Optically detected Auger recombinations in erbium- and ytterbium-doped InP

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Microwave-induced impact ionization of excitons and shallow donors is studied in Er- and Yb-doped InP. The experimental results indicate a high efficiency of free-electron-related Auger recombination. Yb and Er intrashell emissions are deactivated due to an energy transfer to either free or bound carriers. A new Auger-type nonradiative process is suggested in which the rare-earth-related photoluminescence decays via an energy transfer to a free carrier which has become localized via a short-range potential.

Rare-earth (RE)-doped III-V semiconductors such as InP and GaAs doped with erbium (Er) or ytterbium (Yb) attract an increasing interest due to their possible application in light-emitting devices. The most promising property of these materials is the possibility of excitation of sharp RE intrashell emissions by injection of minority carriers (electroluminescence). For example, the 1.54 μm photoluminescence (PL) of Er^{3+} is likely to find wide application in silica-fiber-based communication systems. Recently, room-temperature light-emitting diodes have been made on the basis of Er-doped GaAs and GaAlAs double heterostructures.[1] However, until now the efficiency of such devices is too low for practical applications.

To improve light output of these devices, the excitation mechanisms should be understood and optimized. It was demonstrated that RE PL could be observed in III-V devices by impact excitation of RE ions with energetic electrons accelerated by an electric field.[2] In an Auger-type energy transfer, energy of a recombining ion is given to either a free or bound carrier, which is then highly excited into the continuum of the conduction-band (CB) or valence-band (VB) states.[3] In this way, Auger processes provide a deexcitation mechanism alternative to PL. The efficiency of RE photoluminescence is thus determined by a competition between impact excitation and an Auger-type energy transfer from excited RE ions to free or bound carriers.

In this letter we prove that indeed such free-carrier-related Auger-type processes limit the efficiency of RE emissions. We show the efficiency of these processes to be high by performing optically detected cyclotron resonance (ODCR) measurements. The theoretical background of ODCR is given by Romestain and Weisbuch[4] and, in application to impact ionization studies, by one of the authors.[5] Microwave power is applied to accelerate photoexcited electrons which may reach energies sufficient to impact ionize excitons and shallow centers. Recently, we applied this technique to verify the excitonic excitation mechanism of Yb PL in InP.[6] As will be shown, an efficient Auger deexcitation channel also exists for Er and is therefore likely to be characteristic for RE^{3+} ions in general.

The samples used in this study were grown by metal-organic chemical vapor deposition (MOCVD). The samples were kindly provided by Dr. F. Scholz of Universität Stuttgart, Germany—details of the growth procedure can be found elsewhere.[7] PL was excited with a cw 514.5 nm Ar^+-ion laser, dispersed by a high-resolution 1.5 m F/12 Jobin–Yvon THR-1500 monochromator (600 grooves/mm grating blazed at 1.5 μm), and detected by a nitrogen-cooled North-Coast EO-817 Ge detector. Impact ionization measurements were performed at 35 GHz with the samples at 2.1 K mounted in a split-coil Oxford Instruments SM 4 superconducting magnet in a cylindrical TE_{001} cavity. Microwaves were generated by a Gunn oscillator (maximum power 220 mW), and on-off modulated with a *p-i-n* diode at 730 Hz.

