is 185 $GW\,cm^{-2}$) there is a fast recovery of the deflection which might be interpreted in terms of carrier recombination and/or a reduction in the density gradient. Similar behavior was observed in CdS. Because the density gradients were small we argued that the signal

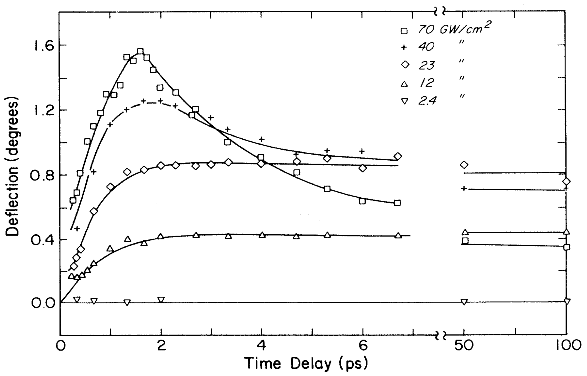

FIG. 1. Time-resolved deflection of a probe beam in $CdS_{0.75}Se_{0.25}$. The pump irradiances are evaluated at the location of the probe pulse and correspond to the (temporal) peak values.

decays could not be explained by conventional ambipolar diffusion (diffusion coefficients greater than 5×10^5 $cm^2 s^{-1}$ would be required to explain the picosecond decay time; the low density value of the diffusion coefficient has been measured to be[17] 5 $cm^2 s^{-1}$). It was also argued, however, that rapid recombination with a rate related to the *local* electron-hole density (e.g., through Auger processes, spontaneous radiative recombination, plasmon-assisted recombination) could not provide an explanation since the time-dependent deflection curves corresponding to values of I_{loc} greater than the threshold irradiance *cross* curves corresponding to smaller values of I_{loc}. It was considered more likely that processes with threshold characteristics such as stimulated emission or recombination via photoexcited metastable defects might account for the behavior.

The dependence of the threshold value of I_{loc} on the position of the probe spot has now been investigated. As the probe spot approaches the center of the pump spot the threshold value of I_{loc} increases. For example, from the data discussed above the local threshold is $I_{loc}=25$ GW cm^{-2} for the probe spot at the e^{-2} radius of the pump beam (corresponding irradiance at the center of the spot equal to 185 GW cm^{-2}). If the probe spot is at approximately $\frac{1}{3}$ of the e^{-2} radius of the pump beam a local threshold $I_{loc}=110$ GW cm^{-2} (irradiance at center of pump spot is 140 GW cm^{-2}) is measured, and for the probe located at the center of the pump spot (in this case the "deflection" consists of a defocusing of the transmitted probe light) the threshold is $I_{loc}=120$ GW cm^{-2}. These results suggested that a *nonlocal* mechanism such as stimulated emission recombination should be responsible for the rapid decays.

To investigate possible decay mechanisms for steeper density gradients we have performed four-wave mixing experiments with the samples at temperatures between 295 and 80 K. Here the pump pulse was divided to produce two equal irradiance pulses which were focused onto the sample (60±15 μm spot size) to write a density grating. A time-delayed probe pulse was focused (spot size less than 15 μm) onto the *center* of the induced grating structure, and the diffracted probe light was detected by either a fast photodiode or photomultiplier. Gratings with periods between 1.2 and 2.9 μm were investigated.

Figure 2 shows the time-dependent diffracted probe beam intensity for $CdS_{0.75}Se_{0.25}$ (100 μm thick) at 295 K for a 1.2 μm grating period and for several discrete pump excitation levels (the excitation levels are described by I_0, the temporal peak irradiance evaluated at the maxima in the grating structure). A rapid recovery similar to that observed in the beam deflection experiments occurs for $I_0>200$ GW cm^{-2}, and the curve-crossing effect is also observed. Similar behavior has been observed in CdS (100 μm thick) and ZnSe (20 μm thick) with nearly identical irradiance thresholds but with decay times in the thin ZnSe sample as small as 4 ps. As the lattice temperature is decreased both the recovery time and the critical irradiance for the onset of rapid recoveries decrease. At 80 K, for example, the shortest decay time is two times smaller than at 295 K, and the critical value of I_0 is 2.5 times lower. Despite the large difference in carrier density gradients, the decay times measured using the grating technique are of the same order of magnitude as those measured using the deflection technique. Also, Fig. 3 shows the time-resolved diffraction signals for grating spacings of 1.2, 2.0, and 2.9 μm for an above threshold value of I_0; the decay times are virtually identical to within experimental uncertainty. That the decay times are independent of the carrier density gradients suggests that conventional diffusion does not play an important role in the ultrafast recovery.

