PHOTOLUMINESCENCE AND KINETIC OF MOCVD GROWN P-TYPE GaAs:Nd AND Nd-IMPLANTED SEMI-INSULATING GaAs.

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To my parents, brothers & sisters
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CHAPTER 1
RARE EARTH ISOELECTRONIC TRAP

1.1 Introduction

The study of rare earth (RE) elements incorporated into Group III-V and Group IV semiconductor is of current interest due to their potential applications in optoelectronics and photonics in the visible and near infrared spectral region. Although the luminescence properties of RE (4f) ions in solids have been studied in great detail for decades, the research was almost entirely concerned with the optical properties of 4f ions in dominantly ionic host crystals such as fluorides and oxides [1 & 2]. To a lesser extent, luminescence of 4f ions in more covalently bonded hosts, such as tetrahedral II-VI semiconductors has also been investigated [2]. However, in spite of their potential as 4f-doped light-emitting diodes (LED) and lasers, it was not until the early 1980s that the luminescence properties of 4f-ions in III-V semiconductors and silicon were investigated to any significant extent.

The doping of III-V compound semiconductors, such as gallium arsenide (GaAs), gallium phosphide (GaP), and indium phosphide (InP), and silicon (Si) with such RE elements as ytterbium (Yb), erbium (Er) and neodymium (Nd) allows for sharp optical transitions, with accompanying narrow line-widths [3]. The emission wavelengths are not determined by the host semiconductor bandgap but the transition energies within the 4f levels of the RE ion. Because the 4f shell is well-shielded from the external environment by filled 5s and 5p shells, these transition energies tend to be only weakly
affected by the presence of the external perturbations. Thus, a RE doped semiconductor source would be compatible with integrated optics applications, as this laser medium may be incorporated into any host material, and the emission wavelength is relatively insensitive to the host material [4] or temperature [5].

Recent developments in this new research area could result in light-emitting diodes (LED) and perhaps a wide array of injection lasers which would operate with much narrower line width in those spectral regions important to present silica based fiber optics. Both Whitney [5] and Rolland [6] reported the fabrication of Er-doped GaAs LEDs operated at 1.54 μm; Haydl et al. (7) and Dmitrieve et al. [8] reported on Yb-doped InP LEDs emitting at 1.0 μm. Among the RE ions, Nd has stimulated wide spectroscopic interest in the past, mainly because of its intense luminescence which also enables laser operation in the near infrared. Before we go into a detailed discussion of RE ions in III-V semiconductors, one should have a background in the nature of the semiconductors and conduction process in solids. Next section provides the concepts and fundamentals of semiconductor materials and processes of radiative and nonradiative transition.

1.2 Basic review of solid state physics

1.2.1 Band structure

Semiconductors are materials that have electrical conductivity intermediate between insulators and metals. Their conductivity can be varied in many orders of magnitude by changing temperature, optical excitation and impurity content. Every solid
has its own characteristic energy band structure, valence band and conduction band (Fig. 1), and this variation in band structure is responsible for the wide range of electrical characteristics observed in different materials. At $0^\circ$ K, a semiconductor material has its valence band filled with electrons and its conduction band empty. Semiconductor materials, unlike insulators, have relatively small bandgaps ($E_g$) that allow electrons to be excited from the valence band to conduction band by reasonable amount of excitation energy.

![Figure 1: Typical band structure of a semiconductor.](image)

1.2.2. Radiative transitions

In this section a comprehensive survey of the known electron-hole (e-h) radiative recombination mechanisms will be explained. Luminescence emission involves radiative transitions between electronic energy levels of the material, and the emission is
characteristic of the material. Electron hole recombinations usually occur predominantly at impurities or lattice defects, either introduced intentionally or otherwise, but radiative intrinsic interband e-h recombinations, which occur in perfect crystals, have been observed. When an electron makes a transition from valence band to conduction band (Fig 2a), the transition may occur radiatively (emitting photon) or non-radiatively (no emission of photon). In direct bandgap semiconductors when an electron from the conduction band (CB) recombines with a hole in the valence band (VB), it emits a photon. This process is called band to band recombinations or transitions (Fig. 2b).

![Diagram](image)

**Figure 2:** Radiative recombination processes. (a) e-h pair generation, (b) band to band recombination, (c) free electron to bound hole at acceptor level, (d) bound electron at donor level to free hole, and (e) donor acceptor recombination.
Radiative transitions may occur between an impurity level and a band, for example, transition between CB and acceptor level (Fig. 2c), and donor to VB (Fig. 2d). When an electron from the donor energy level recombines with a hole in the acceptor energy level, it is called donor-acceptor transition (Fig. 2e). The emitted photon energy due to this transition is described by the following equation.

\[ h\nu = E_g - (E_d + E_a) + \frac{q^2}{\epsilon r} \]  

(1)

where \( E_g \) is the bandgap in eV, \( E_d \) is donor energy level in eV, \( E_a \) is acceptor energy level in eV, \( q \) is the electron charge in Coulomb, \( \epsilon \) is the dielectric constant, and \( r \) is the separation between the donor and acceptor in nanometer.

1.2.3. Non-radiative transitions

A. Phonon emission

A non-radiative transition occurs when an electron makes a transition from an upper state to a lower state without emitting photon. Such a process has a low emission efficiency. An electron can make a transition from a higher energy level to a lower energy level by emitting or absorbing a phonon. A phonon is the elastic wave of the lattice vibration. If the energy gap between the two levels is high enough then this non-radiative process is less probable.

B. Auger effect

The Auger process occurs when a recombining electron transfers its energy to another electron, causing it to move to a higher energy state. This excited electron then will return to a lower energy state by the multiple phonon emission mechanism. As we can see from Figure 3, energy transfer is not confined only to particles in the same state.
Auger energy transfer processes involving three particles, for example, two electrons and a hole (for n-type semiconductors), or an electron and two holes (for p-type semiconductors) are shown by the dashed arrow in Figure 3.

As mentioned in the introduction, a RE doped III-V semiconductor is of particular interest due to its sharp, independent of host, and temperature stable emission lines. Since the main topic of this thesis is about photoluminescence of rare-earth impurity doped semiconductors, we must know the definition of isoelectronic impurities and their
electronic properties in III-V semiconductors. Also, some theories of isoelectronic trap will be discussed in Section 1.4.

1.3 Isoelectronic impurities

Isoelectronic impurities are substitutional impurities which have the same valence electron structure as the atom they replace. Therefore, isoelectronic impurities are neutral impurities in the semiconductor host crystal. For example, oxygen (O\(^{2-}\)) impurities in zinc tellurium (ZnTe) semiconductor replaces Te\(^{2-}\) and creates an isoelectronic trap [9]. The electronic configurations of Te\(^{2-}\) and O\(^{2-}\) are:

\[
\begin{align*}
\text{O}^{2-} & : \quad [\text{He}] 2s^2 2p^2 \\
\text{Te}^{2-} & : \quad [\text{Kr}] 4d^{10} 5s^2 5p^2
\end{align*}
\]

From the electronic configuration we can see that both O\(^{2-}\) and Te\(^{2-}\) have the same valence electron in the outer shell. But the total number of electrons of the atom to be substituted and the substitutional isoelectronic impurity differ, sometimes by a large amount.

According to Thomas [9], there are two classes of isoelectronic impurities. One is isoelectronic impurities of the first kind which give rise to discrete levels (bound exciton state) in the forbidden gap (energy level between the valence band and conduction band). The second is the isoelectronic impurity of the second kind which produce band states. The isoelectronic impurities of the second kind are more abundant in nature than isoelectronic impurities of the first kind. Due to the interest of this paper only first case will be discussed here. The isoelectronic impurities which produce localized states within the band gap are called “isoelectronic traps”.

Since isoelectronic traps are neutral, according to Hopfield and Thomas [10], they can be attractive either for electrons and holes and become negatively or positively charged trap, respectively. By long range Coulomb interaction charged trap will capture a carrier of opposite sign [9] and this leads to creation of exciton bound to the isoelectronic trap. When an electron and a hole orbit each other in a crystalline solid at distances large compared with atomic dimensions, it is called exciton. Exciton bound to the isoelectronic trap is shown by an ellipse in Figure 4.

![Figure 4: Bound exciton due to the isoelectronic trap.](image)

The striking feature of excitons bound to isoelectronic traps is a long luminescence decay time, ranging from a few hundred to few thousands nanoseconds. The lifetimes of a neutral donor or acceptor bound excitons in the direct-gap semiconductors are in the range of nanoseconds. For example, the decay time of excitons bound to neutral donors or acceptors in InP are 0.5 and 1.5 ns, respectively [11]. The lifetime of an exciton bound to a neutral donor in GaAs is 1.07 ns [12]. By contrast, the lifetime of an exciton bound to a Bi isoelectronic trap in InP is about 200 ns [13]. If the isoelectronic traps are bound strongly, the wave function of the second carrier bound will be acceptor-like for an electron trap or donor-like for a hole trap. For example, O in ZnTe creates an
iso-electronic electron trap, whereas bismuth (Bi) in gallium phosphide (GaP) creates a hole trap [9].

So far, we have discussed the formation of isoelectronic traps when an isoelectronic impurity substitutes for the anion sites. However, isoelectronic impurities on cationic sites exist. Recently it has been established that ytterbium (Yb) in indium phosphide (InP) replaces indium on a substitutional site and creates an 30 meV isoelectronic electron trap below the conduction band (Fig. 5a). Also, recent studies show that erbium (Er) in InP [14a] and Yb in GaAs [14b] create isoelectronic electron traps at 60 and 63 meV below the conduction band. According to Taniguchi [15] the isoelectronic trap level in GaAs:Nd is about 80 - 120 meV below the conduction band (Fig. 5b).

\[ Eg = 1.344 \text{ eV} \quad \text{at 300 K} \]

\[ Eg = 1.424 \text{ eV} \quad \text{at 300 K} \]

Figure 5: Isoelectronic trap level in (a) InP:Yb and (b) GaAs:Nd.
1.4 Theory of isoelectronic traps

First, Faulkner [16] attempted to give a detailed theoretical study of the isoelectronic trap N in GaP. In his study the impurity potential was assumed to be the difference in the atomic pseudopotentials of nitrogen and phosphorus. According to Faulkner the interaction between charge carriers and impurities is due to a potential derived as the difference between the pseudopotentials for nitrogen and phosphorus. But the theoretical binding energy (1 eV) was 100 times larger than observed from the experimental data. According to Phillips [17] the lattice deformation will practically compensate the binding forces due to the pseudopotential difference, and therefore, will considerably reduce the binding energy. However, Allen [18] proposed that the difference of the pseudopotentials of any two isoelectronic atoms practically vanishes unless one of the atoms comes from the first row of the periodic table. Therefore, in general, the isoelectronic impurity potential does not come from pseudopotential difference. The concept of electronegativity rule appears to be successful for some experimental data stated in Czaja’s article [9]. Using the electronegativity rule, an isoelectronic impurity may bind a hole (electron) only if the electronegativity is smaller (larger) than that of the host atom it replaces. Using this rule for the isoelectronic impurities on cation site's example (InP:Yb), we see from Table I that the electronegativity of In and Yb are 1.78 and 1.10, respectively. According to electronegativity rule Yb impurity in InP introduces an acceptor-like electron trap. But the weakness of the electronegativity rule is that it does not indicate which systems actually have a bound state.
1.5 Properties of Rare-Earth (RE) ions

The rare-earth or lanthanide ions all have relatively similar chemical and physical properties, and their atomic numbers range from 58 to 71 inclusive, commencing with cerium (58) and ending with lutetium (71). The chemical properties are similar because the outer electron shells are identical in the 5s\(^2\) 5p\(^6\) configuration; the differences in the elements result from the filling of the 4f shells. Table I shows the electron configuration of RE atoms, RE\(^{3+}\) ions with their ionic and covalent radius, and Pauling’s electronegativity.

