Optically detected microwave-induced impact ionization of ytterbium bound excitons in InP

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Optically detected microwave-induced impact ionization of excitons and shallow donors is studied in Yb-doped InP grown by metalorganic chemical vapor deposition. The experimental results directly confirm that Yb^{3+} intrashell emission is induced by nonradiative recombination of Yb bound excitons due to an impurity Auger effect. Yb^{3+} ions in InP are found to bind excitons with the electron being localized first, followed by subsequent hole capture.

A new, very efficient photoluminescence excitation (PLE) mechanism of transition metal (TM) and rare-earth (RE) intrashell emissions was evidenced recently.[1] In this PLE process TM and RE intrashell emissions are induced by an energy transfer from a bound exciton (BE) excited state of an impurity to its core states resulting in nonradiative BE recombination and core states excitation (impurity Auger effect). Such energy transfer process was proposed recently[2] for Yb^{3+} PLE in InP. In this letter we verify this hypothesis using optically detected microwave-induced impact ionization spectroscopy.

RE-doped III-V compounds are intensively studied due to their possible application to light-emitting devices and lasers with emission wavelengths insensitive to device processing. Although Yb-doped InP is the most studied material of this group, there still is a controversy on its electrical and optical properties. Yb-induced PL is well known to occur near 1.0 μm, being due to intra-4f-shell transitions of trivalent Yb^{3+} ($4f^{13}$) ions on In sites. Recently it was proved that the Yb^{2+} level is not localized in the band gap,[3] leaving the 3+ state as the only stable charge state of Yb in InP. The Yb dopant is believed to introduce either an acceptor-like electron trap which can capture an electron at a level of about 30 meV below the conduction band,[2-5] or a donor-like state at 30 meV above the valence band.[2] To explain this behavior it was proposed that Yb in InP acts as an isoelectronic center with a short-range attractive potential either due to a lattice distortion around the Yb site or to a difference in electron affinities of Yb and In.[5] Until very recently the dominant Yb PLE mechanism was not understood, although different mechanisms have been proposed.[2,5,6]

The sample used in this study was grown by the metalorganic chemical vapor deposition method (MOCVD, for details see Ref. 2). Luminescence was excited with the 514.5 nm Ar^{+} laser line. The signal was dispersed by a 1.5 m Jobin–Yvon monochromator (grating blazed at 1.5 μm) and detected by a nitrogen-cooled Ge detector (North-Coast EO-817). Impact ionization measurements were performed at 2.1 K in a 35 GHz TE_{001} cavity using a split-coil superconducting magnet (Oxford Instruments SM4).

In Fig. 1(a) a typical PL spectrum is shown. In the near-edge region it consists of three peaks (L_1–L_3) at 1417.5, 1387.5, and 1344.6 meV, attributed to donor bound exciton (DBE) recombination, donor-acceptor pair (DAP) recombination and its LO phonon replica, respectively.[7,8] A second group of lines (L_4–L_7) is observed at 1248.6, 1242.5, 1238.1, and 1230.7 meV and is ascribed to Yb^{3+} intra-4f-shell ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) transitions.[9] The introduction of magnetic field (B), by setting it to 0.5 T, causes no change of PL intensity—see Figs. 1(a) and 1(b). A simultaneous introduction of maximum microwave power (P_μ) of 220 mW yields a 5–6% decrease of the overall PL intensity. Careful analysis of the spectra of Fig. 1 reveals that whereas the intensity of the DBE and DAP PL is reduced (by 8% and 6%, respectively), the Yb^{3+}-related PL intensity is slightly enhanced (by 1%). This could be directly monitored by recording the change of PL intensity while scanning through the luminescence—see Fig. 2.

