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EXCITATION OF RARE EARTHS IN SEMICONDUCTORS BY THE EXCITONIC AUGER RECOMBINATION

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Abstract. The role of the electron trap (AE) for the excitation and de-excitation mechanism of rare earths in a semiconductor host is studied by photoluminescence and microwave-induced impact ionization methods. A direct evidence for an AE-mediated excitonic e-e-h Auger recombination process of Er^{3+} ion in the ground state which is responsible for the low luminescence efficiency of erbium-doped silicon is given.

Introduction

Rare earth (RE) elements incorporated into semiconductor host material give rise in photoluminescence (PL) to sharp, atomic-like spectra, whose energy position is independent of the host crystal and temperature. The RE-doped semiconductors belong to the perspective optoelectronic materials. They attract much attention because of possible applications to new optical devices characterized by sharp and temperature-stable luminescence, such as light emitting diodes or lasers. Recently, considerable attention has been given to the erbium-doped silicon system, due to the fact that Er emission at 0.806 eV coincides with the optical window of glass fibers currently used for telecommunications, and such a system can be easily integrated with devices manufactured using the standard silicon technology. In addition to optical also successful excitation by minority carrier injection has been reported for Er-doped GaAs [1], Yb-doped InP [2] and, recently, also Er-doped Si [3]. However, the luminescence intensity rapidly decreases at high temperatures, thus seriously hampering possible practical applications. In order to overcome this thermal quenching and to increase PL efficiency at high temperatures it is necessary to clarify, and then optimize, the luminescence mechanism of the RE ions.

Experimental conditions

Free carriers are created by optical excitation with energy exceeding the band gap of the host crystal. At low temperatures, the free carriers in the way of de-excitation usually form excitons. In thermal equilibrium each exciton ionization process is counterbalanced by a corresponding formation process. Under application of a microwave field, (photoexcited) free carriers are accelerated by the electric field and some of them gain sufficient energy to impact ionize excitons as well as loosely bound carriers. A critical microwave field exists at which the impact-ionization rate starts to predominate both exciton recombination and ionization by phonon absorption, which is normally the dominant process in thermal equilibrium. As a result the number of low-energy carriers - which are being effectively captured by shallow impurities - diminishes, and simultaneously the effective capture rate of such centers is being reduced, leading to an increase of the free carrier's life time. At the same time an increased number of carriers is available to participate in recombinations via deep centers and free-to-bound transitions.

The impact ionization effect can be measured directly by monitoring the influence of the microwave field on the PL spectrum. In this case, the standard PLspectrum is compared with

the one recorded under the application of constant microwave power; to permit the lock-in detection technique in both cases the laser excitation is modulated. On the other hand, the wavelength (spectral) dependence of the impact ionization can be investigated. To perform this one monitors the changes of the PL spectrum in phase with the on-off modulated microwave field set at different power levels, under constant laser excitation power.

In the present study the following crystals have been used:

i. Czochralski silicon implanted with 1×10^{13} cm^{-2} Er atoms of 1 MeV energy and subsequently annealed in a chlorine-atmosphere.

ii. An InP:Yb single crystal grown by the high-pressure gradient freeze synthesis method. By this method, unintentionally doped samples are n type with a residual electron density of about 5×10^{15} cm^{-3}. When Yb is diluted in the semiconductor with a concentration of about [Yb] = 10^{17} cm^{-3} the crystals remain n type with the carrier density ranging between 10^{16} and 5×10^{16} cm^{-3} at 300 K.

In the experiment the samples were mounted in a TE_{011} microwave cavity with slits for optical access. The carriers were excited with the 514.5-nm line of the Ar^+ laser operating with an output power of typically 50 mW. The luminescence was collected from the laser-irradiated side and was dispersed with a high-resolution 1.5-m F/12 monochromator (Jobin-Yvon THR-1500) with a 600-grooves/mm grating blazed at 1.5 μm. The signals were detected with a liquid-nitrogen-cooled germanium detector (North Coast EO-817) and amplified using the conventional lock-in technique with a modulation frequency at typically 730 Hz. Optically detected impact ionization measurements were performed in the Q microwave band of 35 GHz at liquid-helium temperature.