The PL spectra of Yb- and Er-doped InP are shown in Fig. 1. In the band-edge region the PL spectrum consists of a donor-bound exciton (DBE) at 1417.5 meV and a donor-acceptor pair (DAP) transition at 1387.5 meV with its LO phonon repetition at 1344.6 meV.[8,9] For the Er-doped sample the DBE emission is much weaker. The near-edge part of the PL spectrum is followed by a group of lines around 1240 meV (1.0 μm) and 805 meV (1.54 μm), which are due to Yb^{3+} ($^2F_{5/2}\rightarrow{}^2F_{7/2}$) and Er^{3+} ($^4I_{13/2}\rightarrow{}^4I_{15/2}$) intra-4*f*-shell transitions, respectively. Figure 2 shows the PL intensity changes measured synchronously with chopped microwave power (P_μ), with the magnetic field set at the broad cyclotron resonance signal. The relative changes of the InP:Yb PL intensity are shown in Fig. 3. The threshold dependence on P_μ is observed, as expected for the impact ionization mechanism.[5] For $P_\mu > 5.5$ mW carriers reach energies sufficient to impact ionize shallow donors in InP thus reducing the efficiency of the DAP recombination. Free carriers impact ionized from shallow centers enhance Yb^{3+} PL due to exciton binding by the RE ion.[6] Yb-bound excitons recombine transferring their energy to Yb core states.[6] We note that the impact of bound excitons and shallow donors leads to a 5%–6% decrease of the overall PL intensity. The 8% and 6% reduction of the DBE and DAP emissions, respectively, is accompanied by only a 1% increase in Yb^{3+} PL intensity—see Fig. 3. Since at the same time no additional emission appears, the above observation indicates that, once bound excitons and donors are ionized and the free-carrier concentration is increased,

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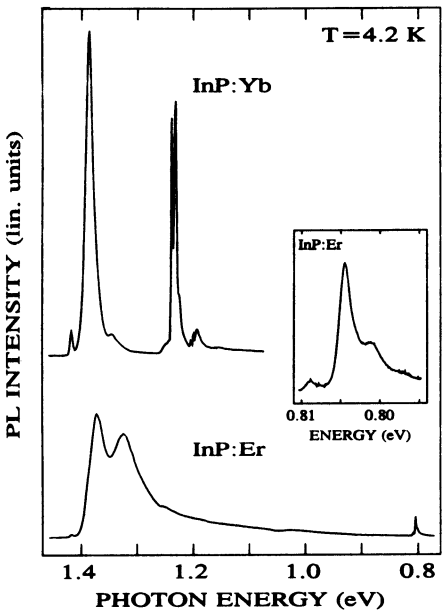

FIG. 1. Photoluminescence spectra of MOCVD-grown InP:Yb and InP:Er measured at 4.2 K under Ar^+ ($\lambda = 514.5$ nm) laser excitation. The inset shows the Er^{3+} PL in more detail.

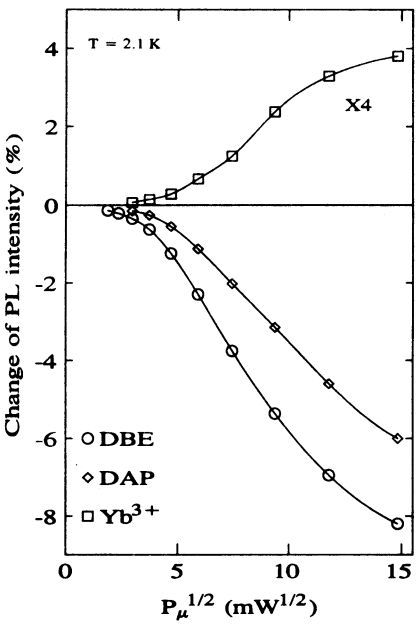

FIG. 3. Microwave power dependence of the relative PL intensity for three different recombinations in InP:Yb (DBE, DAP, and Yb^{3+} intra-4*f* shell). The experiment was performed at 2.1 K with $B = 0.5$ T and constant Ar^+ excitation intensity (50 mW).

some nonradiative recombination channel is promoted.

In the case of Er this nonradiative recombination is even more important. Similarly to Yb, also for Er the exciton binding mechanism was suggested.[10] Thus, the ODCR results are expected to be similar. However, we observe that the impact ionization of excitons and shallow donors does not stimulate recombination via Er^{3+} ions. Instead, an asymmetric derivativelike response of Er^{3+} PL to applied microwaves is obtained—see the inset of Fig. 2: a positive signal at higher energies followed by a negative signal at lower energies. Such response reflects, first, a slight broadening of the Er^{3+} PL and, second, a decay in the intensity once free carriers are promoted into the CB. From the separate PL experiment we find that Er^{3+} PL decreases by about 1% upon application of microwave field. The observed decrease of the Er^{3+} PL intensity means that the above postulated excitonic mechanism of Er^{3+} excitation is less efficient than for Yb^{3+}. An increase in the free-carrier concentration results in an overall decrease of Er^{3+} PL, even though the Er BE formation should be enhanced.