Table I: Electron configuration of RE atoms, RE\(^{3+}\) ions (and some elements), ionic, covalent radii, and electronegativity.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron configuration</th>
<th>Electron configuration of RE(^{3+})</th>
<th>Ionic radius (Å) charge (3+)</th>
<th>Covalent radius (Å)</th>
<th>Electronegativity (Pauling’s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium</td>
<td>4f(^2)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^1)5s(^2)5p(^6)</td>
<td>1.02</td>
<td>1.65</td>
<td>1.12</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>4f(^3)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^2)5s(^2)5p(^6)</td>
<td>1.00</td>
<td>1.65</td>
<td>1.13</td>
</tr>
<tr>
<td>Neodymium</td>
<td>4f(^4)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^3)5s(^2)5p(^6)</td>
<td>0.99</td>
<td>1.64</td>
<td>1.14</td>
</tr>
<tr>
<td>Promethium</td>
<td>4f(^5)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^4)5s(^2)5p(^6)</td>
<td>0.98</td>
<td>1.63</td>
<td>1.13</td>
</tr>
<tr>
<td>Samarium</td>
<td>4f(^6)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^5)5s(^2)5p(^6)</td>
<td>0.97</td>
<td>1.62</td>
<td>1.17</td>
</tr>
<tr>
<td>Europium</td>
<td>4f(^7)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^6)5s(^2)5p(^6)</td>
<td>0.97</td>
<td>1.85</td>
<td>1.20</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>4f(^8)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^7)5s(^2)5p(^6)</td>
<td>0.97</td>
<td>1.61</td>
<td>1.20</td>
</tr>
<tr>
<td>Terbium</td>
<td>4f(^9)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^8)5s(^2)5p(^6)</td>
<td>1.00</td>
<td>1.59</td>
<td>1.20</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>4f(^10)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^9)5s(^2)5p(^6)</td>
<td>0.99</td>
<td>1.59</td>
<td>1.22</td>
</tr>
<tr>
<td>Holmium</td>
<td>4f(^11)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^10)5s(^2)5p(^6)</td>
<td>0.97</td>
<td>1.58</td>
<td>1.23</td>
</tr>
<tr>
<td>Erbium</td>
<td>4f(^12)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^11)5s(^2)5p(^6)</td>
<td>0.96</td>
<td>1.57</td>
<td>1.24</td>
</tr>
<tr>
<td>Thulium</td>
<td>4f(^13)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^12)5s(^2)5p(^6)</td>
<td>0.95</td>
<td>1.56</td>
<td>1.25</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>4f(^14)5s(^2)5p(^6)6s(^2)</td>
<td>4f(^13)5s(^2)5p(^6)</td>
<td>0.94</td>
<td>1.74</td>
<td>1.10</td>
</tr>
<tr>
<td>Gallium</td>
<td>3d(^10)4s(^2)4p</td>
<td></td>
<td>0.62</td>
<td>1.26</td>
<td>1.81</td>
</tr>
<tr>
<td>Indium</td>
<td>4d(^10)5s(^2)5p</td>
<td></td>
<td>0.81</td>
<td>1.44</td>
<td>1.78</td>
</tr>
</tbody>
</table>

The electronic configuration [Pd] 4p\(^5\)s\(^2\)5p\(^6\) may also be used as it is more illustrative in showing the 5s and 5p shielding. The shielding of the f-electrons from the interaction
with the environment is important in determining the spectral characteristics of the rare earth. The sharpness of the RE emission is the result of the lack of interaction between the f-levels and the 4f-orbitals from the crystalline or amorphous surroundings such that the spectrum is very similar to that free atom.

From the table we see that the electronegativity of rare-earth elements is in the range of 1.1-1.25, and is smaller than Ga (1.81) and In (1.78) for which it substitutes. According to the discussion in Section 1.3 and from different investigations we know that Yb substitutes In in an InP crystal and creates an isoelectronic trap. The rare-earth ions in III-V semiconductors can occupy different sites rather than substitutional. The rare-earth isoelectronic trap must not necessarily be the "pure" substitutional center, if the rare-earth ions are very active chemically, they can create a more complex center involving other impurity or native defects. The important roles of oxygen on RE luminescence have been discussed recently [19]. For example, from the experiment, it was noticed that Er-O complexes seemed to be formed in GaAs:Er [19]. Clearly, more experimental and theoretical investigations are required to be familiar with the electrical activities of RE ions in semiconductors.

1.6 Restrictions of 4f transitions

As mentioned before in RE doped semiconductors, we are interested in 4f transition rather than band to band, because their emission lines are sharp, and independent of the nature of the host material, and the emission lines do not dependent on temperature. Since transitions between ground and excited states are governed by the selection rules not every possible transition occurs as an optical transition. Two
important selection rules, which should be obeyed for optical transition are stated in the following:

1. The spin selection rule forbids electronic transitions between levels with different spin states ($\Delta S \neq 0$).

2. The parity selection rule forbids electronic (electric-dipole) transitions between levels with the same parity; examples are electronic transitions within the $d$-shell, within the $f$-shell, and within the $d$ and the $s$ shells.

Therefore, electric-dipole transitions between $4f$ levels of RE are strictly forbidden, because the parity does not change (Laporte’s selection rule). The parity prohibition can be lifted by the influence of the crystal lattice. If the RE ion is located at a site that is a center of symmetry in the crystal lattice, the parity prohibition cannot be lifted and only magnetic-dipole transitions are allowed. For RE ions residing in a lattice site lacking inversion symmetry, such as semiconductors with $T_d$ symmetry, the parity prohibition can be canceled by mixing the $4f^n$ configuration with a state possessing a different parity. Typically, the lifetime of the magnetic-dipole transition is $10^4 - 10^5$ times longer than the lifetime of a level that recombines via an allowable electric-dipole transition. In InP:Yb and GaAs:Nd semiconductors the radiative lifetime at low temperature is in the range of 12 $\mu$s and is probably dominated by electric-dipole transition.

1.7 Objective of the research

In this project we have investigated the photoluminescence of Nd-implanted semi-insulating GaAs at 9K after annealing at 750 °C for different times. The luminescence
kinetics of p-type GaAs:Nd was analyzed at 2K.* In the second part of this project, we developed a kinetic model for p-type semiconductors doped with RE which describes energy transfer and recombination processes. A similar model was proposed by Lozykowski [20] for semi-insulating and n-type semiconductor. We solved the set of kinetic differential equations by numerical method to derive the dependence of the rise and decay kinetics for different excitation intensities. The calculated rise and decay was then fit to the experimental data obtained for p-type GaAs:Nd. By fitting the calculation to the experimental data we can estimate important parameters related to energy transfer from the lattice to RE$^{3+}$ centers, the Auger processes, and temperature quenching mechanisms. A temperature dependence due to the quenching centers was incorporated in the model. Other quenching mechanisms, which are not included in the model but may be responsible for nonradiative decay, are discussed briefly [21].

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* This experiment was performed by H. J. Lozykowski at NTT Basic Research Laboratory, Tokyo.
CHAPTER 2
PHOTOLUMINESCENCE OF Nd-IMPLANTED SI GaAs AND
PHOTOLUMINESCENCE KINETIC OF MOCVD GROWN P-TYPE GaAs:Nd

2.1 Introduction

Photoluminescence was the main investigating technique used in this study. It is a spectroscopic technique that allows the identification of various electronic states in the solid state. Photoluminescence in semiconductors occurs in general as the result of above bandgap excitation of the material, with coherent or incoherent light, and the subsequent recombination of electrons and holes with the simultaneous emission of photons. But as mentioned before in the case of rare earth doped semiconductors, we are interested in the internal emission of the 4f shell rather than electron-hole recombination. Therefore, it is necessary to understand the mechanisms responsible for the rare earth 4f shell excitations. Excitation spectroscopy of the internal RE 4f transitions revealed several possible mechanisms for RE excitation. Among these are:

(1) direct excitation, when a RE 4f shell is excited directly using an infrared tunable laser. For example, we know that luminescence of Nd\(^{3+}\) at \(\sim 0.92\ \mu\text{m}\) arises from the \(^{4}F_{3/2} \rightarrow ^{4}I_{9/2}\) transition. Therefore, it is possible to excite the neodymium 4f shell by a tunable LiF:F\(^+\) color center laser with wavelength range 880-920 nm. In fact, this experiment was done by Wagner [28].

(2) indirect excitation, when a RE 4f shell is excited by the nonradiative energy transfer from the host to the core states. Assuming that the isoelectronic trap is an
electron trap such as Yb$^{3+}$ in semi-insulating InP (see Fig. 5a), the annihilation energy of bound electron to the free hole on the valence band can excite the 4f core states. The bound electron may create a bound exciton (BE), attracting a hole from the valence band, and that BE energy can be transferred nonradiatively to excite the ground state electron of the 4f core states. These processes indirectly excite the 4f core states above bandgap excitation. The detailed study of this process will be discussed in Section 3.2.

Deexcitation of the 4f transitions can be radiative and nonradiative. So luminescence quenching mechanisms, which divert crystal energy away from the 4f shell or cause nonradiative deexcitation of the excited RE, are also of interest and thus discussed in Section 3.2.

In this experiment, both semi-insulating and p-type GaAs doped with neodymium (Nd) were excited indirectly above band gap (excitation process 2) to observe rare earth luminescence. Kasatkin [22] was the first to address the excitation mechanisms of REs in III-V compounds by measuring the excitation spectra of ytterbium (Yb$^{3+}$) and DAP emissions in GaP:Yb and InP:Yb. In GaP he found that the excitation spectra of Yb$^{3+}$ -4f emissions exactly mirrored the excitation spectra of the DAP in the range of 2.3 to 2.6 eV. Photoluminescence spectroscopy allows us to identify the transition of energy levels for interested impurities in the crystal.

However, time dependent photoluminescence kinetics measurements give information about the energy transfer processes from the host to the RE core states, the lifetime of an electron in the excited state of 4f orbital, and radiative and nonradiative processes. It is shown that the study of the rise time at different excitation intensities can
provide important information about the energy transfer processes from the host lattice to the rare earth core states. The most common method of performing such experiments involves monitoring the rise and decay of the sample emission while exciting it with a pulsed or modulated excitation. As a result of such measurements, models will be proposed which describe the system kinetics after the excitation pulse and also allow for the determination of the magnitude of important parameters that are responsible for energy transfer processes from the host to the RE core states during the excitation pulse. Some of these processes will be further examined by performing excitation intensity dependent measurements. In this research we have investigated photoluminescence rise and decay as a function of excitation intensities for p-type GaAs:Nd.

2.2 Background

Among the rare-earth (RE) ions, neodymium Nd$^{3+}$ (4f$^3$) has stimulated wide spectroscopic interest in the past, mainly because of its intense luminescence that also enables laser operation in the near infrared. That work, however, strongly concentrated on the luminescent properties of Nd in dominant ionic hosts, such as Y$_3$Al$_5$O$_{12}$ (YAG) (for review see ref. [23]). In addition early attempts have been reported [24] to incorporate neodymium by ion implantation into classical semiconductors such as GaAs. This was done presumably with the intention to excite the characteristic intra 4f-shell luminescence of Nd$^{3+}$ (4f$^3$) by minority-carrier injection in an Nd-activated p-n junction. The results were discouraging since no Nd-specific photoluminescence could be observed [24].
However, recent investigations have shown that intra-4f-shell luminescence of rare-earth elements can, in fact, be optically excited in properly RE-doped III-V semiconductors as well as in RE-doped silicon [25]. The first observation of intra-4f-shell luminescence for Nd-implanted GaAs was reported by Muller [26] and confirmed by others. The complete PL spectrum of Nd-implanted, recorded by Lozykowski, is shown in Figure 6. Figure 7 shows the 4f transition of each set of Nd emission lines.

