Electrical and optical properties of rare earth dopants (Yb, Er) in n-type III–V (InP) semiconductors

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Abstract. Rare earths (REs) diluted into MBE grown and synthesised n-type InP samples create an acceptor-like level (at 30 meV for Yb and 60 meV for Er) below the conduction band; the activation energies are deduced from temperature dependent Hall effect measurements. From EPR experiments where we observe resonance due to the Yb^{3+} ground state in n-type samples, we deduce that this acceptor-like level is not the Yb^{2+}/Yb^{3+} acceptor level. We propose that the RE creates an attractive potential for electrons in III–V semiconductors. We discuss the consequences of this property for the luminescence excitation mechanism of the luminescence.

In recent years a large number of studies have been devoted to the properties of rare earths (REs) diluted into semiconductors; this is because of their potential properties in opto-electronic devices. While spectroscopic photoluminescence (PL) and electron paramagnetic resonance (EPR) properties are now well documented (for a review see, for example, [1] and references therein), very little is known about RE electrical activity in III–V semiconductors. This problem is important, because it partly governs the mechanisms driving the RE luminescence. At low concentrations the REs give rise to a 'gettering' effect for shallow donor impurities, like silicon and sulphur [1]. It has been observed [2] that high levels of RE doping induce p-type conductivities: it was proposed that the acceptor level Yb^{3+}/Yb^{2+} would be near the top of the valence band (VB). This interpretation was strongly supported by theoretical calculations [3] which predict a hole binding energy of roughly 250 meV for the neutral Yb acceptor. In fact this p conductivity is due to contaminant acceptors, such as Mg and Ca, which are present in the RE source metal.

Recently, by using thermally dependent Hall (TDH) effect and DLTS measurements [4] it was found that in n-type MOCVD grown InP layers Yb introduces an acceptor-like level at 30 meV below the conduction band (CB). The authors proposed that this level would be the acceptor level Yb^{3+}/Yb^{2+}. However, we have recently shown by EPR measurements [5] that the Yb^{3+}/Yb^{2+} acceptor level is not in the band gap of InP. In order to resolve this apparent contradiction we have performed TDH experiments on the same samples as were used in our EPR experiments. We also generalise our results to Er-doped n-type InP samples: we find evidence for a RE related acceptor-like level near the bottom of the CB. It is proposed that the appearance of this electron trap level is related to the fact that the RE creates an attractive potential for electrons. Finally we discuss the

consequences of the presence of these acceptor-like levels on the RE related PL excitation mechanism.

Electrical properties were measured by the Van der Pauw method. The mobility and carrier concentration were obtained by TDH measurements. The photoluminescence (PL) due to RE^{3+} internal transitions was obtained with the samples fixed into a continuous He flow cryostat allowing a temperature variation in the range 2 K–300 K. The PL was excited by the 4880 Å line of an Ar^+ ion laser and detected by a liquid nitrogen cooled Ge detector associated with a lock-in detection. The RE (Yb and Er) concentrations were determined by spark source mass spectroscopy (SSMS) and secondary-ion mass spectroscopy (SIMS).

RE-doped InP samples were obtained in two ways:

(i) *InP (RE) synthesised crystals.* Taking into account the fact that the enthalpy of formation of the rare earth phosphorus (RE)P is much higher than that of RE(InP), the RE and indium are beforehand vacuum baked at 700 °C in a silica crucible to obtain In–RE alloy. Then InP(RE) crystal is grown by the high pressure gradient freeze method [6]. It is thought that this process prevents the formation of RE(P) if the RE concentration in as-grown InP is lower than its solubility limit.

The RE (Yb and Er) concentrations in as-grown InP crystals, as determined by SSMS and SIMS, depend on the RE content in the starting melt. For instance, when the Yb concentration in the starting melt (Yb_m) is 0.143 g per 100 g InP, the Yb content varies over the InP ingot in the range of [Yb] from 2×10^{16} to 10^{17} cm^{-3}. In this case SIMS investigations reveal that Yb is relatively well diluted in the ingot. However, increasing Yb_m up to 1.49 g per 100 g InP does not result in a Yb concentration in monocrystalline parts of the ingot higher than 10^{17} cm^{-3}. This value corresponds to the Yb solubility limit in InP.