The temperature dependence of the main line related to Er^{3+} PL is plotted in Fig. 4. It can be fitted to the relationship

$$I(T) = I(0)/[1 + A_1 \exp(-E_1/kT) + A_2 \times \exp(-E_2/kT)], \quad (1)$$

yielding a dominant quenching mechanism with $E_1 \approx 9$ meV and a weaker one with $E_2 \approx 0.9$ meV. The fact that $A_2 \ll A_1$ indicates that process 2 is of less importance.[13] The thermal activation energy of process 1 is reasonably equal to the 7.31 meV donor ionization energy in InP. Our earlier study on InP:Yb[6] and also results by other groups,[11,12] show that the DAP→RE energy transfer is not the dominant process: therefore one has to conclude that the creation of free carriers introduces an efficient nonradiative recombination of the RE ion. This provides a clear evidence for the high efficiency of the Auger-type transfer process. Klein[13] and Takahei *et al.*[14] proposed that such energy transfer may proceed to an electron bound to the RE ion in its excited state by a short-range potential. In this case RE intrashell emission is quenched due to a very efficient intracenter Auger energy transfer to the bound

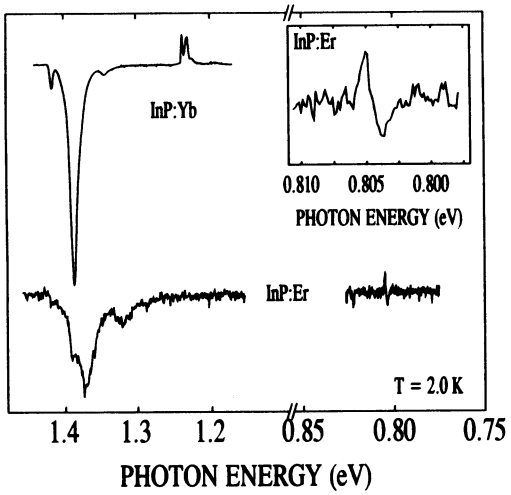

FIG. 2. Spectral dependence of the impact ionization spectra measured at 2.1 K using constant laser excitation power (50 mW for InP:Yb, 250 mW for InP:Er) and 220 mW of microwave power. The magnetic field was set at the broad cyclotron resonance signal ($B = 0.5$ T for InP:Yb, $B = 0.36$ T for InP:Er). The inset shows the response of Er^{3+} PL to applied microwaves.

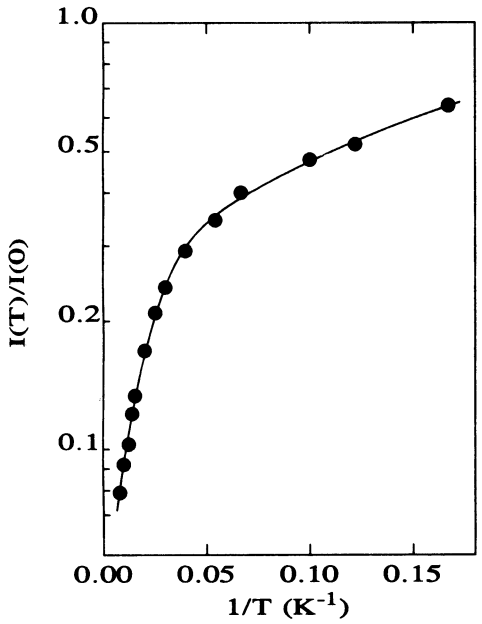

FIG. 4. Semilogarithmic plot vs reciprocal temperature of the main Er^{3+} intrashell emission line. The solid curve is a fit to the data using the analytical expression (1) with fitting parameters: $E_1 = 8.8 \pm 0.9$ meV, $A_1 = 20 \pm 4$, $E_2 = 0.9 \pm 0.2$ meV, and $A_2 = 3.0 \pm 0.5$.