![Figure 6: Complete PL spectra of Nd$^{3+}$ in GaAs.](image)

These emission lines correspond to the Nd$^{3+}$ ion intra-4f-shell transitions $^4F_{3/2} \rightarrow ^4I_{13/2}$ at 0.9 eV, $^4F_{3/2} \rightarrow ^4I_{11/2}$ at 1.1 eV, and $^4F_{3/2} \rightarrow ^4I_{9/2}$ at 1.346 eV respectively. Sharp luminescence spectra due to the intra-4f shell transitions of Nd were observed in GaAs [26 & 27], and GaP [26 & 28]. In all of their experiments, the spectra were complex,
suggesting the presence of at least two Nd centers. Unfortunately, there are no experimental data that could help us resolve the structure of the Nd centers. In particular, substitutional location of the Nd atoms has not been proved.

![](image)

Figure 7: Energy level scheme and radiative transition of Nd$^{3+}$. Note higher energy level above $^4F_{3/2}$ are not shown.

In this research two different samples of GaAs:Nd were investigated to observe the Nd$^{3+}$ emission. From figure 6 we see that three sets of Nd$^{3+}$ emission lines occur in the infrared region. But we were able to observe one set of emission line ($^4F_{3/2} \rightarrow ^4I_{9/2}$) located in the nearest infrared region. This is because our detector can detect up to 1100 nm. Neodymium (Nd$^{3+}$) emission was observed for Nd-implanted semi-insulating GaAs (sample A) at 9 K after annealing at 750 °C for different time. Also, photoluminescence kinetic was investigated for p-type GaAs:Nd (sample B) at 2 K.
2.3 Ion implantation and annealing

Ion implantation is a common technique of doping in semiconductors in which high-energy ions are projected onto the wafer surface. The principle advantages of doping by ion implantation are: (1) it is possible to introduce into the lattice a single impurity type only, and (2) it is possible to define accurately both the area and the depth of the implanted region. The impurity is initially ionized through various techniques and is accelerated through a high potential. The ions are directed in a nonchanneling direction to ensure that their collision with the host lattice and their energy determine the average penetration depth. The distribution of the ion is controlled through the mass of the implant ion, the potential field, and the implant time. The depth from the surface to which the impurity ion comes to rest is calculated by integrating the energy loss along the path of the implanted atom. The distribution of the implanted atoms in the wafers can be described by both Pearson and Gaussian distributions. Using these distributions, we can simulate how the impurity concentrations are distributed over distance from the surface.

The damage caused by the high-energy ions during implantation makes the material almost amorphous. To restore single crystal structure and to remove the defects, the implanted wafer is annealed. During this process the samples are heated to high temperature (typically 700 °C to 1000 °C) through various techniques (e.g., conventional and rapid thermal annealing) so that the damaged layer may reorder itself and aid the impurity in moving into its proper site. Rapid thermal annealing is the common technique to activate implanted dopants in both GaAs and InP crystals. In this case
typical annealing times are a few seconds to few a minutes. We have used this annealing
technique to anneal our Nd-implanted semi insulating GaAs samples.

2.4 Photoluminescence of Nd-implanted SI GaAs

2.4.1 Sample description

The material used for Nd implantation was semi-insulating (SI) GaAs doped with
crchromium (Cr) with the concentration of (0.1 - 2.0)×10^{16} \text{ cm}^{-3}. The semi-insulating GaAs
wafers, one side polished, were provided by Wacker-Chemitronic GmbH (Germany). Nd
was implanted in the polished side of the sample grown in the <100> direction. The
implantation process was performed at Lawrence Berkeley Laboratory, California.
Implantation was performed at room temperature (RT) with an energy of 150 keV and a
dose of 7.5×10^{13} \text{ ion/cm}^2. The Pearson (Fig. 8a) and Gaussian distributions (Fig. 8b) of
Nd^{3+} ion in the GaAs crystal were simulated in the computer using PROFILE software to
see the surface thickness of Nd^{3+} ion layer in the sample. From the simulated profiles it
can be noticed that the maximum Nd^{3+} ion concentrations occur at 409 \text{ Å} (for Gaussian
distribution) and 363 \text{ Å} (for Pearson distribution) from the surface. At these depths the
maximum Nd concentrations are 1.59×10^{19} and 1.52×10^{19} \text{ ion/cm}^3, respectively. At
greater depths the concentration of neodymium ion decreases. From Figure 6a we see
that at 800 \text{ Å} Nd concentration is about 1.2×10^{18} \text{ ion/cm}^3. Therefore, with such a low
implantation energy (in our case 150 keV) the penetration depth of Nd ion in GaAs is
low, and after the annealing process the implanted region may degrade and be responsible
for the absence of RE luminescence.
Figure 8: Simulation of Nd ion distribution in a GaAs wafer. (a) Pearson and (b) Gaussian distributions. The implantation energy is 150 keV.

2.4.2 Sample preparation

First the GaAs samples were cut to small pieces (4 mm × 4 mm) with a diamond cutter. Then the samples were cleaned by acetone, alcohol, and distilled water. The samples were then annealed by rapid thermal annealing technique. Small pieces of GaAs crystal were placed in the circular groove of the graphite susceptor (Fig.9). This was done to protect the GaAs wafer from escaping arsenic (As). The graphite box was covered with a graphite lid of 1 mm thickness and placed on the molybdenum strip heater. The temperature was measured by a microprocessor-controlled temperature indicator, OMEGA model 650, through a thermocouple placed inside the bottom of the graphite box. The temperature was controlled by the AC voltage applied to molybdenum strip heater. The samples were annealed at 750 °C for 3, 4, 5, 6, 7, 8, 9, 10, and 12 minutes at a time in nitrogen (N₂) ambient.
2.4.3 Experimental setup

To investigate the photoluminescence (PL), all the samples were mounted on a sample holder situated in the inner most of the cryostat, where the samples were cooled by a closed-cycle helium gas. The system was evacuated down to a pressure of 5 - 10 microns (0.05 - 0.1 torr). It took about 45 min to 1 hour to cool down the samples to 9 K. A Laser Ionics model 553A argon-ion laser operating at 514.5 nm was used for PL excitation. The excitation power was about 150 mW. The laser beam was filtered through a laser filter monochromator (Photo Physics 2300) to suppress all the plasma lines and make it monochromatic (see Figure 10). A 665 nm filter was placed in front of the Monochromator slit which cuts all the wavelength below 665 nm so that the detector would be able to detect any signal above 665 nm. The emission was dispersed by a Jarrel Ash model 78-490, 0.75M, scanning monochromator equipped with a 1180 grooves/mm.
A DC step motor (S.M.) controlled by a computer drives the scanning system through the
gear assembly. The detecting electronics consisted of a thermoelectrically cooled
Hamamatsu R632-01 photomultiplier. The signals from the photomultiplier were fitted
through a fast preamplifier to a dual channel gated photon counting system controlled by
a computer, which also controlled the scanning monochromator. The complete block
diagram of this experimental setup is shown in Figure 10. The procedure for this
experiment is stated in Appendix A.

![Figure 10: Photoluminescence experimental setup of semi insulating Nd-implanted GaAs.](image)

After performing the experiment, we calibrated our monochromator to check if there was
any discrepancy between the actual emission wavelength of the sample and the measured
value. To calibrate the monochromator, we scanned the monochromator from 540 to 580
nm with the ORIEL mercury spectral lamp. The actual wavelength was obtained from
the data sheet given by manufacturer. We found a little discrepancy between the actual and the measured wavelength.

2.4.4 Results & discussions

The emission spectra of Nd-implanted GaAs are presented in Figures 11 and 12 for different annealing times. Since the photo counting system with photo multiplier has the long wavelength limit at about 1100 nm, one set of Nd$^{3+}$ emission (the lowest wavelength) was detected. The PL emission at $\sim 920.23$ nm arises from the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition of Nd$^{3+}$. The line at 829.66 nm (1.4944 eV) in Figure 10a or 11a arises from the donor-acceptor recombination emission.

Figure 11: PL spectra of Nd-implanted GaAs. (a) Donor-acceptor (DA) recombination and Nd$^{3+}$ transition and (b) closer look of Nd$^{3+}$ $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions. The sample was annealed for 3 min at 750 °C.
Figure 12: PL spectra of Nd-implanted GaAs. (a) Donor-acceptor (DA) recombination and Nd$^{3+}$ transition and (b) closer look of Nd$^{3+}$ $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions. The sample was annealed for 12 min at 750 °C.

Muller [26] has also observed the same line at 1.494 eV in Nd implanted GaAs. Both Figure 11a and 12a show DA recombination with its phonon replica at 849.7 nm (1.4592 eV) and 851.3 nm (1.4564 eV), respectively. It needs to be justified that 1.4592 eV (or 1.4564 eV) is a phonon replica of DA recombination. According to the model of Keil [29], in adiabatic approximation, the initial and final state adiabatic potentials for emission transition, which are the excited ($E_b$) and ground ($E_a$) state potentials respectively, are shown in Figure 13. At $T = 0K$, the only occupied initial state is $m = 0$ and the probability for transition to the final-state ($E_\alpha$) gets lower when the energy level, $n$, increases. This leads to emission spectra consisting of a series of evenly spaced lines at $E_n = E_0 - n\hbar\omega$, where $E_0$ is the DA recombination energy.
Assuming the same model in our case, we can do the following calculation.

In our case, $E_0 = 1.4944 \text{ eV}$ and $E_n = 1.4592 \text{ eV}$.

Therefore, $n\hbar\omega = E_0 - E_n = 1.4944 - 1.4592 = 0.0352 \text{ eV}$.

Since the highest energy of longitudinal optical (LO) phonons in GaAs occurs at approximately 291 cm$^{-1}$ (36.08 meV), the 0.0352 eV energy may correspond to the generation of one LO phonon. Transverse optical (TO) phonon energy in GaAs is 269 cm$^{-1}$ (33.33 meV) suggesting the low probability of TO phonon emission. The generation of one LO phonon for this DA recombination is explained by the configurational coordinate diagram (Figure 13). However, radiative DA recombination can occur under the conditions of strong electron-phonon coupling. In that case multiple phonon emission may occur under DA recombination. For example, Lozykowski, et al.,
[30] have observed four phonon replicas in their electroluminescence experiment of ZnSe MOS diodes.

From Figure 11a and 12a it is easily seen that the intensity of DA recombination decreases but that the intensity of Nd emission increases. Therefore, it is very clear that the donor-acceptor pair recombination energy transfers nonradiatively to the Nd core states for the sample that was annealed for longer time. The samples annealed at higher temperature shows the low intensity of the DAP recombination. Looking at Figures 11-12 and 14-17, we can see that the highest PL intensity of Nd$^{3+}$ occurs when the annealing time is 9 min. In all samples we have observed Nd$^{3+}$ emission transition $^4F_{3/2} \rightarrow ^4I_{9/2}$ consisting of six lines peaking at around 904.41, 908.02, 917.64, 920.04, 923.45, and 922.65 nm. Looking at the photoluminescence spectra of all the samples, we note that the relative intensities of various lines depend on the annealing time.

