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Kinetics of free-exciton luminescence in GaAs

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Exciton-polariton photoluminescence kinetics under short-pulse excitation in nominally undoped GaAs has been investigated. A delayed onset revealing the energy relaxation of electrons and polaritons has been observed. In an ultrapure sample ($N_D \sim 10^{12}$ cm^{-3}) the maximum luminescence is reached after a considerable delay of 4 ns. Energy relaxation speeds up with an increase in impurity concentration and depends on the type of conductivity. At a high repetition rate, the next excitation pulse causes fast quenching of polariton luminescence in the vicinity of exciton resonance because of heating of excitons by photoexcited hot electrons.

At low temperatures excitons constitute the final state in energy relaxation of the photoexcited crystal. In GaAs the main channel of exciton formation after excitation above the energy gap E_g is binding of thermalized electrons and holes.[1] Various processes are involved in exciton kinetics: energy relaxation of the photoexcited charge carriers, electron-hole binding, energy relaxation and trapping of free excitons, spatial diffusion, etc., and also polariton effects.[2,3] A direct way to determine the contribution of the mentioned processes is to study the time behavior of free-exciton luminescence at different luminescence energies after pulse excitation at variable photon energy. In previous papers devoted to free-exciton luminescence kinetics in GaAs most attention was paid to the luminescence decay[4] and time-resolved spectra.[2] We have focused on the luminescence onset as in Ref. 5; however, better spectral resolution and variation of the excitation energy were obtained and ultrahigh-purity samples were used.

Luminescence was excited by a synchronously pumped mode-locked Styryl-9 dye laser. Optical pulse duration was $\Delta t_p = 5$ ps, and cavity dumping rates $f = 82$ and 4.1 MHz were used. The average excitation power density $I_{av} \sim 1$ W/cm^2. Photoluminescence was measured at $T = 1.7$ K by a time-correlated photon-counting system with a time resolution of 300 ps (FWHM). The spectral linewidth of excitation (~ 0.7 meV) and spectral resolution (~ 0.1 meV) permitted tunable excitation and luminescence energies. The samples were pure epitaxial layers grown by vapor phase epitaxy in a chloride system with various residual impurity concentration and conductivity types. In the purest sample G13 (Refs. 6 and 7) shallow-donor concentration was estimated to be $\sim 10^{12}$ cm^{-3},[6] whereas reference samples with $N_D \approx 10^{14}$ cm^{-3} and $N_A \approx 10^{14}$ cm^{-3} were also measured. A characteristic of the low-temperature photoluminescence spectrum of the ultrapure sample obtained under cw excitation is a distinct exciton-polariton line, with an intensity comparable to the bound-exciton lines usually dominant in the spectrum.[7]

Time-integrated luminescence spectra and the corresponding luminescence time behavior of different samples are depicted in Fig. 1. The latter were measured at energies denoted by arrows 1,2 and correspond to the emission from lower and upper polariton branches. In all samples a slowing of the onset with decreasing polariton luminescence energy is observed. The dependence of the delay time of the pulse maximum Δt_{max} on the luminescence en-

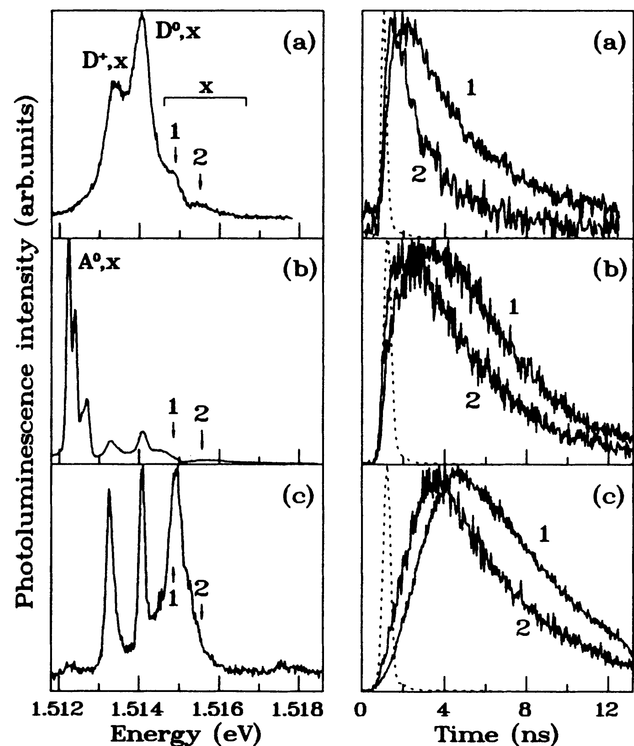

FIG. 1. Time-integrated photoluminescence spectra (on the left) and corresponding time behavior (on the right) of different GaAs samples. (a) n^0-GaAs, $N_D \sim 10^{14}$ cm^{-3}. (b) Y1, p^0-GaAs, $N_A \sim 10^{14}$ cm^{-3}. (c) Sample G13, $N_D \sim 10^{12}$ cm^{-3}. The dashed line represents the excitation pulse. Excitation energy is 1.554 eV. Traces 1 and 2 correspond to the luminescence energies denoted by arrows on the spectra.