Relative changes of the PL intensities for $B = 0.5$ T and for different P_μ are shown in Fig. 3. As expected for the impact ionization mechanism of microwave-induced PL intensity changes, the threshold dependence on P_μ is observed.[10] The threshold values are 2.2 and 5.5 mW for the DBE and DAP transitions, respectively. The observed increase of the Yb^{3+} PL saturates for $P_\mu > 100$ mW indicating that the threshold for Yb^{3+} quenching is around this value. Such ordering of impact ionization threshold values agrees well with the ordering of binding and ionization energies for DBEs, shallow donors, and Yb BEs in InP. The Yb BE binding energy was suggested to be 9–15 meV,[2] i.e., a factor of two larger than the donor ionization energy. As a consequence, with the increase of microwave power, free carriers first reach energies sufficient for DBE impact ionization and quench the DBE PL. For $P_\mu > 5.5$ mW shallow donors are impact ionized reducing the efficiency of DAP recombination. Once the DAP transition becomes less effective, Yb^{3+} PL is enhanced—see Fig. 3. This is clearly inconsistent with a DAP→Yb energy transfer being the dominant channel for Yb^{3+} PLE, as proposed by Kasatkin and Savel'ev.[6]

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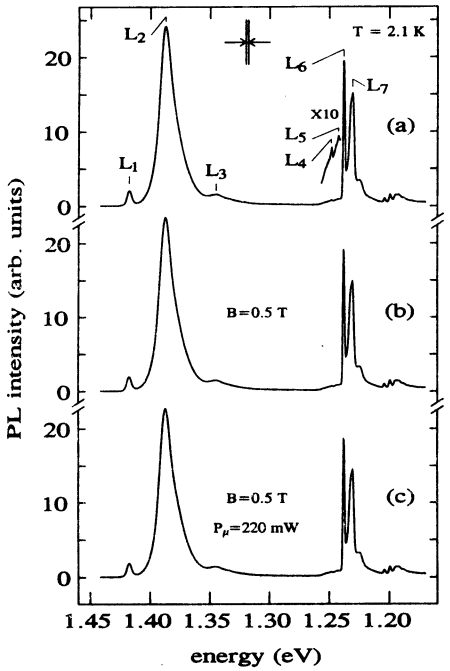

FIG. 1. Photoluminescence (PL) spectrum of MOCVD-grown InP:Yb measured at 2.1 K under Ar^+ ($\lambda = 514.5$ nm) excitation (a) without magnetic field B and microwave power P_μ, (b) with $B = 0.5$ T and $P_\mu = 0$ mW, and (c) with $B = 0.5$ T and $P_\mu = 220$ mW.

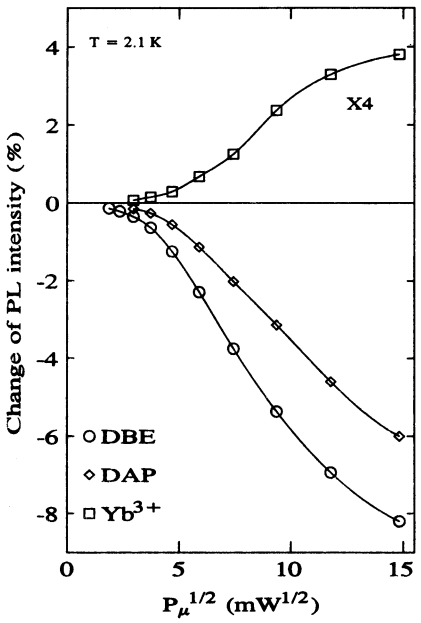

FIG. 3. Relative PL intensity vs the square root of applied microwave power chopped at 730 Hz for DBE recombination at 1417.5 meV, DAP recombination at 1387.5 meV, and Yb^{3+} intra-4f-shell emission at 1238.1 meV (multiplied by 4 for clarity). The experiment was performed at 2.1 K with $B = 0.5$ T and constant Ar^+ laser excitation power of 50 mW.

The decay time of Yb^{3+} PL is 13 μs (Ref. 2) instead of ms as expected for parity forbidden intra-4f-shell transitions. Takahei *et al.*[5] proposed that the Yb^{3+} decay time may be controlled by a nonradiative two-center Auger-type process involving Yb^{3+} in its excited state and a nearby occupied donor. It seems that impact ionization of shallow donors would reduce the concentration of centers active in such an Auger process, thus increasing Yb^{3+} PL. However, Auger-type energy transfer to bound carriers was found to be approximately two orders in magnitude less efficient than the one involving free carriers.[11] Impact ionization of shallow donors increases the free-electron concentration and should result in Yb^{3+} PL quenching rather than in its enhancement as observed in the experiment.