Figure 14: PL spectra of Nd-implanted GaAs @ 750 °C for annealing time (a) 4 min and (b) 5 min.
Figure 15: PL spectra of Nd-implanted GaAs @ 750 °C for annealing time (a) 6 min and (b) 7 min.

Figure 16: PL spectra of Nd-implanted GaAs @ 750 °C for annealing time (a) 8 min and (b) 9 min.
In a crystal field of cubic symmetry (e.g., $T_d$), the $^4F_{3/2}$ term does not split, whereas the spin orbit level $^4I_{9/2}$ splits into three crystal field states (Fig. 18). Thus, if the Nd$^{3+}$ ion experiences a crystal field of the cubic symmetry in GaAs, one would expect three lines for $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition. But the number of emission lines is much larger than one would expect for one single Nd$^{3+}$ center in a cubic crystal field. Therefore, in cubic hosts GaAs any splitting of the $^4F_{3/2}$ level is indicative for association of the Nd impurity with other defects. In non-cubic symmetry the luminescent level $^4F_{3/2}$ and the $^4I_{9/2}$ ground state are split into two and five states, respectively. Therefore, five emission lines should appear in the PL spectrum if one type of Nd center is involved in a crystal field of noncubic symmetry.

Figure 17: PL spectra of Nd-implanted GaAs @ 750 ºC for annealing time 10 min.
Wagner [28], et al., explained in their paper the existence of two dominant non-cubic Nd centers in GaP which arise presumably from the association of Nd with radiation damage centers. Although more than one type of center is certainly involved in the spectrum shown in Figures 11-12 and 14-17, we did not yet succeed in assigning individual lines to specific luminescent centers. From Figure 17 we can see that seven lines appear for Nd$^{3+}$ transition $^4F_{3/2} \rightarrow ^4I_{9/2}$ which differs from the other samples. On the other hand, Alshawa & Lozykowski [31] observed nine sharp peaks corresponding to the same transitions of Nd in Nd-implanted cadmium sulfide crystal CdS (II-VI semiconductor). The 907.62 and 908.02 nm lines of Nd$^{3+}$ emission (Fig. 17) may be overlapping in other samples. Wagner et al., [28] proved that two dominant non-cubic Nd$^{3+}$ centers are involved in GaP. A similar situation may be applied for the Nd-related luminescent centers in GaAs.
In order to identify the Nd$^{3+}$ centers in GaAs crystal, PL experiments with selective excitation and photoluminescence excitation (PLE) spectroscopy (combination of absorption and emission spectra) are required. However, for microscopic identification of the various types of rare-earth centers formation in the crystals, additional methods, such as Zeeman spectroscopy and electron-spin resonance techniques will be mandatory.

2.5 Photoluminescence kinetic of MOCVD grown p-type GaAs:Nd

2.5.1 Sample preparation and experimental technique

Nd-doped p-type GaAs (sample B) epitaxial layers were grown by low-pressure metal organic chemical vapor deposition (MOCVD). In the case of MOCVD, the constituent atoms are delivered to the substrate as a gaseous flow within a growth reactor furnace. The concentration of hole is $1.4 \times 10^{14}$ per cm$^3$ at room temperature. The PL measurements were carried out using an argon-ion laser (Ar+) operating at 514.5 nm. The pulse excitation for kinetics measurements was obtained by an acousto-optic light modulator, model A140 CS. The detecting electronics consisted of a Hamamatsu R632-1S photomultiplier. The signals from the photomultipliers were fitted through to the photon counters SR430, which was the fastest commercially available multichannel scaler to measure the photoluminescence rise and decay kinetics. The experimental setup of the PL kinetic model is shown in Figure 19.
2.5.2 Results & discussions

Figure 20 shows PL emission lines peaking at 921.0 nm (1.346 eV) which are attributed to the transition $^4F_{3/2} \rightarrow ^4I_{9/2}$ of the Nd$^{3+}$ ion. The PL rise and decay kinetics of Nd$^{3+}$ transition $^4F_{3/2} \rightarrow ^4I_{9/2}$ at 921 nm as a function of excitation intensity was investigated for p-type GaAs doped with neodymium. This wavelength was chosen since the photon counting system with photomultiplier had the long wavelength limit at about
1100 nm. Figure 21 shows rise and decay kinetics of PL as a function of excitation intensity.

Figure 20: PL spectra of MOCVD grown p-type GaAs:Nd is attributed to transition $^4F_{3/2} \rightarrow ^4I_{9/2}$ peaked at 921 nm.

Figure 21: Photoluminescence rise and decay of GaAs: Nd @ 921 nm for four different excitation intensities. The excitation pulse duration is 71.4 µsec.
The excitation intensity was varied from 0.02436 mW to 13.691 mW with pulse duration 71.4 μsec. The profiles show the buildup of luminescence, allowing the process to reach a steady-state value for a given excitation intensity, and the decay after switching off the excitation pulse. All profiles shown in Figure 21 are normalized to unity at maximum.

A faster rise time of luminescence intensity is noticed when the excitation intensity increases. The rise time gives information about the energy transfer from the host to the core states of the 4f electron, whereas the decay time indicates the lifetime of the electron in the excited state of the 4f shell. The PL rise and decay of Nd³⁺ at 921 nm are shown in Table II. At higher excitation intensity we see the fast decay of electron from its excited state to its ground state. Now it is intended to develop luminescence kinetics equations of rare-earth doped p-type semiconductors, which will be used to fit the experimental data discussed above. As mentioned before, by fitting the calculation to the experimental data, we can estimate important parameters related to energy transfer from the lattice to RE³⁺ centers, the Auger processes, temperature quenching mechanisms, and other important parameters.

Table II: Rise and decay time of Nd³⁺ emission at 921 nm for sample B.

<table>
<thead>
<tr>
<th>Excitation power (mW)</th>
<th>Rise time (μsec)</th>
<th>Decay time (μsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1.91</td>
<td>9.421</td>
</tr>
<tr>
<td>2.243</td>
<td>5.4</td>
<td>10.23</td>
</tr>
<tr>
<td>0.24</td>
<td>9</td>
<td>13.1</td>
</tr>
<tr>
<td>0.02436</td>
<td>15.75</td>
<td>13.3</td>
</tr>
</tbody>
</table>
In the next chapter the theoretical kinetic model of p-type III-V semiconductor doped with RE will be developed to fit the experimental data.
CHAPTER 3

KINETIC MODEL FOR P-TYPE III-V:RE

3.1 Introduction

In this chapter, we develop the photoluminescence kinetic model for p-type III-V semiconductor doped with RE which describes the energy transfer and recombination processes from the host lattice to the core states of rare earth (RE) centers. A similar model was proposed by Lozykowski [20] for semi-insulating III-V semiconductor doped with RE. This model account for energy transfer from the host to the 4f core states through localized states in the forbidden gap and for the dependence of the rise time on excitation intensities and temperature, including non-radiative recombination centers. A set of kinetic differential equations of RE luminescence in p-type semiconductor is derived. The RE luminescence rise time of the RE doped semiconductors, excited indirectly above the band gap, contain information about the energy-transfer processes from the host to the 4f\textsuperscript{th} electron system. Studying the rise time at different temperatures, excitation intensities, and excitation pulse duration can provide important information about the energy transfer, radiative, and non-radiative processes, respectively. A numerical approach was used to solve the kinetic equations. The calculated rise and decay were then fitted to experimental data. A trial and error method was used to fit the calculated rise and decay. The fitting parameters are related to energy transfer from the lattice to RE\textsuperscript{3+} centers, the Auger processes, temperature quenching mechanisms, and other important parameters, and these are discussed in Section 3.2.
According to Lozykowski [20], the “simple” isoelectronic center in III-V materials can exist in three possible states. In the case of rare-earth isoelectronic traps the kinetics model is even more complicated because of energy transfer processes between the localized state in the forbidden gap of the host and the localized core states of structured isoelectronic impurities. There are three possible mechanisms of energy transfer. The first is the energy-transfer process from excitons bound to “structured” isoelectronic centers to the core electrons. The second mechanism is transfer of energy to the core electrons involving the “structured” isoelectronic trap occupied by electron (hole) and free hole (electron) in the valence (conduction) band. The third mechanism is the transfer through an inelastic scattering process in which the energy of a free exciton near a “structured” trap is given to the localized core states [32]. If the initial and final states are not resonant, the energy mismatch must be accommodated in some way, such as phonon emission or absorption [32]. According to Robbins and Dean [32], if the atomic core excitations are strongly coupled to the host phonons, the energy transfer probability is likely to be higher. Strong phonon coupling may also be desirable in ensuring that relaxation down the ladder of core excited states occurs quickly; thus preventing back transfer. However, for efficient radiative recombination, the phonon coupling should not be strong in order to prevent core deexcitation by nonradiative multiple phonon emission.

3.2 Kinetic Model & Energy Transfer Processes

“Simple” traps can exist in three possible states, which are empty, electron (hole) occupied, and exciton occupied. In this model we have assumed that the isoelectronic
trap is an electron trap such as Yb$^{3+}$ in InP. In the case of RE$^{3+}$ “structured” isoelectronic centers, the model is more complicated because the center can exist in six possible states. These are: (1) neutral unoccupied trap (concentration $N_o$), (2) negatively charged (concentration $N_-$), (3) exciton occupied (concentration $N_x$), (4) neutral excited (concentration $N_0^*$), (5) excited negatively charged (concentration $N_-^*$) and (6) excited exciton occupied (concentration $N_x^*$). The total concentration of isoelectronic traps $N$ is given by the following equation:

$$N = N_o + N_+ + N_x + N_0^* + N_-^* + N_x^*$$  \hspace{1cm} (2)

In p-type semiconductor before the excitation, the isoelectronic trap will be empty at low temperature as shown in Figure 22a. When the sample is excited above the bandgap, an electron from the valence band will go to the conduction band first. And this electron may be captured into the isoelectronic trap with time $\tau_{et} = (v_{th} \sigma_{RE} N)^{-1}$, where $v_{th}$ is the thermal velocity of the free electron and $\sigma_{RE}$ is the cross section for the capture of electrons by unoccupied traps and transformed into negatively charged trap, $N$. (Fig. 22b).

![Figure 22: Schematic diagram of (a) electron trapping into the structured rare-earth isoelectronic electron traps (represented by ellipse) with the atomic like 4f$^n$ core states and (b) formation of negatively charged trap.](image-url)
The capture rate of electrons by the isoelectronic trap is \( (n/\tau_{el})(N_o/N) \), where \( n \) is the free electron density.

Now the annihilation energy of the bound electron with free hole in the valence band can be transferred nonradiatively through an Auger process to the rare-earth core states (Fig 23a) with a rate, \( r_T = B_T N \cdot p \), where \( B_T \) is the energy-transfer coefficient, and \( p \) is the free hole density. The result of this energy transfer process to the core states of the structured impurities is the neutral core excited state, \( N_o^* \) (Fig. 23b). We know that the energy transfer can only occur if the annihilation energy is equal (resonance condition) to the energy differences between the ground- and excited states of the 4f core states.

Figure 23: A schematic representation of energy-transfer processes to RE core states. (a) Auger energy-transfer process where annihilation energy of the bound electron with the free hole is transferred to the RE core states. (b) formation of RE neutral core excited state (result of part (a)).

