Thermal quenching of luminescence in erbium doped semiconductors

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Abstract. The nature of the temperature dependence of luminescence intensity from Er\(^{3+}\) ions in GaInAsP, Si, InP, GaAs, AlGaAs, ZnTe, as observed by Favennec et al.\(^{1}\) has been examined in terms of a double exponential model. The smaller activation energy is found to be 58–100 meV, characteristic of a localized energy barrier at the Er\(^{3+}\) centre while the higher activation energy is approximately 0.8\(E\)\(_{g}\), attributed to an Auger non-radiative process of carrier excitation into bands. This model has been found to describe the observed temperature dependences with reasonably good agreement.

Keywords. Luminescence; rare earths; semiconductors.

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1. Introduction

There has been growing interest in rare earth (RE)doped III–V and II–VI semiconductors due to the uniqueness of optical and electrical properties of rare earth impurities in semiconductor hosts [1–11]. It is well-known that the wavelength (energy) of rare earth luminescence emission is insensitive to device processing and ambient temperature. Rare earth elements have partially filled 4\(f\)-shells which are deeply buried and screened by outer closed 4s\(^2\) and 5p\(^6\) orbitals that the energy levels of 4\(f\)\(^n\) configuration are only slightly perturbed compared to free ion energy levels. If the RE ions replace the element from column III in III–V compounds that are isovalent with respect to outer electrons of RE\(^{3+}\) ions, they create isoelectronic traps in III–V semiconductors. The luminescence emission arises from intraconfigurational \(f\)–\(f\) transition in the core of the isoelectronic impurities. The presence of low-lying empty core orbitals in rare earth impurities introduces new excitation and recombination phenomena.

Yb in InP replaces In on a substitutional site [7] and acts as an isoelectronic trap. It has been confirmed that the Yb ion creates an electron trap 30 meV below the conduction band [8]. Er implantation in InP has been observed to introduce electron traps 60 meV below the conduction band [9, 10] while in GaAs two hole traps occur 84 and 340 meV above the valence band. Rochaix et al. [5] observed that the Er\(^{3+}\) emission wavelength remains unchanged with a wavelength of 1.54 \(\mu\)m in binary, ternary and quaternary III–V semiconductors with band gaps ranging from 0.807 eV
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to 1.73 eV. This emission wavelength is also constant with temperature. Favennec et al [1] extended this work by incorporating the results of II–VI semiconductors.

In this paper we have attempted to describe the variation of Er$^{3+}$ emission intensity against temperature as observed by Favennec et al [1]. They used single crystal substrates of Si, GaAs, InP, ZnTe as host bulk material, while for the alloys epitaxial layers of AlGaAs, GaInAsP were used. Implantation of Er ions was carried out at room temperature using a beam making an angle 7° with the normal to the sample surface. The beam energy was 330 keV and doses varied from $10^{13}$ to $10^{14}$ Er$^+$ cm$^{-2}$. After implantation, samples were annealed using rapid thermal annealing technique. The photoluminescence emission intensity at 1.53 μm was measured vs. temperature between 77–400 K. To the best of our knowledge, these results have not been explained before quantitatively.

2. Model

Variation of Er$^{3+}$ emission intensity against temperature in Si, GaAs, InP, ZnTe, AlGaAs, GaInAsP shows that the intensity of emission for all the semiconductors is high at low temperatures. However, at higher temperature the intensity depends strongly on the nature of the host semiconductor. It has been observed that narrower the band gap the faster the decrease of luminescence intensity with temperature and the weaker the intensity at higher temperatures.