Unfortunately, in synthesised InP:Er, we detect no Er with concentrations [Er] > 5×10^{15} cm^{-3} (the Er solubility limit in InP seems to be 5×10^{15} cm^{-3}), as we vary the Er concentration in the starting melt from 0.317 g per 100 g InP to 1.56 g per 100 g InP. We find that the absence of Er appears to be systematic in 'equilibrium' growth techniques and seems to be related to the higher temperature stability of Er phosphide as compared with Yb phosphide. In these synthesised InP samples the Er^{3+} related luminescence, at around 1.54 μm, was not detected.

(ii) *InP(Er) MBE grown layers.* Er doped InP epitaxial layers have been successfully obtained by the MBE technique. In order to perform TDH measurements a 10 μm thick Er doped InP layer was grown onto [001] oriented si-InP with a growth temperature of 495 °C and a growth rate of 2 μm h^{-1}. The Er concentration, measured by SIMS, was found to be at a level of 2×10^{19} cm^{-3}. The poor quality of the Er metallic source (4N) can explain the relatively high n-type concentration at 300 K. The fact that Er was diluted into InP material was attested to by the presence of the Er^{3+} related PL emission at around 1.54 μm.

All RE (Yb, Er) doped samples are n-type at room temperature. These effects have already been observed at $T = 300$ K [7] and it was deduced that REs are not electrically active. When the RE concentration, as determined by SIMS measurements, is higher than the residual doping level ($N_{DS} - N_{AS}$) the carrier concentration diminishes when T decreases. This fact has already been observed for MOCVD InP:Yb layers [4] and has been interpreted as being due to an acceptor-like level which is about 30 meV below the conduction band. The authors of [4] suggested that this level would be related to the Yb^{3+}/Yb^{2+} acceptor level. We have recently performed EPR measurements on
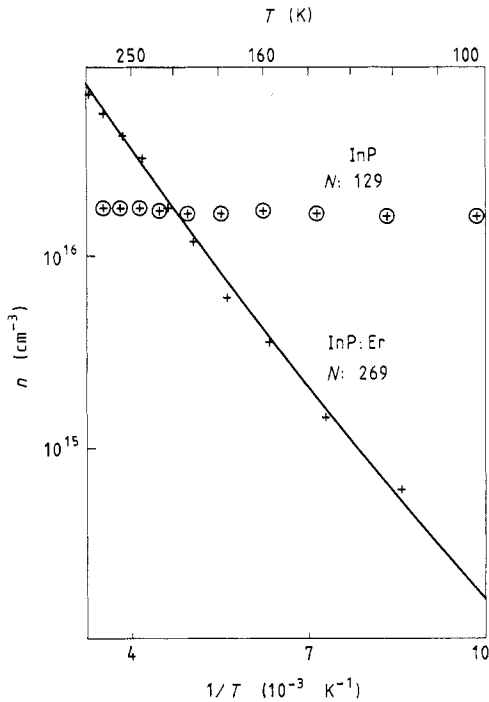
Figure 1. Temperature dependence of the electron concentration n for an MBE grown InP:Er layer (No 269) and an undoped InP layer (No 169). The crosses correspond to experimental measurements and the full curve to a fit to equation (1) with $N_{DS} - N_{AS} = 2 \times 10^{17}$ cm^{-3}, $N_A = 5 \times 10^{18}$ cm^{-3} and $E_{AC} = 60$ meV.
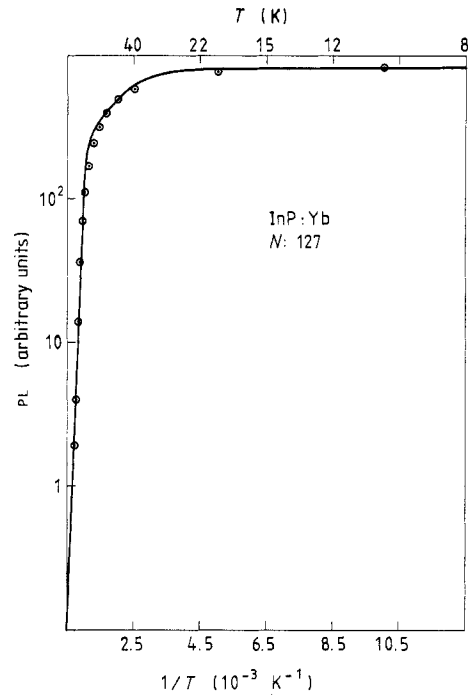
Figure 2. Semilogarithmic plot versus inverse temperature of the PL intensity. A fit of the data obtained using the analytical expression (3) is shown as the full curve. Fitting parameters: $E_1 = 115$ meV, $E_2 = 11$ meV, $A_1 = 4.7 \times 10^7$ and $A_2 = 3.2$.