If the initial and final states are not resonant, the energy mismatch must be accommodated in some way, such as phonon emission or absorption. Also bound electrons can create a bound exciton (\( N_x \)) by Coulombic attraction with the hole in the valence band with capture time \( \tau_{px} \). The second important energy transfer occurs when
the annihilation energy of the bound exciton transferred non-radiatively via Auger process to core states of structured impurity (Fig. 24) with the rate $r_{XT} = B_{XT} N_X$, where $B_{XT}$ is the transfer coefficient, and $\tau_{XT}$ is the characteristic time. Again, if the initial and final states are not resonant, the energy mismatch must be accommodated in some way such as phonon emission or absorption. The result of this process is neutral core excited state (Fig 23b). The radiative recombination of the bound exciton on REI trap has long lifetime compare to the energy transfer time $\tau_{XT}$. That's why we do not observe the luminescence of excitons bound to REI trap.

![Figure 24: Auger energy-transfer process from a bound exciton on a REI-trap (shadow ellipse) to 4f core states.](image)

The bound electron may also recombine radiatively or nonradiatively (via the Auger process) with a hole in the valence band with transition rate $r_{FBI} = B_{FBI} N_p$ and $r_{pp} = B_{pp} N_p^2$, respectively (Fig. 23a). It also may recombine radiatively with a hole trapped on a distant acceptor with characteristics time $\tau_{\text{int}}$. The last three processes transform the $N_x$ center into the $N_0$ neutral trap (Fig 22a). The exciton bound to isoelectronic traps $N_x$ can thermally dissociate by either of the two processes: (1) it can dissociate into a free exciton
(X) and neutral $N_o$, and (2) it can dissociate with the liberation of a hole or electron with time $\tau_{px}$ and $\tau_{et}$, respectively, by the following equations.

$$1/\tau_{px} = (1/\tau_{px})(N_h \beta_h^{-1} \exp[-E_h/kT])(1/N),$$

where, $N_h$ is the effective density of state in the valence band,

$\beta_h$ is the degeneracy of the hole component of the exciton having binding energy $E_h$.

$$1/\tau_{et} = (1/\tau_{et})(N_e \beta_e \exp[-E_e/kT])(1/N),$$

$N_e$ is the effective density of state in the conduction band,

$\beta_e$ is the degeneracy of the electron component of the exciton having binding energy $E_e$.

Since the lifetime of the $N^+_o$ is long (for example, the lifetime of excited Yb$^{3+}$ in InP is about 12 $\mu$sec), an electron may be captured by this time and transformed into an $N^+_e$ center (Fig. 25a). A bound electron on $N^+_e$ center can create an excited bound exciton $N^+_X$ by Coulombic attraction (Fig. 25b).

"Figure 25: A schematic diagram of (a) negatively charged excited trap and (b) excited exciton REI trap."
The RE luminescence is due to the radiative transitions between 4f\textsuperscript{n} core states of the RE element. Total intensity of the RE emission is the sum of the radiative transition of N\textsuperscript{o*}, N\textsuperscript{-}, and N\textsuperscript{x*} (Fig. 26).

![Figure 26: Radiative transition of (a) neutral excited REI-trap, (b) negatively charged REI-trap, and (c) excited exciton REI-trap.](image)

The deexcitation energy of N\textsuperscript{-} may be transferred nonradiatively via Auger process to eject the bound electron into the conduction band (N\textsuperscript{-} \rightarrow N\textsuperscript{o} + e-kinetic energy) with characteristic time \tau_{BT} as shown in Fig. 27a. This is the Auger nonradiative luminescence quenching mechanism of the excited rare-earth isoelectronic trap. The deexcitation energy of RE core state can also be transferred to bound exciton to dissociate with the liberation hole or electron with characteristic time \tau_{BXT} (Fig. 27b) resulting N\textsuperscript{o}. At sufficiently high temperatures, the electron from N\textsubscript{\textsuperscript{o}} and N\textsuperscript{-} may be thermally emitted to the conduction band at a rate (n/\tau_{et})(N/N or N\textsuperscript{-}/N), where n = N\textsubscript{c}β\exp[-E\textsubscript{RET}/kT],
(1/\beta_s) is the degeneracy of the structured isoelectronic trap level at energy \( E_{RET} \) below the conduction band, and \( N_c \) is the conduction band density of states.

Figure 27: Energy back transfer processes. (a) The auto de-ionization Auger quenching mechanism, and (b) The energy back transfer process from the excited REI trap to a bound exciton

Figure 28a shows an example of nonradiative recombination involving the interaction of a core excited isoelectronic trap (\( N_o^* \)) with an electron trapped on a separate center (\( N_\cdot \)), or an electron trapped on a core excited REI trap (\( N_{-}^* \)). The recombination rates of these processes are proportional to \( N_o^* \), and the concentrations of \( N_\cdot \), or \( N_{-}^* \) traps such that

\[
    r_{BT1} = B_{BT1} N_o^* N_\cdot \quad \text{and} \quad r_{BT2} = B_{BT2} N_o^* N_{-}^*,
\]

where \( B_{BT1} \) and \( B_{BT2} \) are the Auger coefficients. The de-excitation energy of \( N_o^* \) may be transferred non-radiatively via an Auger process creating a “hot” hole in the valence band.
by ejecting an electron from the valence band to acceptor level (Fig. 28b), or to a hole by
ejecting it into the deep valance band (Fig. 28c); the energy transfer rates of both
processes are described by the following rate equations.

\[ \begin{align*}
    r_{BT3} &= B_{BT3} N_o^* p \\
    r_{BT4} &= B_{BT4} N_o^* N_A^0,
\end{align*} \]

where \( B_{BT3} \) and \( B_{BT4} \) are the Auger coefficients.

![Diagram](image)

Figure 28: Auger nonradiative recombination involving the interaction of the neutral core
excited REI-trap with (a) an electron trapped on separate centers, (b) an electron in the
valence band, and (c) a hole in the valence band.

Wang and Wessels [33] reported that free carrier Auger processes play a limited role in
determining the Er\(^{3+}\) luminescence efficiency in InP crystals. This is because the
probability of formation of bound excitons at the rare earth centers increases with the
increase of free carrier concentration from \(10^{13}\) to \(10^{17}\) per cm\(^3\). Considering this situation
in our model we have ignored the free carrier Auger processes.

Energy migration due to the quenching center can play an important role in the
quenching of RE luminescence at high temperature. For example, the energy transfer
process from Yb$^{3+}$ to Fe$^{3+}$ ions in InP:Yb is attributed to thermal quenching of the luminescence intensity with an increase in temperature [34]. A similar thermal quenching process may occur in GaAs:Nd. To estimate the thermal energy required to quench the luminescence at high temperature in p-type GaAs:Nd, we have fitted the experimental data (integrated intensity vs. inverse temperature) stated in ref. 15 using equation 2 (Fig. 29).

$$I(T) = a \left[ 1 + b e^{-E_1/kT} c e^{-E_2/kT} \right]^{-1}$$

where, $a = 0.98$, $b = 1092$, $c = 1.03$, $E_1 = 30$ meV, and $E_2 = 2.2$ meV

![Figure 29: (a) The PL integrated intensity of MOCVD grown GaAs:Nd vs. temperature and (b) PL decay times vs. temperature. Data were extracted from reference 15.](image)

Therefore, the activation energy of the quenching trap, $E_q$, is about 30 meV. Similarly, the experimental data stated in the same reference for decay time vs. inverse temperature was fitted using equation 3 (Fig. 29b).
where, $a = 11.55 \times 10^6 \text{ sec}^{-1}$, $E_3 = 12.3 \text{ meV}$, and decay time of Nd$^{3+}$ at low temperature, $\tau_r = 11.74 \mu \text{ sec}$. This model describes the relaxation rate $R_r = 1/\tau_3$ (decay time) of Nd$^{3+}$ luminescence as a function of temperature. We have used these results in our developed kinetic model, although with different samples, as a reference fitting parameter.

From the above discussion the differential equations for the REI-trap energy-transfer processes and recombination kinetics are derived. The differential equations govern the variations with time of the concentrations of various components under band-to-band excitation. The derived kinetic equations are:

$$\frac{dN_0}{dt} = \frac{n}{\tau_{et}} \left( \frac{N_0}{N} \right) + \frac{N^*_x}{\tau_3} + \frac{1}{\tau_{px}} \left( \frac{N_0}{N} \right) \frac{N_x}{\beta_h} \exp \left( -\frac{E_h}{kT} \right) - \frac{1}{\tau_{et}} \left( \frac{N_0}{N} \right) \beta N_x \exp \left( -\frac{E_h}{kT} \right) - \frac{p}{\tau_{px}} \left( \frac{N_0}{N} \right) - B_{FIA}(N_0) - B_{BTA}(N_0) - B_{F1}(N_0)p$$

$$\frac{dN_x}{dt} = \frac{N_x^*}{\tau_3} + \frac{p}{\tau_{px}} \left( \frac{N_0}{N} \right) - N_x \left( \frac{1}{\tau_2} + \frac{1}{\tau_{xT}} + \frac{1}{\tau_{sdT}} \right) - \frac{1}{\tau_{px}} \left( \frac{N_x}{N} \right) \frac{N_x}{\beta_h} \exp \left( -\frac{E_h}{kT} \right)$$

$$\frac{dN^*_0}{dt} = \frac{N_x}{\tau_{xT}} + B_x(N_0)p + \frac{1}{\tau_{et}} \left( \frac{N^*_x}{N} \right) \beta N_e \exp \left( -\frac{E_x}{kT} \right) - \frac{n}{\tau_{et}} \left( \frac{N^*_0}{N} \right) - \frac{N^*_0}{\tau_3} - B_{BTA}(N_0) - B_{BTA}(N^*_0)$$

$$\frac{dN^*_x}{dt} = \frac{n}{\tau_{et}} \left( \frac{N^*_0}{N} \right) + \frac{1}{\tau_{px}} \left( \frac{N^*_x}{N} \right) \frac{N_x}{\beta_h} \exp \left( -\frac{E_h}{kT} \right) - N^*_x \left( \frac{1}{\tau_3} + \frac{1}{\tau_{BTA}} \right) - B_{FIA}(N^*_x)p$$

$$\frac{dN^*_0}{dt} = \frac{p}{\tau_{px}} \left( \frac{N^*_0}{N} \right) - \frac{1}{\tau_{et}} \left( \frac{N^*_0}{N} \right) \beta N_e \exp \left( -\frac{E_x}{kT} \right) - B_{BTA}(N_0) - B_{BTA}(N^*_0)$$

$$\frac{dN^*_x}{dt} = \frac{p}{\tau_{px}} \left( \frac{N^*_0}{N} \right) - N^*_x \left( \frac{1}{\tau_2} + \frac{1}{\tau_3} + \frac{1}{\tau_{sdT}} + \frac{1}{\tau_{BTA}} \right) - \frac{1}{\tau_{px}} \left( \frac{N^*_x}{N} \right) \frac{N_x}{\beta_h} \exp \left( -\frac{E_h}{kT} \right)$$
\[
\frac{dn}{dt} = G + N_x \left( \frac{1}{\tau_{sd}} + \frac{1}{\tau_{BRT}} \right) + \left( \frac{N_x + N^*}{N} \right) \frac{1}{\tau_{\alpha}} \beta N_e \exp \left(-\frac{E_i}{kT}\right) + \frac{N_x}{\tau_{sd}} + \frac{N^*}{\tau_{BRT}} - \frac{n}{\tau_{\alpha}} \left( \frac{N_0 + N^*_0}{N} \right) + B_{BRT} N_0^* (N_-) + B_{BRT} (N_0^*) N^*_0
\]

\[
\frac{dp}{dt} = G + \frac{\beta_A}{\tau_{px}} \left( \frac{N_x}{N} + \frac{N^*_x}{N} \right) - \frac{p}{\tau_{px}} \left( \frac{N_-}{N} + \frac{N^*_-}{N} \right) - B_{FRT} (N_- + N^*_-) p + B_{FRT} N_0^* N^*_A
\]

\[
- \left( 1 - \frac{N_0^*_A}{N_A} \right) \frac{p}{\tau_{pa}} + \left( \frac{N_0^*_A}{N_A} \right) \frac{1}{\beta_A} \frac{N_x}{\tau_{pa}} \exp \left(-\frac{E_A}{kT}\right)
\]

\[
\frac{dN^*_A}{dt} = \left( 1 - \frac{N_0^*_A}{N_A} \right) \frac{p}{\tau_{pa}} - \left( \frac{N^*_0}{N_A} \right) \frac{1}{\beta_A} \frac{N_x}{\tau_{pa}} \exp \left(-\frac{E_A}{kT}\right) - B_{FRT} N_0^* N^*_A
\]

\[
N = N_0 + N_- + N_x + N_0^* + N^*_+ + N^*_x
\]

\[
N_A = N_0^*_A + N_A
\]

\[
p = n + N_- + N^*_+ - \left( 1 - \frac{N_0^*_A}{N_A} \right) N_A
\]