The data are consistent with a recovery process due to stimulated emission. The threshold irradiances for the room-temperature deflection and diffraction experiments correspond to *peak* (i.e., at the center of the excitation spot) surface carrier densities in excess of 10^{19} cm^{-3} [2PA coefficient[15] is equal to 9 (7,6) cm GW^{-1} in $CdS_{0.75}Se_{0.25}$ (CdS, ZnSe)]. These densities are more than a factor of 2 above the threshold densities for optical gain for band-edge radiation [the gain threshold density, calculated within an effective mass approximation using a k-conserving model for the gain coefficient is equal to $5(6,4)\times10^{18}$ cm^{-3} for $CdS_{0.75}Se_{0.25}$ (CdS,ZnSe) at room temperature]. Also, the gain threshold density at 80 K is roughly $\frac{1}{7}$ of the room-temperature value, consistent with the factor of 2.5 decrease in the threshold value of I_0 at

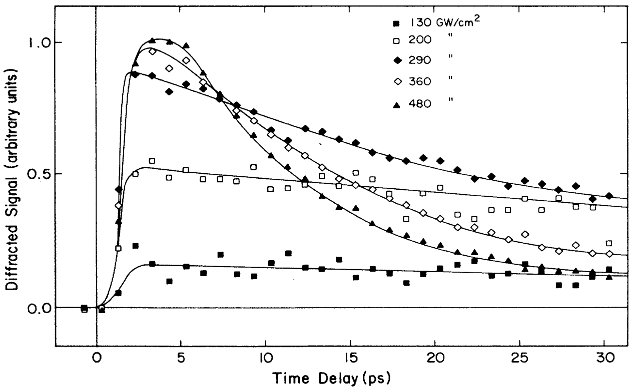

FIG. 2. Time-resolved diffraction efficiency for a grating written by a pair of identical pump pulses in $CdS_{0.75}Se_{0.25}$ at 295 K. The pump irradiances are evaluated at the grating maxima and correspond to the (temporal) peak values.

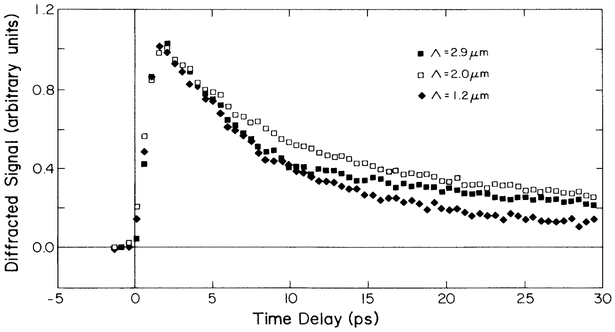

FIG. 3. Time-resolved diffraction signals from three different period gratings in $CdS_{0.75}Se_{0.25}$ at 295 K. The peak pump irradiance at the grating maxima is ~380 GW cm^{-2}.

80 K. Evidence for stimulated emission was indirectly verified by measuring the time integrated band-edge luminescence from the front surface of CdS at 295 K as a function of excitation irradiance (single beam excitation). The yield is observed to very supralinearly with irradiance up to 110 GW cm^{-2} (corresponding to a surface carrier density of 1.1×10^{19}) consistent with spontaneous emission following two photon absorption, but thereafter varies sublinearly consistent with stimulated emission occurring in the transverse direction. This is reasonable since the lateral extents of the regions which display gain are predicted to be between four and six times larger than their depths.

Although the *peak* carrier density for the onset of rapid decays is well correlated with the gain threshold density, the *local* carrier density at the location of the probe in the deflection experiments may be much lower than that required for gain. For example, the onset of a rapid decay in Fig. 1 occurs for a *peak* carrier density of the order of 2.8×10^{19} cm^{-3} while the density at the location of the probe is of the order of 5×10^{17} cm^{-3} (an order of magnitude below that necessary to produce gain). In order to explain the observation of decays here, it is necessary to consider the redistribution of carriers produced by the reabsorption of light produced by stimulated emission near the center of the excitation spot. Since the volume has its greatest extent in the radial direction (at the threshold in Fig. 1 the gain region has a diameter equal to 52 μm while the depth extends to 14 μm), stimulated emission and reabsorption occur preferentially in planes parallel to the surface. This will continue until the carrier distribution is everywhere nondegenerate after which processes such as spontaneous emission and conventional diffusion govern the kinetics. Figure 4 depicts what the initial and "final" carrier distributions should look like. In the final state carriers in the volume where emission and reabsorption have occurred will have a density near the gain threshold value. For the data in Fig. 1 the radial extent of this volume is calculated to be slightly larger than 40 μm and hence extends beyond the position of the probe spot. Since the carrier distribution sampled by the probe beam in this near-surface region is radially uniform, the near-surface contribution to beam deflection vanishes. The total deflection does not completely vanish since the gain region does not extend to the back surface of the sample (i.e., radial carrier redistribution does not occur at all depths). With increased excitation strength the depth of the uniform density region increases, leading to the curve-crossing effect whereby the "final" deflection values lie below those achieved for lower excitation strengths.