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ergy of sample G13 is shown in Fig. 2(a). This dependence reveals the effect of a polariton bottleneck due to a reduced energy relaxation rate in the vicinity of the exciton resonance.[8] Unlike the results concerning the polariton bottleneck in CdS,[9-11] the decay time here weakly depends on the luminescence energy. In ultrapure sample G13 this decay time reaches the value of 4–5 ns. It is worth noting that this value exceeds the radiative exciton lifetime in GaAs obtained by 't Hooft *et al.*[4] A weak dependence of the luminescence onset on the exciton luminescence energy in GaAs was observed by Steiner *et al.*[2] and attributed to energy-dependent diffusion of polaritons from the bulk to the surface. To determine the contribution of the polariton diffusion to the observed delayed onset of the polariton luminescence we measured the temporal evolution of the exciton luminescence accompanied with LO-phonon emission. Because of the small absorption coefficient and high group velocity, spatial distribution of polaritons should not affect the time behavior of this emission. No essential difference in the onset of the luminescence at the exciton resonance and corresponding energies of the LO-phonon replica was found in sample G13. This fact rules out the contribution of the polariton diffusion to the observed delayed onset of luminescence.

The luminescence onset essentially depends on the excitation energy, so that Δt_{max} is increased (approximately by the value 2 ns) with increasing excitation energy above the band gap for all luminescence energies [Fig. 2(b)]. It is natural to attribute this part of the delay time to the energy relaxation of electrons. At the same time we could not resolve the process of exciton formation from cold electrons and holes since the values of the delay time are practically the same for the excitation at the band edge and $n=2$ excited state of the free exciton [experimental points corresponding to two smallest values of excitation energy in Fig. 2(b)].

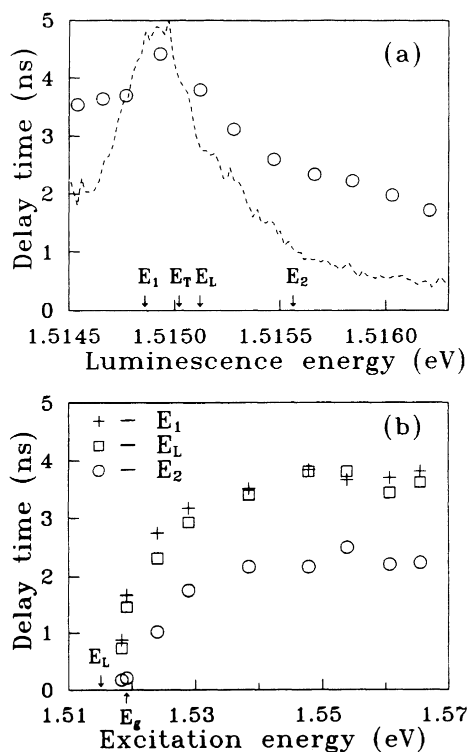

FIG. 2. The dependence of the luminescence maximum time delay on (a) the luminescence energy and (b) excitation energy for sample G13. (a) Excitation energy is 1.554 eV; the dashed line represents the polariton luminescence spectrum. (b) Luminescence energies correspond to those denoted in (a). E_L and E_T are longitudinal and transverse exciton energies, respectively.

As it is seen in Fig. 1, the onset of the polariton luminescence depends on impurity concentration. It is usually assumed[5] that the energy relaxation of electrons in GaAs with energy less than the energy of optical phonon is governed by the emission of acoustical phonons. This process, however, is rather slow because of the small value of the electron effective mass (according to calculations carried out by Ulbrich[12] the energy relaxation rate via emission of acoustical phonons for the electron temperature $T_e=10$ K is determined to be $S\sim0.1$ meV/ns). The observed impurity concentration dependence in our experiments clearly points to the role of extrinsic processes in the electron energy relaxation. The noticeable decrease in Δt_{max} and the appearance of a fast initial rise with increasing impurity concentration is caused by an enhancement of the electron energy relaxation rate due to inelastic impurity scattering. Furthermore, in the n-type sample [Fig. 1(a)] the luminescence onset is considerably faster than in p-type sample [Fig. 1(b)], with a comparable total impurity concentration. This appears reasonable, since inelastic scattering by neutral donors is more probable because of the smaller binding energy.