synthesised n-type InP:Yb samples that rule out this model. In the same sample we detect *both* the EPR signal due to the neutral shallow donor D_S^0 (located at about 7 meV below the conduction band) and the Yb^{3+} ground state related EPR signal; this result indicates that it is not possible to locate the acceptor Yb^{3+}/Yb^{2+} state at 30 meV below the conduction band. How then is it possible to explain the acceptor-like behaviour of such a centre near the bottom of the CB? An explanation is that REs diluted into III–V semiconductors create a potential that is attractive for the electrons. The RE would act as an isovalent substituent which would create an electron trap [4]; at high temperature this trap is neutral and at low temperature when it has trapped an electron it is negatively charged. The origin of this electron trap is not known—is it due to a distortion of the InP lattice caused by the large RE mass or to differences in electron affinity [4]? It is a challenge for theoreticians to solve this problem.

The TDH measurements performed on our synthesised InP:Yb samples confirm that Yb is responsible for an acceptor-like level at 30 meV below the conduction band, the concentration of which is in reasonable agreement with Yb introduced into the sample [4]. In order to generalise this result we have performed TDH measurements on MBE grown InP:Er samples. The results are shown in figure 1; a plot of ρ or $nT^{-3/2}$ versus $1/T$ gives a straight line whose slope is $E_0 = 60$ meV. Also shown on figure 1 is the free

electron concentration for an undoped InP (No 129). This result indicates that Er behaves as Yb in n-type InP, and that Er doping induces an electron trap that acts as an acceptor level below the bottom of the conduction band.

In such a case we can compute $n(T)$; if the acceptor level is below the shallow donors and closer to the CB than to the VB (similar to the case for the iron acceptor level Fe^{3+}/Fe^{2+}), we obtain [8]

$$0 = n - (N_{DS} - N_{AS}) + nN_A/(n + \varphi_{AC}) \tag{1}$$

where N_A is the concentration of deep acceptors (Yb concentration) and N_{AS} and N_{DS} are the concentrations of shallow acceptors and shallow donors, respectively. Also φ_{AC} is defined [8] as the 'modified' density of states function

$$\varphi_{AC} = (g_{A0}/g_{A1})N'_C T^{3/2} \exp(-E_{AC}/kT) \tag{2}$$

where $N'_C = 2(2\pi m_n^* k)^{3/2}/h^3$ and E_{AC} is the acceptor ionisation energy with respect to the conduction band. For the computation we took $g_{A0}/g_{A1} = 2$ and an effective mass $m_n^*/m = 0.077$. The result is shown in figure 1 as a full curve; the best values for $N_{DS} - N_{AS}$ and N_A have been chosen: $N_{DS} - N_{AS} = 2 \times 10^{17} \, \text{cm}^{-3}$ and $N_A = 5 \times 10^{18} \, \text{cm}^{-3}$; with regard to the different hypotheses made, these results are in reasonable agreement with the different impurity concentrations determined by SSMS and SIMS. These electrical results indicate that REs introduced in n-type InP create a potential that is attractive to the electrons.

