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THE ROLE OF FREE CARRIERS IN THE LUMINESCENCE OF RARE EARTH IONS IN SEMICONDUCTING HOSTS

I. TSIMPERIDIS, T. GREGORKIEWICZ, and C.A. J. AMMERLAAN
Van der Waals-Zeeman Institute, University of Amsterdam
Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands

In the paper the influence of the free carrier concentration on the energy transfer from the semiconducting host to the RE ion, and on the subsequent relaxation of the excited RE core, is studied for InP:Yb and Si:Er systems. To this end the PL intensity quenching due to an increase of electron and lattice temperature and the PL decay characteristics are investigated.

1 Introduction

Rare earth (RE) ions imbedded in semiconducting hosts receive much attention due to their interesting physical properties and possible applications in optoelectronics and telecommunications. Photoluminescence (PL) of RE ions is due to internal transitions within the energy manifold of their incompletely filled 4f shell, split by the spin-orbit interaction and the local ligand field of the host crystal. Since the magnitude of the local field is small, the PL spectrum of a given RE ion is always observed in the same spectral range, regardless of the host. Due to the internal character of the transitions one expects also that the radiative recombination time τ_R of RE's is host- and temperature-independent. The experimentally measured thermal variations of the excited state lifetime are then generally attributed to the nonradiative component of the relaxation process, which can involve participation of free carriers.

The small magnitude of the RE ion interaction with the host crystal implies also that the energy transfer between the two, leading to the excited state of the 4f-shell, is complex. The actual excitation mechanism is subject to a considerable debate. For the two most investigated systems - Yb in InP and Er in Si - similar processes are usually considered. For Yb in InP a generally accepted model assumes that following an electron capture at an Yb-related electron trap, at approx. 30-40 meV below the bottom of the conduction band (CB), a pseudo acceptor system is formed with the secondary particle hole localized in the Coulomb field of the electron. A nonradiative recombination of the electron-hole pair with a simultaneous phonon emission leads to the Yb core excitation. Also for Er in Si a donor level is reported, but with a considerably bigger ionization energy of ~200-260 meV (Fz-Si), or ~150 meV (Cz-Si). Following an electron capture, the donor center converts into its neutral charge state and can bind an exciton. In a nonradiative recombination of the exciton the Er core excitation is achieved and the excess energy, of approx. 300 meV, is absorbed by the donor electron which is then removed into the continuum of states in CB.

Both above outlined excitation mechanisms depend crucially on the presence of free electrons. For InP:Yb an electron capture initiates the formation of a pseudo acceptor system; for Si:Er an electron capture is necessary for an exciton trap formation. Electrons are also important in the de-excitation process. For Yb in InP an effective shortening of the excited state lifetime by two orders of magnitude is commonly observed. This effect is ascribed to an effective Auger quenching of the core excitation. For Er in Si the situation is even more complex, as the lifetimes of the excited Er, but also the Er BE state intermediating the core excitation, can effectively be shortened by an Auger process. In a recently proposed model [1], which accounts well for experimental data, the effective lifetimes of both states are assumed to contain a term corresponding to an energy transfer to CB electrons: $(\tau)^{-1} = (\tau')^{-1} + c * n$, where c is a coefficient reflecting the efficiency of an Auger process, and n is the concentration of CB electrons.

2 Experimental Results and Discussion

In the paper the particular role of conduction electrons in the energy transfer mechanism for InP:Yb and Si:Er systems has been studied by investigating the changes of the PL intensity as induced by variation of electron and lattice temperature. Additional information has been obtained from the PL decay characteristics. Details on sample preparation can be found elsewhere [2].

2.1 Electron temperature effect

When a laser-illuminated sample is simultaneously exposed to a microwave field the heating of the electron gas takes place. The increased effective temperature of electrons might affect the recombination channels; this effect will be observed as a change of the intensity of individual bands of the total PL spectrum. In the experiment an increase of the RE-related PL upon application of microwaves has been observed for both studied systems. The effect can only partially be attributed to the blocking of the more shallow recombination channels due to impact ionization, and, consequently, a direct influence of the microwave field on the RE PL mechanism is concluded. Here two possible explanations can be postulated: blocking of the nonradiative recombination of the excited Yb core, and an increased efficiency of the exciton trapping by the Er-related donor level in the bandgap of Si [3]. Yet another possibility would be the effective blocking of the energy transfer from the Er BE to CB electrons. Regardless of the particular mechanism involved, the experimentally observed microwave field effect evidences a direct involvement of CB electrons in the PL mechanism of a RE ion in a semiconductor host.

2.2 Lattice temperature effect

It is well known that RE PL exhibits a very pronounced thermal quenching effect. Since the effective lifetime decreases at a higher temperature, the PL intensity quenching has to be ascribed to the lowering of the concentration of RE ions in an excited state. By studying the temperature dependence of the PL intensity the particular processes responsible for that effect can be identified by their individual activation energies.

For Si:Er the low-temperature quenching mechanism has been identified as the free exciton dissociation ($E_1 \approx 15$ meV), indicating importance of excitons in the process of the energy transfer from a Si crystal to Er. In the high temperature range the quenching mechanism was found to be characterized by a considerably larger activation energy $E_2 \approx 150$ meV. While it is possible to link the relevant process to the thermalization of an electron from the Er-related donor to CB [4], a more likely explanation interprets E_2 as the energy which is required for an electron in CB to initiate the *so-called* backtransfer process, in which the BE state is recreated at an expense of the core excitation. In addition to these two processes, for Cz-Si material a very significant quenching has been ascribed to a mechanism with an activation energy $E_3 \approx 2E_1$. It can be shown[5] that such an activation energy value is a fingerprint of an Auger process transferring energy from Er BE to electrons in CB. This experimental result confirms then the process whose existence has been assumed in the form of the effective lifetime of Er BE[1], as mentioned earlier, and illustrates the role of electrons in a promotion of relaxation paths alternative to Er-related PL and hampering its intensity.

2.3 PL decay measurements

A crucial role of free electrons in limiting the efficiency of the excitation mechanism can also be derived from the saturation behavior of the PL intensity in an oxygen-rich material with a high concentration of the optically active Er [1,5]. It is, however, best revealed by the Er PL decay measurements. Fig.1 compares the Er PL decay as measured upon a complete and a partial termination of the argon laser excitation. (In order to exclude possible saturation effects, small power has been used.) For the curve obtained in the dark a delay of approx. 0.08 ms of the decay onset can be noticed; it is illustrative of a consi-

Figure 1: Decay of Er-related PL without - upper curve, $\tau \approx 0.8$ ms, and with background excitation - lower curve, $\tau \approx 0.3$ ms, T=4.2 K.

derable lifetime of the BE state mediating the core excitation. Following that, a relatively slow decay with the time constant of $\tau \approx 0.8$ ms can be seen. When a background illumination (of approx. 50% of the original excitation power) is maintained, the decay curve is clearly changed - the delay practically disappears, and the decay time is shortened to ~0.3 ms. The effect depicted in Fig.1 shows that both characteristic lifetimes involved in the mechanism of Er PL in Si - that of the exited Er core and of the Er BE state - depend critically on the free carrier concentration[2], and can be shortened upon its increase. The presented evidence illustrates that electrons in CB have crucial role in the PL mechanisms of RE in semiconductors. Their presence influences both the excitation mechanism of the energy transfer from the semiconductor host to the RE, but also controls the reverse processes leading to the effective lowering of the PL intensity.

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