Experimental results

The PL spectrum of the n-type Si:Er crystal is presented in Fig. 1a; it is characterized by a weak Er band luminescence at 806.6 meV, and a relatively strong band edge luminescence. The latter emission consists of several peaks: two peaks at 1150 meV and at 1091.8 meV are no-phonon (NP) and TO phonon lines of phosphorus bound excitons, respectively. The peaks at 1132.6 meV and 1085 meV are most probably related to excitons bound to lithium and thermal donors (TD), respectively. At high chopping frequencies a new line, probably also related to erbium, appears at 873 meV. Fig. 1b shows the PL spectrum as recorded for the other material used in this study: n-type bulk crystal of InP. It shows characteristic strong Yb^{3+} luminescence band at 1240 meV and no band edge luminescence.

The application of a microwave field influences the observed PL spectra. In the n-type Si:Er crystal microwave power of 200 mW decreases the band-edge and increases the Er^{3+} and TD related luminescence; the total radiative luminescence of the crystal enhances by 10 %. For both materials the change of PL was directly recorded with constant laser excitation and on-off modulated microwave power at a frequency of 730 Hz. Spectral dependencies obtained in this way are depicted in Figs. 2a and 2b for Si:Er and InP:Yb crystals, respectively. For the Si:Er crystal the microwave-field influence on both groups of PL lines can be seen: it is negative for the band-edge luminescence and positive for Er^{3+} and TD-related PL. For the InP:Yb crystal only enhancement of the Yb band can be seen. In this case the total increase of PL for the maximum value of the microwave field is 5%.

Discussion

Zeeman analysis of the Er-related characteristic 1540 meV emission band and Yb-related band

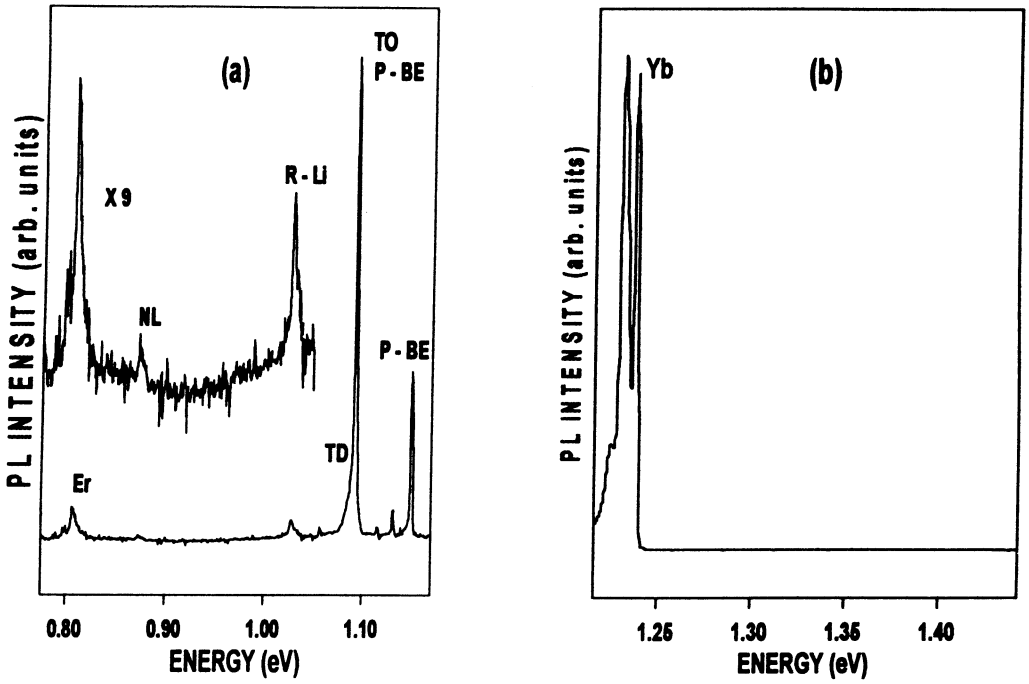

Figure 1: Photoluminescence spectra of the (a) Er-doped silicon, and (b) Yb-doped InP.