electron. A similar explanation should also be valid if the first carrier localized is a hole, as suggested by Thonke *et al.*[7]

The current results also allow us to explain the earlier experimental data for Yb in InP[7,13,14] where the decay of Yb^{3+} PL was found to be nonexponential, with the decay time being of the order of μs.[13,14] This can be understood if the Yb^{3+} decay time is controlled by a nonradiative process due to an Auger-type transition involving Yb^{3+} in its excited state and either a RE-bound or free carrier. The excited Yb^{3+} decays via this Auger-type energy transfer (localized Auger quenching).

The present study shows that for Yb in InP exciton binding and the subsequent BE$\rightarrow 4f$ core energy transfer is more efficient than the competing localized Auger quenching. Consequently, high efficiency of Yb^{3+} PL can be obtained. This is not the case for Er^{3+}: the postulated exciton binding followed by energy transfer to the Er core states is less efficient than the competing Auger process. This is likely to be due to a misfit between the energies of the Er^{3+} BE and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ intraion transition. As a consequence, BE$\rightarrow$RE core transfer, nearly resonant in the case of Yb^{3+} in InP with the misfit of only 145 meV,[7] is far less efficient for Er^{3+}.

Concluding, we presented a direct evidence for a highly efficient Auger-type energy transfer from RE ions to either free or bound carriers which limits the RE-related emission. In this way we have established the physical origin of the low PL efficiency of Yb- and Er-doped InP which presents an important drawback and seriously hampers potential application of these materials for carrier-injection optoelectronic devices.

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[1] P. Galtier, J. P. Pocholle, M. N. Charasse, B. de Cremoux, J. P. Hirtz, B. Groussin, T. Benyattou, and G. Guillot, Appl. Phys. Lett. **55**, 2105 (1989).
[2] H. Isshiki, H. Kobayashi, S. Yugo, T. Kimura, and T. Ikoma, Appl. Phys. Lett. **58**, 484 (1991).
[3] A. Suchocki and J. M. Langer, Phys. Rev. B **39**, 7905 (1989).
[4] R. Romestain and C. Weisbuch, Phys. Rev. Lett. **45**, 2067 (1980).
[5] H. Weman, M. Godlewski, and B. Monemar, Phys. Rev. B **38**, 12525 (1988).
[6] B. J. Heijmink Liesert, M. Godlewski, A. Stąpor, T. Gregorkiewicz, C. A. J. Ammerlaan, J. Weber, M. Moser, and F. Scholz, Appl. Phys. Lett. **58**, 2237 (1991).
[7] K. Thonke, K. Pressel, G. Bohnert, A. Stąpor, J. Weber, M. Moser, A. Molassioti, A. Hangleiter, and F. Scholz, Semicond. Sci. Technol. **5**, 1124 (1990).
[8] J. U. Fischbach, G. Benz, N. Stath, M. H. Pilkuhn, and K. W. Benz, Solid State Commun. **11**, 721 (1972).
[9] J. U. Fischbach, G. Benz, N. Stath, and M. H. Pilkuhn, Solid State Commun. **11**, 725 (1972).
[10] B. Lambert, A. Le Corre, Y. Toudic, C. Lhomer, G. Grandpierre, and M. Gauneau, J. Phys.: Condense Matter **2**, 479 (1990).
[11] J. E. Colon, D. W. Elsaesser, Y. K. Yeo, R. L. Hengehold, and G. S. Pomrenke, to appear in Proceedings of 16th Int. Conf. Defects in Semiconductors, Bethlehem, PA, 1991.
[12] W. Körber and A. Hangleiter, Appl. Phys. Lett. **52**, 114 (1988).
[13] P. B. Klein, Solid State Commun. **65**, 1097 (1988).
[14] K. Takahei, A. Taguchi, H. Nakagome, K. Uwai, and P. S. Whitney, J. Appl. Phys. **66**, 4941 (1989).