All the experiments described above were performed at a low repetition rate of excitation pulses $f=4.1$ MHz. At $f=82$ MHz the polariton luminescence signal of the ultrapure GaAs sample does not decay completely during the time interval between two successive excitation pulses $\Delta t=12.2$ ns. In this case we observed interaction of newly created excitations with those left from the preceding pulse. Figure 3 presents the luminescence kinetics of sample G13 at different energies, E_1, E_L, and E_2 (see also Fig. 2). It is seen in Fig. 3(b) that at luminescence energies in the vicinity of the exciton resonance the next excitation pulse causes a fast luminescence quenching. This effect disappears when the excitation energy approaches the band gap [Fig. 3(a)]. Luminescence quenching is also observed in the bound-exciton luminescence kinetics, especially in the case of (D^0,x) line (exciton bound to neutral donor).

The magnitude of the dip in the luminescence kinetics is the greatest in the vicinity of the exciton resonance. At the same time at higher luminescence energies the expected rise of the luminescence intensity after the excitation pulse is observed. We propose the following explanation of the observed phenomenon. Photoexcitation with photon energy well above the band gap leads to creation of hot electrons. Exciton-electron interaction causes scattering of the polaritons accumulated in the states with small energies to the states with higher energies. Due to this heating effect the thermalized population of excitons around E_T is reduced, which is reflected in the luminescence kinetics. The greatest effect should be expected at

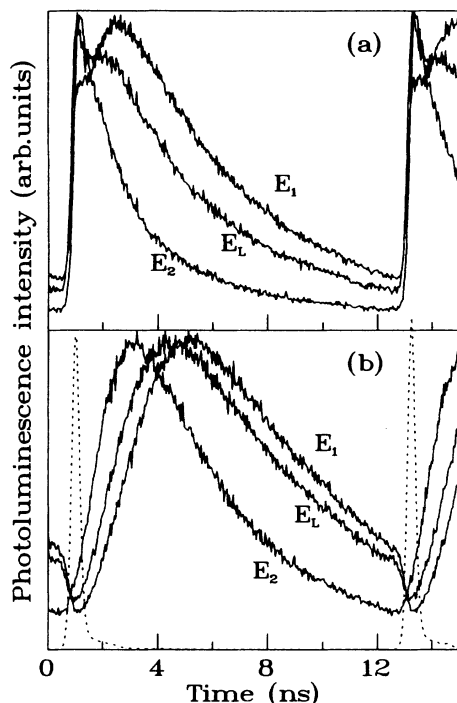

FIG. 3. Time behavior of the polariton luminescence of sample G13 at a high repetition rate. Excitation energy is (a) 1.520 eV, equal to the energy gap and (b) 1.554 eV. The dashed lines represent the excitation pulses. Traces are measured at the luminescence energies denoted in Fig. 2(a).

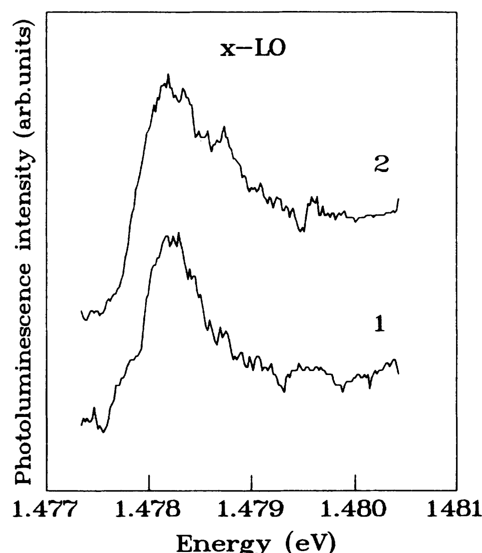

FIG. 4. Time-integrated LO-phonon replica of exciton emission of sample G13. Curves 1 and 2 correspond to excitation energies 1.520 and 1.554 eV, respectively.

the energy of the maximum of the polariton distribution function in the vicinity of the exciton resonance. Polariton heating also causes a decrease in bound-exciton concentration, because the exciton trapping probability decreases with increasing polariton energy.[13] In the case of excitation close to the band edge cold electrons are created and polaritons are not heated.

The proposed interpretation requires a dependence on the excitation density. Such a dependence really exists. The magnitude of the dip in the luminescence kinetics is a function of excitation density with a maximum at the average density ~ 2.5 W/cm^2. A decrease in the magnitude of the dip at lower excitation density is natural due to a reduced rate of exciton-electron scattering. At higher excitation densities the effect is not observed because of an increase in the electron energy relaxation rate (due to the same processes of exciton-electron interaction) and a concurrent fast increase in exciton population.