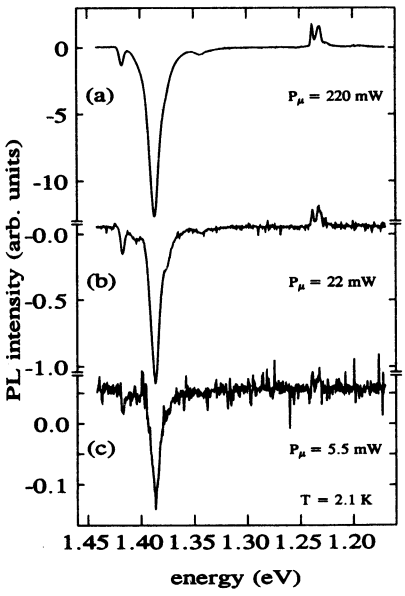

FIG. 2. Spectral dependence of the impact ionization spectra measured at 2.1 K and with $B = 0.5$ T using 50 mW of constant laser excitation power. Spectra (a), (b), and (c) are plotted for three different microwave powers $P_\mu = 220$, 22, and 5.5 mW, respectively. The PL signal was detected in phase with applied microwaves on-off modulated at 730 Hz.

Retrapping of electrons impact ionized from shallow donors should enhance the recombination via a competing electron trap (no free to bound emission was observed). Indeed, Yb^{3+} PL starts to be enhanced at exactly the same threshold value of P_μ which leads to DAP quenching (see Fig. 3), suggesting that electrons ionized from shallow donors are retrapped by Yb^{3+} centers. Yb^{2+} involvement can be ruled out since this level is not localized in the InP band gap.[3] Capture thus occurs via an acceptor-like Yb trap state as discussed in Refs. 2–5. It is very unlikely that trapped electrons recombine with holes on acceptors giving rise to DAP-like transitions, as proposed recently by Takahei *et al.*[5] This should result in a mirror-like decrease of the DAP emission and increase of the new Yb-related DAP transition, which has not been observed. We conclude therefore that once Yb^{3+} traps an electron, Yb^{3+} transforms to some intermediate state. Further, this state must have relatively shallow character allowing for the observed impact ionization (impact ionization of Yb^{3+} core states is not expected in InP).

All data shown in Fig. 3 are consistent with a mechanism of exciton binding by isoelectronic Yb^{3+} centers. Yb^{3+} PL is then excited due to nonradiative recombination of such a BE state (impurity Auger effect). In fact, accompaniment of Yb^{3+} decay by an Auger-type transition is implied by the quenching of the DBE and DAP

transitions leading to a 5–6% decrease of the total PL intensity. A model for excitons bound to isoelectronic centers was introduced by Hopfield *et al.*[12] First a carrier (either an electron[5] or a hole[2]) is bound by a short-range attractive potential which is followed by binding of a second carrier by the long-range Coulomb attractive potential. The electron capture cross section of the Yb-related acceptor-like state is $\approx 4\times 10^{-16}$ cm^2 (Ref. 4) which is a typical value for electron trapping by neutral centers. The lack of electric field effects on the emission rate of this state[4] supports such assignment. This observation together with our data indicates that the Yb BE state is formed first by electron capture followed by subsequent hole binding. The cross section for hole capture is unknown but must be relatively large in order to dominate over a competing Yb-related DAP transition discussed above. A BE state intermediating Yb^{3+} PLE may also result in enhancing Yb^{3+} PL excitation. The Yb-BE system as a whole does not have rotational nor space symmetry. As a consequence, the symmetry rules are broken and due to the impurity Auger effect highly efficient excitation of the Yb center may occur.

In conclusion, we have shown that the dominant PLE mechanism of the Yb^{3+} ($4f^{13}$)-related emission is due to the impurity Auger effect. Ytterbium in InP binds an exciton which intermediates Yb core states excitation. Exciton binding affects the selection rules leading to very efficient intra-4*f*-shell excitation. This observation is of particular importance in view of the potential applications of RE- and TM-doped III-V compounds for light-emitting devices.

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