at 1240 meV had shown that they are arising from intra-4f-shell transitions of the RE^{3+} ions [4, 5]. In the PL spectrum of the Si:Er crystal, Fig. 1a, there appears a PL emission at 0.873 eV which is probably also related to Er. It seems to have a fast decay since it can be detected only for high chopping frequencies. We suggest that this line may be related to the t_2 level predicted theoretically in the gap of silicon. This level is created by the interaction of the 5d orbitals of an interstitial Er atom in Si with the bulk silicon antibonding states and it is expected to lie $\approx$ 200 meV below the conduction band [6]. It has been argued that the core excitation of the 4f shell of rare earths in a semiconductor host can involve the participation of the 5d orbitals. Further study, currently on the way, is necessary to clarify the origin of this PL emission.

It is generally assumed that the excitation mechanism of RE^{3+} ion in a semiconductor host involves capture of a free exciton at the AE trap and excitation of the intra-4f-shell by the Auger energy transfer. Such a model is based on the spatial localization of an electron-hole pair subject to an attractive Coulomb interaction thus forming an exciton [7]. We propose that upon interaction of a free exciton with the AE trap of Er^{3+} the electron may be captured into the deep level whereas the hole takes the excess energy and is excited highly into the valence band. The electron localized at the AE trap (200-290 meV) of the Er^{3+} ion can follow two alternative routes of de-excitation:

i. recombination with a free hole with the efficient energy non-radiative transfer to the 4f shell of erbium. Relaxation of the excited 4f shell will give the characteristic luminescence.

ii. recombination with a hole which participates in a free exciton; in this case the energy of the recombination will excite the electron into the conduction band (AE-mediated excitonic Auger recombination). In this case the Er^{3+} ion remains in the ground state.

The above outlined scenario is fully consistent with our experimental results. The application of a microwave field increases the temperature of the photo-created electrons and holes