Exciton-electron interaction was already considered to influence the polariton luminescence line shape under cw excitation.[14,15] The importance of exciton-electron scattering to exciton dephasing at comparable, moderate excitation level was shown by Schultheis *et al.*[16] Exciton-electron interaction also was revealed in our study of the line shape of the time-integrated phonon replica of the polariton luminescence at different excitation energies. As it is shown in Fig. 4 the effective polariton temperature determined from the high-energy tail of the phonon replica increases with an increase in excitation energy. This result directly indicates the close relation between electron and exciton temperatures.

It is important to note that efficient exciton-electron interaction implies coincidence of excitons and electrons in time and space. Under pulse excitation concentration maxima of excitons and hot electrons are separated in time. This is the reason why the dip, usually observed at longitudinal exciton energy in the polariton luminescence spectrum under cw excitation,[7] is absent in the ultrapure sample even at rather high excitation densities. Due to spatial separation of excitons and electrons luminescence quenching by the next excitation pulse is not observed in the kinetics of LO-phonon replica of exciton emission. Unlike the resonance polariton luminescence its LO-phonon replica originates from the bulk. During the time between two succeeding excitation pulses polariton spatial distribution shifts inside the crystal due to diffusion, while hot electrons are created at the surface.

In conclusion, we have shown that the maximum of polariton luminescence from high-purity GaAs is reached after a considerable delay (up to 4 ns) from the excitation pulse. This delay is caused by the energy relaxation of the photoexcited electrons and slow thermalization of excitons around a polariton bottleneck. The energy relaxation rate in samples with higher impurity concentration is increased due to inelastic impurity scattering. The electron-exciton interaction provides another channel of electron cooling and is evidenced by a quenching of the polariton luminescence by the next excitation pulse.

[1]C. Weisbuch, Solid State Electron. **21**, 179 (1978).

[2]T. Steiner, M. L. W. Thewalt, E. S. Koteles, and J. P. Salerno, Phys. Rev. B **34**, 1006 (1986).

[3]W. J. Rappel, L. F. Feiner, and M. F. H. Schuurmans, Phys. Rev. B **38**, 7874 (1988).

[4]G. W. 't Hooft, W. A. J. A. van der Poel, L. W. Molencamp, and C. T. Foxon, Phys. Rev. B **35**, 8281 (1987).

[5]R. Höger, E. O. Göbel, J. Kuhl, K. Ploog, and H. J. Queisser, J. Phys. C **17**, L905 (1984).

[6]V. G. Golubev, Yu. V. Zhilyaev, V. I. Ivanov-Omskii, G. R. Markaryan, A. V. Osutin, and V. E. Chelnokov, Fiz. Tekh. Poluprovodn. **21**, 1771 (1987) [Sov. Phys. Semicond. **21**, 1074 (1987)].

[7]Yu. V. Zhilyaev, G. R. Markaryan, V. V. Rossin, T. V. Rossina, and V. V. Travnikov, Fiz. Tverd. Tela (Leningrad) **28**, 2688 (1986) [Sov. Phys. Solid State **28**, 1506 (1986)].

[8]Y. Toyozawa, Progr. Theor. Phys. Suppl. **12**, 111 (1959).

[9]P. Wiesner and U. Heim, Phys. Rev. B **11**, 3071 (1975).

[10]F. Askary and P. Y. Yu, Phys. Rev. B **28**, 6165 (1983).

[11]Ya. Yu. Aaviksoo, Ya. E. Lippmaa, A. M. Freiberg, and S. F. Savikhin, Fiz. Tverd. Tela (Leningrad) **31**, 203 (1989) [Sov. Phys. Solid State **31**, 462 (1989)].

[12]R. Ulbrich, Phys. Rev. B **8**, 5719 (1973).

[13]E. F. Gross, S. A. Permogorov, V. V. Travnikov, and A. V. Sel'kin, Fiz. Tverd. Tela (Leningrad) **14**, 1547 (1972) [Sov. Phys. Solid State **14**, 1331 (1972)].

[14]K. Aoki, T. Kinugasa, and K. Yamamoto, Phys. Lett. **72A**, 63 (1979).

[15]K. Aoki, Y. Okuyama, T. Kobayashi, and K. Yamamoto, J. Phys. C **12**, 647 (1979).

[16]L. Schultheis, J. Kuhl, A. Honold, and C. W. Tu, Phys. Rev. Lett. **57**, 1635 (1986).