The most probable non-radiative mechanism quenching the rare earth luminescence in III–V semiconductors is the Auger energy back-transfer mechanism [12]. The rare earth excited isoelectronic trap occupied by an electron or exciton can transfer energy to the trapped electron and exciton rather than to the radiative field. The electron is consequently ejected deep into the conduction band. If the RE isoelectronic trap is $E_n$ eV below the conduction band of the host material the intensity of emission ($\eta$) can be expressed as function of temperature ($T$) following the relation

$$\eta = \frac{1}{1 + \Sigma_n C_n \exp (-E_n/kT)}$$

(1)

Lozykowski [12] has recently carried out a detailed analysis of the kinetics of luminescence in rare earth doped III–V compounds considering a variety of models. He has also involved an Auger mechanism of non-radiative energy transfer. The final expression used to explain thermal quenching however is of the form given by (1). This has been used to explain luminescence of Yb in InP [13].

3. Results

Figures 1–6 represent experimental data along with the theoretical data (solid line) as predicted by the relation (1). These figures indicate that (1) explains reasonably well the nature of temperature dependence of Er$^{3+}$ emission intensity for various host semiconductors. The deviation of the theoretical data with respect to the experimental data is slightly more in the high temperature range. The fitted parameters corresponding to various semiconductors are listed in table 1.
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Figures 1–6. Plot of emission intensity vs $1/T$ of Er$^{3+}$ ions in GaInAsP, Si, InP, GaAs, AlGaAs, ZnTe hosts respectively. Experimental data are indicated by the discrete points while solid lines indicate the theoretical data as predicted by relation (1).
Table 1. List of fitted parameters $C_1, E_1, C_2, E_2$ of relation (1) corresponding to different host materials.

<table>
<thead>
<tr>
<th>Hosts</th>
<th>$E_g$ (eV)</th>
<th>$C_1$</th>
<th>$E_1$ (eV)</th>
<th>$C_2$</th>
<th>$E_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaInAsP</td>
<td>0.807</td>
<td>40</td>
<td>0.0600</td>
<td>100</td>
<td>0.65</td>
</tr>
<tr>
<td>Si</td>
<td>1.120</td>
<td>40</td>
<td>0.0580</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>InP</td>
<td>1.270</td>
<td>40</td>
<td>0.0650</td>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.430</td>
<td>30</td>
<td>0.0675</td>
<td>10</td>
<td>1.30</td>
</tr>
<tr>
<td>AlGaAs</td>
<td>1.670</td>
<td>40</td>
<td>0.0720</td>
<td>200</td>
<td>1.40</td>
</tr>
<tr>
<td>ZnTe</td>
<td>2.260</td>
<td>40</td>
<td>0.1000</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

The fitted parameter $E_1$ (0.065 eV) for InP and $E_2$ (1.3 eV) for GaAs are consistent with the reported data [9, 10] of electron and hole trap levels in InP and GaAs respectively. It is found that the $E_1$ values increase very slowly with band gap, with the slight exception of Si. These values varying from 58–100 meV represent energy barriers to ejection of electrons from the excited state of Er$^{3+}$ as in a configuration coordinate model. Multiphonon emission has been shown to have low probability as a non-radiative energy transfer mechanism.

At relatively high temperatures, a different mechanism viz. Auger energy back transfer as postulated by Lozykowski [12] comes into play with $E_2$ for GaInAsP, InP, GaAs, AlGaAs being of the order of 0.8 $E_g$. These energies represent those required for non-radiative energy transfer from Er$^{3+}$ to carriers in bands in the semiconductors. It is observed that a single exponential model is adequate to explain the data for Si and ZnTe in this temperature range but not much significance can be attributed to this, although of these materials, Si has the only indirect gap and ZnTe is the only $p$-type material.

It is observed that there is not much variation in the pre-factor $C_1$ between the different semiconductors but the pre-factor $C_2$ varies strongly between the binary and the alloy semiconductors. This indicates that the nature of the localized centre is very similar in all these materials but the nature of the non-radiative mechanism at high temperatures is different, possibly due to additional defects in the alloys.

In conclusion, the nature of temperature variation of Er$^{3+}$ emission for various semiconductors and alloys has been described quantitatively using a double exponential model with reasonably good agreement. The thermal quenching mechanisms involve localized centres at low temperatures and Auger mechanism at high temperatures.

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References

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