Now the following question arises: What are the influences of these RE properties on the luminescence emission? It is well known that neutral isoelectronic traps (for example N in GaP [9]) and deep impurities (e.g. Cu or Ag [10] in II–VI compounds) can trap excitons. We have looked carefully for such bound exciton related emission in our RE doped InP samples but we detect no such emission lines. This can be explained by the fact that bound excitons are often strongly coupled to the lattice and consequently their related lines are too weak to be detected.

The fact that at low temperature the RE related state traps electrons seems to be related to the PL properties of internal RE^{3+} transitions; it is well known in III–V compounds that the RE^{3+} PL intensity increases strongly when the temperature is lowered. The mechanism could be the following: at low temperature, carriers are trapped on RE related states and so the energy is more easily transferred to producing RE^{3+} internal transitions at the same lattice site where the energy transfers are known [11] to be very efficient—in other words we can say that excitons are bound to REs and transfer their energy to the REs. Our RE luminescence excitation model is strongly supported by the fact that it has been shown that carriers were needed to excite RE centres [2]. So the actual excitation might proceed by direct capture of electrons and/or holes; our explanation does not need the introduction of impact excitation by hot carriers as suggested in [2]. We have to note that at present we do not know whether REs show a potential attractive to the holes. It has to be realised that even if a potential attractive to holes is lacking, RE^{3+} luminescence excitation could occur: first, electrons are trapped and, secondly, holes are attracted by the negatively charged state.

We have studied the temperature dependence of the PL intensities related to the RE^{3+} internal transitions. The most complete results are obtained for InP : Yb and the results are reported in figure 2. The results can be fitted to the relationship

$$I(T) = I_0/[1 + A_1 \exp(-E_1/kT) + A_2 \exp(-E_2/kT)]. \tag{3}$$

Similar features have been observed by Klein [12] in Yb implanted Si-InP : Fe ($E_1 = $

115 meV, $E_2 = 11$ meV, $A_1 = 4.7 \times 10^7$ and $A_2 = 3.2$). We fit our results with the same activation energies but with different coupling coefficients ($A_1 = 2 \times 10^6$ and $A_2 = 9$). As already remarked by Klein [12], the fact that $A_2 \ll A_1$ indicates that quenching process 2 is mostly ineffective. At present, the origin of this weak quenching process is not understood. The dominant mechanism with $E_1 = 115$ meV has been suggested [12] to be related to the hole binding energy for the neutral Yb acceptor. Our EPR experiments [5] on n-type InP : Yb indicate that there is no Yb^{3+}/Yb^{2+} acceptor level in the InP band gap, so we have to reject this suggestion. A problem we have to solve is the following: arguments given above would imply that the thermal energy found in the variation of the PL intensity, $I(T)$, with temperature would be the same as the one found by TDH measurements. The two energies are not the same (30 meV and 115 meV respectively). For the moment, we have no explanation; perhaps the 115 meV activation energy is related to a potential attractive to holes. We hope that a complete study of electrical activity of REs in III–V semiconductors (in particular in p-type samples) will help in solving this important problem.

We have also studied the $PL(T)$ intensity variations of the main line related to Er^{3+} transition; the intensity variations can be fitted using the same law as given by the relationship (3). However, due to the lower signal to noise ratio a precise value for E_1 cannot be given; we can only indicate that $E_1 \gtrsim 100$ meV.

In conclusion, our results indicate that rare earths introduced in n-type InP (or other III–V semiconductors) create a potential attractive to electrons; the EPR results rule out the suggestion that this acceptor-like level is related to the RE^{3+}/RE^{2+} acceptor level. These level concentrations are in reasonable agreement with RE concentrations as deduced from SIMS and SSMS measurements.

Acknowledgments

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