The final state monitored by the diffraction experiments can be considered in a similar fashion. Here, however, the gain volume consists of long, submicrometer wide ribbons. Stimulated emission will occur preferentially along these ribbons transferring carriers away from the location of the probe spot which explains why no change in the decay behavior is observed as the grating period is changed. The refractive index grating will decrease to a uniform value in the near-surface region and remain unchanged for depths beyond the extent of the original gain volume. Calculations of the diffraction efficiency have been performed by integrating the coupled equations for the propagation of scattered light in a thick grating[18] (the sample thickness and gain volume depth are both much greater than the inverse of the mismatch between the wave vectors of the scattered and unscattered beams). The results indicate that the diffraction efficiency should fall rapidly to near zero for values of I_0 in the vicinity of the threshold in agreement with the experimental results. It should also be noted that the higher irradiance thresholds observed for the diffraction experiments are consistent with this interpretation since stimulated emission here is essentially one dimensional whereas in the deflection geometry it is two dimensional.

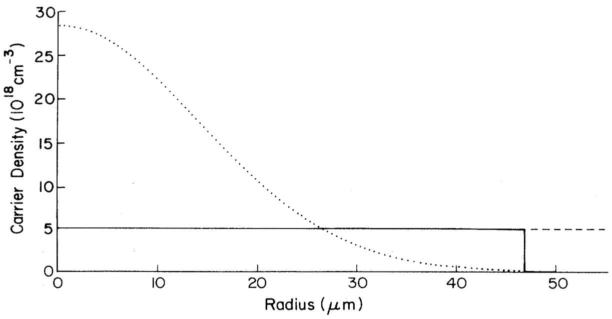

FIG. 4. A schematic diagram of the initial and "final" radial carrier distributions following the carrier transfer process. The dotted line corresponds to the density threshold for optical gain. The integrated carrier densities (weighted by the radius) under the two curves to a radius 48 μm are the same.

We now consider details related to the temporal behavior of the problem. The self-consistent temporal evolution of stimulated emission radiation and *spatially homogeneous* carrier distributions in semiconductor lasers has been considered theoretically[14] and is generally considered to be a formidable problem because of the delicate balance between a number of microscopic processes which allow gain to exist. For the *inhomogeneous* distributions considered here the problem is even more difficult since the radiation field varies both with position and direction. After the excitation pulse the carriers have a temperature of the order of 10^4 K and stimulated emission cannot occur until a degenerate distribution is created by carrier cooling. For CdS, $\mathrm{CdS_{0.75}Se_{0.25}}$, and ZnSe the cooling times[16] are of the order of 2 ps consistent with the 2 ps delay in the appearance of signal recoveries. If no stimulated emission were to take place until the carriers had fully cooled then gains in excess of 3×10^4 cm^{-1} would result and gain depletion would occur on a subpicosecond time scale. However, the processes of carrier cooling and gain depletion are tightly coupled so that the temporal dependence of the gain is determined by a balance between continued carrier cooling (which increases the gain), stimulated emission (which reduces the gain) and carrier heating via free carrier absorption and from recombination of near-band-edge carriers (which decreases the gain). In addition, the size and shape of the gain region evolve with reabsorption-induced carrier generation at a rate which depends on the frequency of the absorbed light and on the location of the quasi-Fermi levels. The theoretical simulation of this problem would be computationally intensive, and would also require the use of models for the processes just outlined for which the number of free parameters would make fits to the data of questionable relevance. However, we point out that the 4–20 ps decay times measured here are of the same order of magnitude as those which have been predicted for homogeneous[11] and inhomogeneous[12] plasmas.

In conclusion we have presented results which indicate that the relaxation of a degenerate electron-hole plasma is accompanied by a rapid expansion of the plasma in directions parallel to the sample surface. We stress that the process of carrier transfer cannot be considered within the framework of conventional ambipolar diffusion since the strength of the induced currents is not proportional to the local gradient in carrier density (i.e., the problem is considerably more nonlocal in nature). However, the results are consistent with a photon-assisted carrier transfer process in which carrier recombination and light generation are produced by stimulated emission in the degenerate plasma followed by reabsorption of the light in the nondegenerate wings of the plasma. This interpretation explains the main features of both the beam deflection and induced diffraction experiments and may contribute to the understanding of other experimental studies whose interpretation is based on enhanced diffusion processes.

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