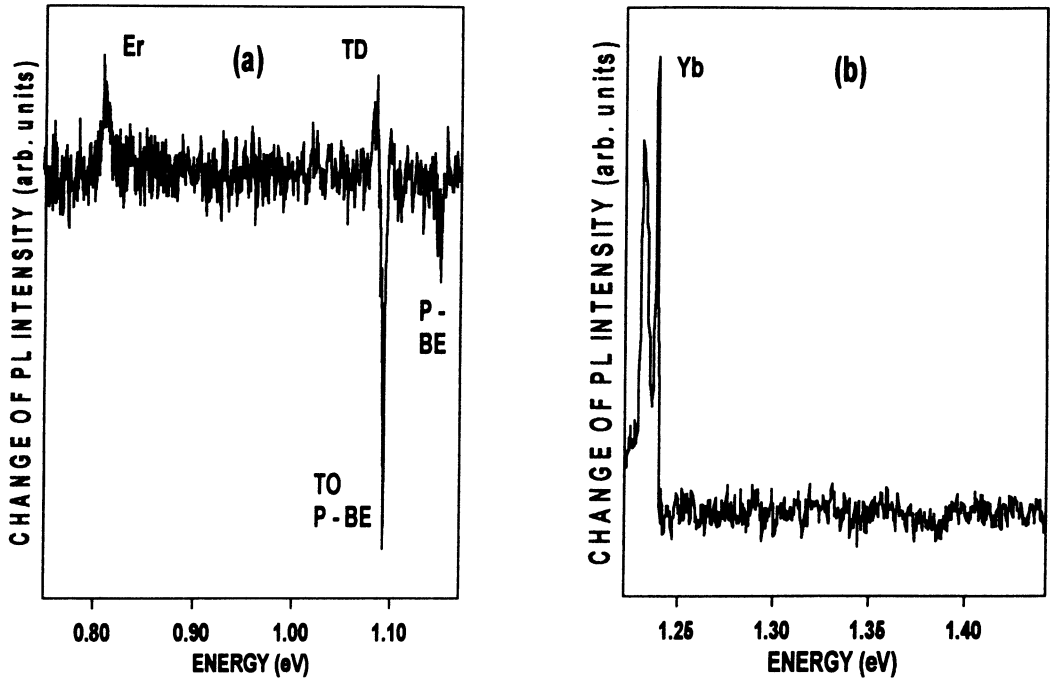

Figure 2: Spectral dependence of the impact ionization signal for (a) Er-doped silicon, and (b) Yb-doped InP. The microwave frequency is $\nu \approx 35$ GHz, microwave power P=200 mW, and the measurement temperature is T=1.8 K.

before they thermalize into a Boltzmann distribution by intercarrier scattering. Subsequent energy loss by acoustic phonons favors single particles rather than bound and free exciton processes amongst the available recombination channels. In that way diffusion into the crystal will decrease the exciton density. Since in an exciton an electron and a hole are tied together the transition probability varies linearly with exciton density. This corresponds to a capture coefficient being independent to carrier density. As a result an electron localized at the AE trap has bigger probability to recombine with a free hole. Consequently upon application of microwave field the e-h pair recombination at the AE trap will be enhanced, leading to more efficient energy transfer to the 4f shell of erbium. In such way the AE-mediated excitonic Auger recombination process will be partly blocked, resulting an enhancement of Er^{3+} luminescence, as confirmed by our experimental results depicted in Fig. 2a: the efficiency of the intra-4f-shell Er^{3+} PL is enhanced, with the total PL efficiency of the studied crystal being increased by 10 %.

For the InP:Yb crystals DLTS measurements have shown presence of an AE trap 30-40 meV below the conduction band minimum. In that case the exciton can be localized at the AE trap and the energy of the recombination will be efficiently transfered by Auger process to the 4f shell of Yb^{3+}. As a result InP crystals doped with Yb give sharp intra-4f-shell emission at low temperatures. The excitonic e-e-h Auger recombination at the AE of Yb in InP is not competing strongly and enhancement of Yb PL in the order of 1 % has been observed in the past by application of microwave field [8].

Lifetime measurements have shown that the Yb PL decay is of the order of 10μs. Since the $^2F_{5/2}$ to $^2F_{7/2}$ transition is parity forbidden, a lifetime of a few ms should be expected.

The transition becomes allowed because the crystal field mixes states of opposite parity. The shortening of Yb PL lifetime has been explained by a nonradiative de-excitation involving a localization of carrier at the $(AE)^*$ trap of the Yb ion in the excited $^2F_{5/2}$ configuration. Our experimental results Fig. 2b give direct indication of the mechanism where, upon an increase of the microwave power, impact ionization of a carrier participating in the nonradiative Auger process occurs. This effectively blocks the nonradiative recombination channel and, consequently, radiative recombinations of the Yb^{3+} ions is strongly enhanced. As has been experimentally observed, the Yb^{3+} PL is enhanced by up to 5 % while practically no other bands can be found in the PL spectrum of this material.

Conclusions

The RE^{3+} ions incorporated into the semiconductor host introduce an AE trap, which can bind a carrier and therefore plays an important role in their excitation and de-excitation mechanisms. In particular, the luminescence efficiency of Er^{3+} in silicon is low due to the AE-mediated excitonic Auger recombination process. Also an Auger mechanism is found to be responsible for the nonradiative recombination of the excited $(Yb^{3+})^*$ ion in InP. In this process an electron is being captured by Yb^{3+} in an excited state; the electron trap is similar to that formed by Yb^{3+} in its ground state. It is further shown that in both cases the nonradiative mechanism can be blocked by microwave field, leading to enhancement of RE^{3+} ions luminescence.

Acknowledgments

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