Equations (4-8) govern: the negatively charged rare earth isoelectronic trap populations (1), the neutral exciton occupied rare earth isoelectronic trap populations (2), the neutral core excited rare earth isoelectronic trap populations (3), the negatively charged core excited rare earth isoelectronic trap populations (4), and the exciton occupied core excited rare earth isoelectronic trap populations (5), respectively. Equations 9, 10 and 11 represent the changes in the total free electron, and free hole populations, and density of neutral acceptor, respectively. Equations 12 and 13 state the constancy of the total concentrations of REI-traps, and acceptors, respectively. Equation 14 is the neutrality condition equation. \( G = gf(t-T) \) is the generation rate of free electrons and holes by the
above band gap laser excitation. The electron hole pair generation rate is controlled by a unit step function $f(t-T)$, where $T$ is the pulse width which takes on the value of zero or unity according to whether its argument is less than or equal to zero or greater than zero. The volume generation rate is approximated by the following equation.

$$G(z) = \Phi_0 \alpha \eta e^{-az},$$

where $\Phi_0$ is the photon flux in photons per cm$^2$ per sec.

or, $G = \int_0^{1/\alpha} \Phi_0 \alpha \eta e^{-az} \, dz$, where $1/\alpha$ and $\eta$ are the penetration depth and quantum efficiency, respectively.

or, $G = 0.63212 \Phi_0 \eta$.

To calculate the e-h pair generation rate, we must take care of the reflection of the incident power by the mirror and the sample itself. The refracting indexes of a silica window and GaAs crystals at 514.5 nm (excitation wavelength) are 1.48 and 4.1, respectively.

The above systems of coupled first order stiff nonlinear differential equations require specialized numerical integration routines, designed specially for stiff equations. The kinetic equations were solved numerically (see Appendix B) for certain excitation intensities and pulse duration using the fitting parameters (the time constants and rate coefficients) defined in Table III. The luminescence intensities are proportional to $N'_0$, $N'_i$ and $N'_e$. For simplicity, we ignored the above band-gap excitations have taken place at low enough temperatures (since experiment was performed at 2K); so the thermal activation of the trapped carriers is negligible. In other words, terms explicitly dependent
on the temperature were ignored, and only trapping, transferring and recombination transitions were considered.

Table III: Parameters describing Rise and Decay kinetics of GaAs: Nd

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ₃</td>
<td>second</td>
<td>11.7×10⁻⁶</td>
</tr>
<tr>
<td>τ₂</td>
<td>second</td>
<td>400×10⁻⁹</td>
</tr>
<tr>
<td>τ_BT</td>
<td>second</td>
<td>500×10⁻⁹</td>
</tr>
<tr>
<td>τ_XT</td>
<td>second</td>
<td>1×10⁻⁹</td>
</tr>
<tr>
<td>τ_BXT</td>
<td>second</td>
<td>9×10⁻⁶</td>
</tr>
<tr>
<td>τ_e</td>
<td>second</td>
<td>1×10⁻⁸</td>
</tr>
<tr>
<td>τ_p</td>
<td>second</td>
<td>4.91×10⁻¹²</td>
</tr>
<tr>
<td>τ_x</td>
<td>second</td>
<td>1×10⁻¹²</td>
</tr>
<tr>
<td>τ_p</td>
<td>second</td>
<td>500×10⁻⁹</td>
</tr>
<tr>
<td>B_T</td>
<td>cm²/second</td>
<td>3×10⁻³</td>
</tr>
<tr>
<td>B_FBI</td>
<td>cm²/second</td>
<td>1×10⁻¹⁵</td>
</tr>
<tr>
<td>B_BT1</td>
<td>cm²/second</td>
<td>1×10⁻¹⁴</td>
</tr>
<tr>
<td>B_BT2</td>
<td>cm²/second</td>
<td>1×10⁻¹⁴</td>
</tr>
<tr>
<td>B_BT4</td>
<td>cm²/second</td>
<td>4×10⁻¹⁸</td>
</tr>
</tbody>
</table>

3.3 Results & Discussion

A MATLAB computer program was developed to solve the system of kinetic equations (Appendix B). The numerical solution was obtained using the fitting parameters described in Table III. All the parameters are not sensitive to fit to the experimental rise and decay. These parameters describe best the experimental rise and decay. The electron trapping time (τ_e) in InP: Yb was estimated to be 50 picosecond, but in the case of Nd in p-type GaAs this time is found to be 10 nanosecond. For GaAs: Nd, the characteristic time of energy back transfer process from the excited REI trap to a bound exciton, τ_BXT, is 9 μs, which is higher than that of InP: Yb (0.5 μs). Therefore, a
slower rise time may be expected for GaAs:Nd. From Table III we note the Auger energy transfer coefficient of bound electron to free hole \( (B_T) \) is \( 3 \times 10^{-5} \) cm\(^3\) per sec. But for semi-insulating (SI) InP:Yb, \( B_T \) was equal to \( 4 \times 10^{-10} \) cm\(^3\) per second [20], which indicates that the transfer rate of the annihilation energy of bound electron to free hole to the core states is faster in p-type GaAs:Nd than in SI InP:Yb. From this parameter the energy mismatch can be described. Energy mismatch is the energy difference between the energy transfer from the host to core states and radiative 4f transition. For example, the energy mismatch for InP:Yb and GaAs:Nd are calculated in the following.

For p-type InP:Yb, energy required to excite Yb\(^{3+}\) from \( ^2F_{7/2} \) to \( ^2F_{5/2} \) = 1.264 eV
But, energy transfer to core states of structured impurity = \( E_g - E_t = 1.423 - 0.03 = 1.393 \) eV. Therefore, energy mismatch is 1.393 - 1.264 = 0.129 eV.

For p-type GaAs:Nd, the energy required to excite Nd\(^{3+}\) from \( ^4I_{9/2} \) to \( ^4F_{3/2} \) = 1.346 eV
But, \( E_g - E_t = 1.519 - .085 = 1.434 \) eV. Therefore, energy mismatch = 1.434 - 1.346 = 0.088 eV. We see that a lower energy mismatch occurs when energy transfer from the host to the 4f shell of Nd ion. Auger quenching processes with the coefficients \( B_{BT1} \) and \( B_{BT2} \) have a profound influence on the rise and decay kinetics of RE luminescence. If we make higher the values stated in Table III, the rise and decay is different from the experimental data. Also, if the radiative process of bound electron to the free hole, \( B_{FBI} \) is greater then \( 1 \times 10^{-15} \) cm\(^3\)/sec, the rise and decay time get slower. Overall, all the parameters used to fit rise and decay describes the experimental data well. Therefore, estimated fitting parameters describe the energy transfer processes from the host to RE 4f
core states. The proposed kinetic model can be used to approximate some energy transfer process and lifetime.

The experimental and numerically simulated luminescence rise and decay are shown in Figure 30 as a function of excitation intensities.

![Fitting curves](image)

**Figure 30:** Fitting curves. (a) experimental and (b) simulated luminescence rise and decay as a function of time, for three excitation intensities, A) 18 mW, B) 2.24 mW and C) 0.24 mW. Pulse width is 71.4 micro sec.

All profiles are normalized to unity at maximum. The rise and decay time of the dominant component of the double exponential fitting are shown in Table IV. From Table IV it is easily noticed that the computed rise time is always higher than the
experimental rise time. However, the decay time almost match with the experimental data. In conclusion, the developed PL kinetic model for p-type semiconductor doped with RE gives estimation of the energy transfer process to core states when fitted with the experimental data.

Table IV: Theoretical and experimental rise and decay times as a function of time.

<table>
<thead>
<tr>
<th>Excitation power</th>
<th>Rise time (μ sec.)</th>
<th>Decay time (μ sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Theoretical</td>
</tr>
<tr>
<td>18 mW</td>
<td>1.91</td>
<td>3.1</td>
</tr>
<tr>
<td>2.243 mW</td>
<td>5.4</td>
<td>9</td>
</tr>
<tr>
<td>0.24 mW</td>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>

3.4 Other quenching mechanisms

Other mechanisms of the nonradiative recombination of the excited states of localized centers in semiconductors are the multiphonon relaxation processes and a migration of energy and cross relaxation processes. The probability of multiple phonon relaxation processes is dependent upon the type of coupling with the lattice vibrations and the phonon frequency distribution. The ion-host lattice interaction for RE$^{3+}$ 4f$^p$ electrons is characteristic of weak coupling, and the multiphonon emission rates exhibit an approximately exponential dependence on the energy gap to the next lowest level. For a single frequency p phonon process, the nonradiative rate for narrow-line emission is described by Kiel’s formula [27]

$$W_{nr}^p (T) = W_{nf}^p (0)[1+n]^p,$$
where $W_{\nu}(0)$ is the rate at low temperature, $p$ is the number of phonons involved, $n$ is the occupancy of the phonon modes:

$$n = [\exp(h\omega/kT)-1]^{-1},$$

and the average phonon energy $h\omega=\Delta E/p$. The single frequency model seems to be an oversimplification, and taking a weighted average over the phonon's spectrum, or consideration of the continuous nature of the phonon spectrum, would be more appropriate [35].

The results of many studies indicate that for given host crystals, the most critical parameter affecting the rate of multiphonon emission is the energy gap to the nearest lower level. Since the energy gap of RE 4f core states are large, the nonradiative multiphonon rate is negligible as compared to the radiative rate. For example, in GaAs:Nd$^{3+}$ the $^4F_{3/2}-^4I_{9/2}$ energy gap is 10864 cm$^{-1}$ (1.346 eV). The highest energy of longitudinal optical (LO) phonons in GaAs is 291 cm$^{-1}$ (36 meV). Therefore, nonradiative decay for this case would require the generation of $(1.346/0.036)$ or 37 LO phonons. Studies in different host materials [36] show that nonradiative decay involving the generation of more than five phonons is weaker than the radiative process. Oxygen atoms due to ability of forming strong bonds create impurity complexes and show IR absorption spectra. Oxygen can also create complexes with rare earth ions [37]. Also, there is an experimental evidence that oxygen creates a complex with Er in GaAs:Er [19]. In GaAs oxygen related centers produced the IR absorption bands centered at 845 cm$^{-1}$ (104.7 meV) and 715 cm$^{-1}$ (88.6 meV) due to localized vibrational modes (LVM) [37].
Nonradiative decay in such a case would require the generation of 13 or 15 LVM phonons. Therefore, we see that probability of non-radiative multiple phonon emission increases in the presence of other impurities. The very high energy optical phonons, derived from internal vibrational modes of the oxygen complexes, may interact with the RE ions differently from the low-energy lattice LO phonons [38].

When the concentrations of the rare-earth luminescent ions are higher, or centers create pairs, allowance must be made of the possibility of interaction between centers. This interaction may be too weak to modify the energy levels, but yet be adequately strong to enable transfer of energy from one to another [20]. In Nd$^{3+}$ doped GaAs the energy of a single excited ion may be transferred to the same level of an identical ion (resonant energy migration), and finally to the quenching center [20]. The second possible degradation of excitation energy is the cross relaxation process. The presence of appropriate intermediate levels in the Nd$^{3+}$ ion ($^{4}I_{11/2}$ and $^{4}I_{13/2}$) between the ground $^{4}I_{9/2}$ and excited $^{4}I_{5/2}$ states makes effective the cross relaxation process and increases the probability of nonradiative quenching processes [20]. Another important consideration for Nd$^{3+}$ is the existence of pairs of transitions which give rise to self-quenching. This process is shown in Figure 31a and can cause serious reduction in luminescence lifetime and quantum efficiency at rare earth concentrations greater than or equal to 1%.

The rate of self-quenching for a given rare earth ion density is dependent upon the oscillator strengths and the spectral match of the two transitions. If transitions are sufficiently nonresonant, self-quenching is reduced and materials with Nd$^{3+}$ concentrations up to 100% can be used for lasers. Energy transfer is possible even when
the energy differences between pairs of transitions become large. Energy transfer transitions of the type illustrated in Fig. 31b can also occur radiatively wherein a photon emitted by one ion is absorbed by a second ion. This leads to radiation trapping but not to lifetime shortening. All the above discussed transfer processes, dependent on temperature and concentration of the RE ions, are useful in explaining the quenching of luminescence of rare earth in semiconductors. These non-radiative processes are not incorporated in the developed kinetic model.

Figure 31: Pairs of energy transitions for rare earth arising from ion-ion interactions. (a) Self-quenching and (b) Energy migration.
CHAPTER 4
CONCLUSIONS

Rare earth doped III-V semiconductor are attractive materials because they have the potential to combine the advantages of optical properties of RE$^{3+}$ ions and semiconductor hosts. In this case we are interested in internal emission of RE ions rather than the band to band emission. As pointed out earlier, there are three main advantages of RE doped semiconductors. These are: 1) the RE emission lines are very sharp, 2) the position of emission lines does not depend on temperature, and 3) the emission lines depend slightly on the host material. Among the rare earth elements, Er$^{3+}$ is very promising because of its 1.54 μm emission, which is well adapted to silica based fiber telecommunication. Nd$^{3+}$ can be useful for lasers application due to its four level laser scheme.

From the experimental result of Nd-implanted semi insulating GaAs we have found that the positions of the near infrared of Nd emission lines (around 920 nm) agree with earlier published work, even though we have used different annealing conditions. This set of emissions corresponds to Nd$^{3+}$ transition $^4F_{3/2} \rightarrow ^4I_{9/2}$. All the lines found are very sharp compared to other reports [23, 24, and 25]. We see the highest emission intensity occurs for the sample which was annealed at 750 °C for 9 min. Different number of lines are observed for different annealed samples. The sample annealed at 750 °C for 10 min shows seven lines, whereas six lines appear in the rest of the samples, suggesting that more than one type of Nd$^{3+}$ center is involved in GaAs. Also, we have
observed that the decrease of donor acceptor pair emission intensity decreases with the increase in the intensity of Nd$^{3+}$ emission. This relation probably shows how the energy transfer occurs from host to the 4f core state, which is the indirect excitation process of RE ion. However, further study is required to prove this energy transfer process to the 4f core state. We have not succeeded in assigning individual lines due to the complex form of Nd in a GaAs semiconductor. But, certainly the Nd$^{3+}$ ion experiences a crystal field of non cubic symmetry (as discussed in the Section 2.4.4). However, for microscopic identification of the various types of RE centers formed, additional method such as Zeeman spectroscopy and electron-spin resonance techniques will be mandatory.

In this work we have developed a kinetic model that describes energy transfer processes from the host lattice to the localized core states of rare-earth isoelectronic structured traps for p-type rare earth doped III-V semiconductors. The presence of low-lying empty core orbitals in rare-earth impurities introduces new excitation and recombination phenomena. The total intensity of the RE emission is the sum of the radiative transition of $N^+_o$, $N^-_e$, and $N^+_x$ (Fig. 26). The developed model was solved numerically and fit to the experimental data obtained for MOCVD grown p-type GaAs:Nd. The fitting parameters as shown in Table III best describe the experimental rise and decay. The initial values of the parameters chosen for the calculations are estimated from experimental data obtained from InP:Yb [20]. Because the data fits the experimental rise and decay we believe that all constants are realistic and characteristic for GaAs:Nd. The kinetics of the luminescence of GaAs:Nd was simulated by repeating
the numerical calculations for 18 mW, 2.243 mW and 0.24 mW excitation power. We simulated the kinetics of the photoluminescence measurement by choosing square generation pulses with 71.4 μsec duration. Both calculated and experimental rise and decay are well approximated by a double exponential curve. The dominant part of the double exponential is used to fit the calculated data with the experimental values. At 0.24 mW excitation intensity, calculated and theoretical rise time are found 10 and 9 μsec, respectively, whereas decay times are 12.52 and 13.1 μsec, respectively. The photoluminescence kinetics of MOCVD-grown p-type GaAs:Nd shows that the decay of Nd\(^{3+}\) is around 12 - 13 μsec at low excitation intensity, which is in the same range of Yb\(^{3+}\) in InP crystal [34].

The energy transfer processes from host to RE core structure and some quenching mechanisms can be approximated from the kinetic model developed in chapter 3 for p-type III-V semiconductor doped with rare earth. We know that radiative recombination of excitons (\(\tau_2\)) bound to "simple" isoelectronic impurities has a long lifetime ranging from a few hundred to few thousand nanoseconds. That time is much longer than the energy transfer time from bound exciton to the 4f core states. From the Table III we note that energy transfer time, \(\tau_{xt}\), is 1 nanosecond (Fig. 24). We did not observe the bound exciton recombination, since \(\tau_{xt}\) is faster than \(\tau_2\). The energy transfer process from the electron trapped on the RE isoelectronic trap to the free hole, which is defined by Auger coefficient \(B_T\), is equal to \(3 \times 10^5\) cm\(^3\)/sec (see Fig. 23). These two energy transfer processes are important to excite the rare earth 4f core states at above bandgap excitation.
The coefficient of radiative recombination of electrons trapped on the isoelectronic trap, $B_{FB}$, is $1 \times 10^{-15}$ cm$^3$/sec; and this radiative process is much lower than $B_T$ (see Fig. 23).

The energy back transfer process from the rare earth core states to the host play an important role in quenching RE luminescence. The 4f de-excitation energy transfers non-radiatively to dissociate the bound exciton with characteristic time, $\tau_{BXT} = 9$ µsec. In this case the de-excitation energy transfer time is longer than energy transfer time from the bound exciton to the 4f core states. The characteristic time to eject an electron trapped on the isoelectronic trap by the de-excitation energy is $\tau_{BT} = 0.5$ µsec. Therefore, this energy back transfer process is much faster than $\tau_{BXT}$. Both the Auger energy transfer rate coefficients from the core excited isoelectronic trap ($N_o^+$) to electron trapped on a separate center ($N_1$), and to the electron trapped on a core excited REI trap ($N_e^+$) are equal to $1 \times 10^{-14}$ cm$^3$/sec (Fig. 28a). The Auger coefficient of the de-excitation energy transfer to the electron in the valence band, $B_{BT4}$ is equal to $4 \times 10^{-18}$ cm$^3$/sec (Fig. 28c). Therefore, we see that the nonradiative energy transfer process to the electron trapped on a separate REI trap center is more responsible for luminescence quenching at high RE concentration. Finally, the quenching mechanisms that were discussed in Section 3.4 can be incorporated in this model for better approximation.
REFERENCES


38 E.D. Reed, H.W. Moos, Phys. Rev. B8, 980 (1973), and references cited therein.
APPENDIX A

Photoluminescence experimental procedure of

Nd-implanted semi-insulating GaAs
Operating vacuum system, cooling system and detector and photocounter

1. Place the samples in the sample holder and place it inside the cryostat and close it.

2. Open the valves of the cryostat and turn on the pump to vacuum inside the cryostat and check the vacuum gage to check the pressure level. Turn off the pump if the pressure level reaches to 5 - 10 micron.

3. Check the CTI-CRYOGENICS for helium pressure level. If the pressure level is 225 psi skip this step. Otherwise set it at that position. This is done by opening valve of the He gas cylinder and carefully adjusting CTI-CRYOGENICS meter to 225 psi. Close the valve of He gas cylinder.

4. Turn on the temperature controller and press PROGRAM button.

5. Turn on the tap water to cool the detector. Do not flow too much water. Turn on the detector controller and press RESET button.

6. At HIGH VOLTAGE POWER SUPPLY machine, apply “1000” volt to the detector.

7. Turn on main power supply.

8. Turn on analogue and digital photocounter.

Laser operation

1. Turn on the tap water flow.

2. Switch on the COOL FLOW machine.

3. Turn on laser main power switch.

4. Use key to turn on laser emission.
5. Turn on the laser control panel and follow the instructions and wait half an hour for stable laser operation.

**Operating Jerrel Ash monochromator and recording spectra**

1. Turn on the monochromator power.

2. In IBM machine go to **specont** directory and type **ashkrom**.

3. Always CHECK the monochromator gear and the gear displays in the computer. If they are not same choose Initialization and set your desired gear and wavelength positions.

4. For Dwell mode operation (recording spectra) make sure use appropriate gear size for desired step as stated below.

<table>
<thead>
<tr>
<th>Monochromator gear size</th>
<th>Step size (nm/step)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>0.1</td>
</tr>
<tr>
<td>250</td>
<td>0.2</td>
</tr>
<tr>
<td>500</td>
<td>0.4</td>
</tr>
<tr>
<td>1250</td>
<td>1.0</td>
</tr>
</tbody>
</table>

5. Go to **spectra** directory of the next computer and type **metawndo** and type **sr465** for the digital photocounter SR 430.

6. press F1 and type 1 to start recording.

7. If you want to abort this operation press ESC in the IBM machine and choose F6 in the other computer for reset.

8. After recording you need to calibrate x axis. Choose F2, F2, F3 and Cal. Always press ESC to one step back of the current menu.
9. Always save the file in a: drive. Do not use any extension, just type the filename. This software will give the filename extension 400 (i.e. filename.400) which is binary file. You need to convert this file to ASCII file for further data processing.

10. In order to that go to the computer located on the other table. Go to profile directory and type bintoprn

11. Type the filename you want to convert. You must use the extension, which is 400 in this particular case and press enter.

12. In the next prompt choose A and next type your filename with extension dat

13. At next prompt choose n.

14. Type y if you want to convert another one.
APPENDIX B

MATLAB CODE
% The following program was used to solve the kinetic equations, derived in chapter 3, % numerically. This program is valid for p-type semiconductor. % User will be asked to enter the excitation power and temperature.
%*******************************************************************
h=6.6e-34; % Planck's constant
c=2.99792458e8; % speed of light in vacuum (in m/s)
lemda=514.5e-9; % excitation wavelength of Ar ion laser
neu=c/lemda;
% Area of the beam size at the sample position in cm^2
A=pi*(7.5e-4)^2;
% Total incident power going into the sample
P=(1-R1)*(1-R2)*Pin;
P=P/A;
% Assume quantum efficiency, eta=0.9
eta=0.9;
G=eta*0.63212*P/(h*neu); % # of photons per cm^3 per second
q=1.6e-19; % Electron charge
k=1.38e-23; % Boltzman's constant in J/K
K=8.617e-5; % Boltzman's constant in eV/K
%*******************************************************************
% Activation energy
%*******************************************************************
Et=0.085; % Isoelectronic trap activation energy in eV
Eh=0.07; % Exciton hole ionization energy in eV
Eq=29e-3; % Energy required to transfer energy from 4f electrons % to nonradiative recombination center in eV
Ea=30e-3; % Acceptor (Mg) ionization energy in eV
Eg=1.42-4.7E-4*(298-T) % Bandgap function of temperature in GaAs.
bt=2; % [1/bt]-degeneracy of the structured isoelectronic trap
bh=2; % The degeneracy of the hole component of the exciton
ba=1; % The degeneracy of acceptor
Tr=300; % Room temperature

N=1.7e17; % Concentration of Nd (in cm^-3) in sample MPF1
ph=1.4e14; % hole concentration in sample MPF1 at room temp.

mo=9.11e-31; % Free electron mass in kg
Mn=0.063*mo; % Electron effective mass of GaAs in Kg (Ref. "Semiconductor Optoelectronic Devices" by P. Bhattacharya, p64)
Mh=0.48*mo; % Hole effective mass kg (Ref. same as above)

Nc=(2*(2*pi*Mn*k*T/h^2)^3/2)/e6; % C.B. density of states [1/cm^3]
Nv=(2*(2*pi*Mh*k*T/h^2)^3/2)/e6; % V.B. density of states [1/cm^3]
Na=ph +ba*(ph^2/Nv)*exp(Ea/(K*Tr)); % Acceptor concentration.
Ncbt=Nc*bt; % Conduction-band density of states x[bt][1/cm^3]
Nvbh=Nv/bt; % Valence-band density of states /[bt][1/cm^3]

Mh=0.48*mo; % Hole effective mass kg (Ref. same as above)

Tpet=1e-6; % tau'(prime) "et"
T2=4e-7; % Exciton recombination time.
Txd=1e-18; % Bound exciton dissociation time.
TXT=1e-9; % The characteristic time for energy transfer from exciton trapped on isoelectronic trap (REI-trap) to % 4f electrons system of REI-trap.
TBXT=9e-6; % The characteristic time for energy back transfer % from 4f electrons system via an Auger process to % dissociate exciton bound on REI-trap.

Tth=(1/5.5287)*1e-6; % Thermal time constant related to the thermal % relaxation time Tr by the relation % Tr(T)=Tth*exp(Eq/(k*T))

T3=11.71e-6/(1+(11.71e-6/Tth)*exp(-Eq/(K*T))); % Recombination time of the rare earth excited centers in GaAs:Nd

TBT=5e-7; % The characteristic time for energy back transfer % from 4f electrons system via an Auger process to % electron bound on REI-trap.

Tet=1e-8; % tau "et", isoelectronic trap electron capture % parameter, can be fitting parameter.

v=((3*k*T/Mh)^3/2)*100; % in cm/sec

Tpx=1/(v*(7.4006e-13)*(T^-m)*N); % Tpx=1/(v[SIGMApx]*N), % SIGMApx=(const.)T^-m =The electron occupied
% isoelectronic center hole-capture cross section.
% occupied with electron Ns^-. 
Tpa=5e-10; % Trapping time constant of electron on neutral acceptor % with concentration Na^0.

% *******************************************************************
Bt=3e-5; % The rate of energy transfer from collapse of electron % on REI-trap and free hole from valence band to the % 4f electrons system of REI-trap.
BFBI=1e-15; % The rate of radiative recombination of electron % on REI-trap with free hole.
BFBA=4e-15;

% *******************************************************************
% Auger coefficients
% *******************************************************************
BT1=1e-14; % Auger quenching rate involving interaction of a % core-excited REI trap with an electron trapped on a % separate center REI-trap (N_) Fig.4.
BT2=1e-14; % Auger quenching rate involving interaction of a % core-excited REI trap with an electron trapped on a % separate center core excited REI-trap (N^*) Fig.4.
BT6=1.2e-18; % Auger quenching rate involving interaction of a % core-excited REI trap with an hole on a neutral % acceptor Fig.5.

% *******************************************************************
% Parameter values
a1=Tpet/T2;
a2=Tpet/T3;
a3=Tpet/TBT;
a4=Tpet/TBXT;
a5=Tpet/Tet;
a6=Tpet/Tpx;
a9=Tpet/TXT;
a10=Tpet/Txd;
a15=Tpet/Tpa;
%f=input('Enter frequency in Hz: ');
period=1/f;
%tau=input('Enter pulse width in second: ');
TAU=tau/Tpet;

% *******************************************************************
g=G*Tpet/N;
c1=Ncbt/N;
c2=Nvbh/N;
c6=Na/N;
c7=Nvba/N;
E1=exp(-Et/(K*T));
E2=exp(-Eh/(K*T));
E4=exp(-Ea/(K*T));
BT=Bt*Tpet*N;
Bfbi=BFBI*Tpet*N;
B1=BT1*Tpet*N;
B2=BT2*Tpet*N;
B6=BT6*Tpet*Na;
Bfba=BFBA*Tpet*Na;

% global parameters for p-type GaAs (pGaAs.m);

global a1 a2 a3 a4 a5 a6 a9 a10 a11 a12 a14 a15 TAU g c1 c2 c3 ...
tau c6 c7 E1 E2 E4 BT Bfbi B1 B2 B3 B4 B6 Bfba T G Tth period Tpet Na

% ******************************************************************************
% p-type GaAs
% ******************************************************************************
[t,y]=ode15s('piso');
y=(y(:,3)*1 +y(:,4)*1 +y(:,5)*1);
y=y./max(y);

%plot(t,y), set(gca,'Xlim',[0 period/Tpet],'YLim',[0 inf]),grid on;
plot(t,y), set(gca,'Xlim',[0 l40],'YLim',[0 inf]),grid on;
%ylabel('y(3 )+y(4)+y( 5)')
%xlabel('Time[X10^-6],piso.m')
%fprintf('N		Ns		Na
');
%fprintf('%e	%e	%e
',N,Ns,Na);
%title([date,',','T=' int2str(T),',','K=',',','G=' num2str(G),',','Pin=',num2str(Pin),',','Na=',num2str(Na)]);
%d=date;
%d=datemark;
%date

save data3.dat t y -ascii
!copy data3.dat c:\tcwin\data3.dat
% End of the main program.
% Uttam Saha
% File: piso.m
% 5:22 PM 3/25/96
% piso: (p-type sem.) Model Luminescence Kinetics of Isoelectronic Trap
% This function solves the system of stiff equations using MATLAB built in function
% ODE15S
% ************************************************************************************
function [out1, out2, out3] = piso(t, y)

global Na Nv Ns bt Ea Et g l period Tpet

K = 8.617e-5;
ba = 1;
x2 = (ba / (Na * Nv)) * exp(Ea / (K * T));
xl = l / Na;
x0 = -l;
% format long e
z = [x2, xl, x0];
r = roots(z);

s = (Na - r(2)) / Na;
if length(t) == 0
    out1 = [0 period/Tpet];
    out2 = [0 0 0 0 0 0 0 0 1 s]';
xr = 1e-5;
ya = 1e-6;
    out3 = odeset('rtol', xr, 'atol', ya);
return;
end

global a1 a2 a3 a4 a5 a6 a9 a10 a11 a12 a14 a15 TAU gc cl c2 c4 ...
c5 c6 c7 E1 E2 E3 E4 BT Bfbi B1 B2 B3 B4 B5 B6 Bfbd Bfba Na
dy = zeros(8, 1);  % preallocate vector dy

% FLAG=0 when TAU-t <= 0 else FLAG=1
FLAG = (TAU - t > 0);

dy(1) = y(6) * a5 * (1 - y(2) - y(3) - y(5) - y(7) + y(6) - c6 + y(8) * c6) + ...
a6 * c2 * E2 * y(2) + a2 * y(4) - (a5 * c1 * E1 + Bfbi * y(7) + BT * y(7) + B1 * y(3)) * y(1);
dy(2) = a2 * y(5) + a6 * y(1) * y(7) - (a1 + a9 + a10 + a6 * c2 * E2) * y(2);
dy(3) = a9 * y(2) + BT * y(7) * y(1) + a5 * c1 * E1 * y(4) - y(3) * (y(6) * a5 + a2) - ...
    B1 * y(1) * y(3) - B6 * y(8) * y(3);
\[
\begin{align*}
dy(4) &= y(3) \cdot y(6) \cdot a_5 - (Bfbi \cdot y(7) + a_2 + a_3 + a_6 \cdot y(7) + a_5 \cdot c_1 \cdot E_1) \cdot y(4) + \\
&\quad a_6 \cdot c_2 \cdot E_2 \cdot y(5) - B_2 \cdot y(4) \cdot y(3); \\
dy(5) &= a_6 \cdot y(4) \cdot y(7) - (a_1 + a_2 + a_4 + a_{10} + a_6 \cdot c_2 \cdot E_2) \cdot y(5); \\
dy(6) &= g \cdot \text{FLAG} + a_4 \cdot y(5) + y(5) \cdot a_{10} + a_3 \cdot y(4) + a_5 \cdot (y(1) + y(4)) \cdot c_1 \cdot E_1 + \\
&\quad a_{11} \cdot y(2) + a_3 \cdot y(4) - a_5 \cdot y(3) \cdot y(6) - B_{fba} \cdot y(6) \cdot y(8) - \\
&\quad y(6) \cdot a_5 \cdot (1 - y(2) - y(3) - y(5) - y(7) + y(6) - c_6 + c_6 \cdot y(8)) + \\
&\quad y(3) \cdot (B_2 \cdot y(4) + B_1 \cdot y(1)); \\
dy(7) &= g \cdot \text{FLAG} - a_6 \cdot (y(1) + y(4)) \cdot y(7) - B_{fbi} \cdot (y(1) + y(4)) \cdot y(7) - \\
&\quad a_{12} \cdot y(7) + B_6 \cdot y(3) \cdot y(8) + a_6 \cdot c_2 \cdot (y(2) + y(5)) \cdot E_2 - B_T \cdot y(1) \cdot y(7) + \\
&\quad y(8) \cdot a_{15} \cdot c_7 \cdot E_4 - (1 - y(8)) \cdot a_{15} \cdot y(7); \\
dy(8) &= (a_{15} / c_6) \cdot (1 - y(8)) \cdot y(7) - (a_{15} / c_6) \cdot c_7 \cdot y(8) \cdot E_4 - B_6 \cdot y(8) \cdot y(3) - \\
&\quad B_{fba} \cdot y(6) \cdot y(8); \\
\text{outl} &= dy; \\
\% \text{End of the function}
\end{align*}
\]
ABSTRACT

Rear earth doped III-V semiconductor is important because their emission lines are sharp, and slightly depend on the temperature and the nature of the host materials. In this case internal emission of the 4f transitions is important rather than band to band transition. In this research very sharp intra-4f-shell luminescence spectra of Nd$^{3+}$ peaking at around 920 nm ($^4F_{3/2} \rightarrow ^4I_{9/2}$) have been observed from Neodymium implanted semi-insulating gallium arsenide crystal. Experimental results show a number emission lines depending on the annealing time and temperature. Also, theoretical kinetic model for p-type III-V semiconductor doped with RE was developed and solved numerically to fit with the experimental data of metal organic chemical vapor deposition (MOCVD) grown p-type GaAs:Nd. Developed kinetic model shows good agreement with the experimental results.