Chapter 1

Introduction

Growth technique and device fabrication skills using GaN and its related materials have matured even further, and have extended the level to launch room-temperature (RT) continuous-wave (CW) blue laser lights with a lifetime more than 10,000 hours[1-1]. On the other hand, thanks to having a partially filled inner shell shielded by completely filled outer orbitals, Lanthanide elements, so-called 'RARE EARTHs', have played an important role in various optoelectronic and photonic applications, ranging from emitting elements in solid-state lasers and in phosphors for color displays to optical fiber communication. The goal of this dissertation is to graft those two materials for the application into novel devices. Basic studies on material characterizations are preceded.

1.1 Introduction and backgrounds

In recent years there have been remarkable advances in nitrided material (GaN and its alloys with In and Al) that have revolutionized optoelectronics[1-2]. The intrinsic properties of wide and direct band gap as well as colorlessness and transparency are practically applied in optical devices such as blue and green light emitting diodes (LEDs)[1-3, 4, 5, 6, 7] and laser diodes (LDs)[1-1, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. Having a high electron drift velocity[1-18]and a large dielectric breakdown voltage[1-19], GaN related material is also applied in electronic devices such as high electron mobility transistors (HEMTs) and heterojunction field effect transistors(HFETs)[1-19, 20, 21, 22]. Nontoxic, high mechanical and thermal stabilities are also some important advantages for which they are applied into devices.

Among versatile devices invented or ones still under development using above superior properties of GaN related materials, commercially available optical devices such as blue and green LED and blue and ultra violet (UV) LD use single quantum well (SQL)[1-23] and multi quantum well (MQL)[1-9, 10, 11, 12, 13, 14, 15, 16, 17] structures in which InGaN plays a pivotal role together with AlGaN or GaN for cladding layer. Larger well depths or high In contents of InGaN well layer need to be asserted to carry the wavelength peak into long wave spectral region, but in that case, following problems which would lower the emission efficiency generally occuer.

Spatially isolation of electron hole pair(EHP)s due to the increase of piezoelectric field in well structures affects recombination probability, and low emission efficiency due to carrier capturing on defects or dislocations caused by large lattice mismatching between InN and GaN and inhomogeneity of emission wavelength due to phase separation between InN and GaN occurs. Due to these problems, red emission LED based on GaN related materials is not commercially available yet.

For those reasons, the full color displays are realized so far by LED using GaN related materials and red LED using the other types of material such as InGaAlP so far(Fig. 1-1(a)).

Using different material requires more complex fabrication procedures and limits minimization of devise size. White LED which already started to gradually increase the market share of illumination industry is also achieved by the structure using InGaN LED chip with yttrium aluminum garnet (YAG) phosphor including epoxy cap[1-24] (Fig. 1-1(b))since red emission is not available. To make the YAG phosphor shine, 2 times of energy conversion, which may lower efficiency, is required. If red emission based on GaN related materials become available, problems mentioned above are expected to be solved.

1.2 Rare Earths (REs).

With the background information above provide, the author introduced rare earth (RE)s doping into GaN. The REs, otherwise referred to as the lanthanides, comprise the series of elements in the

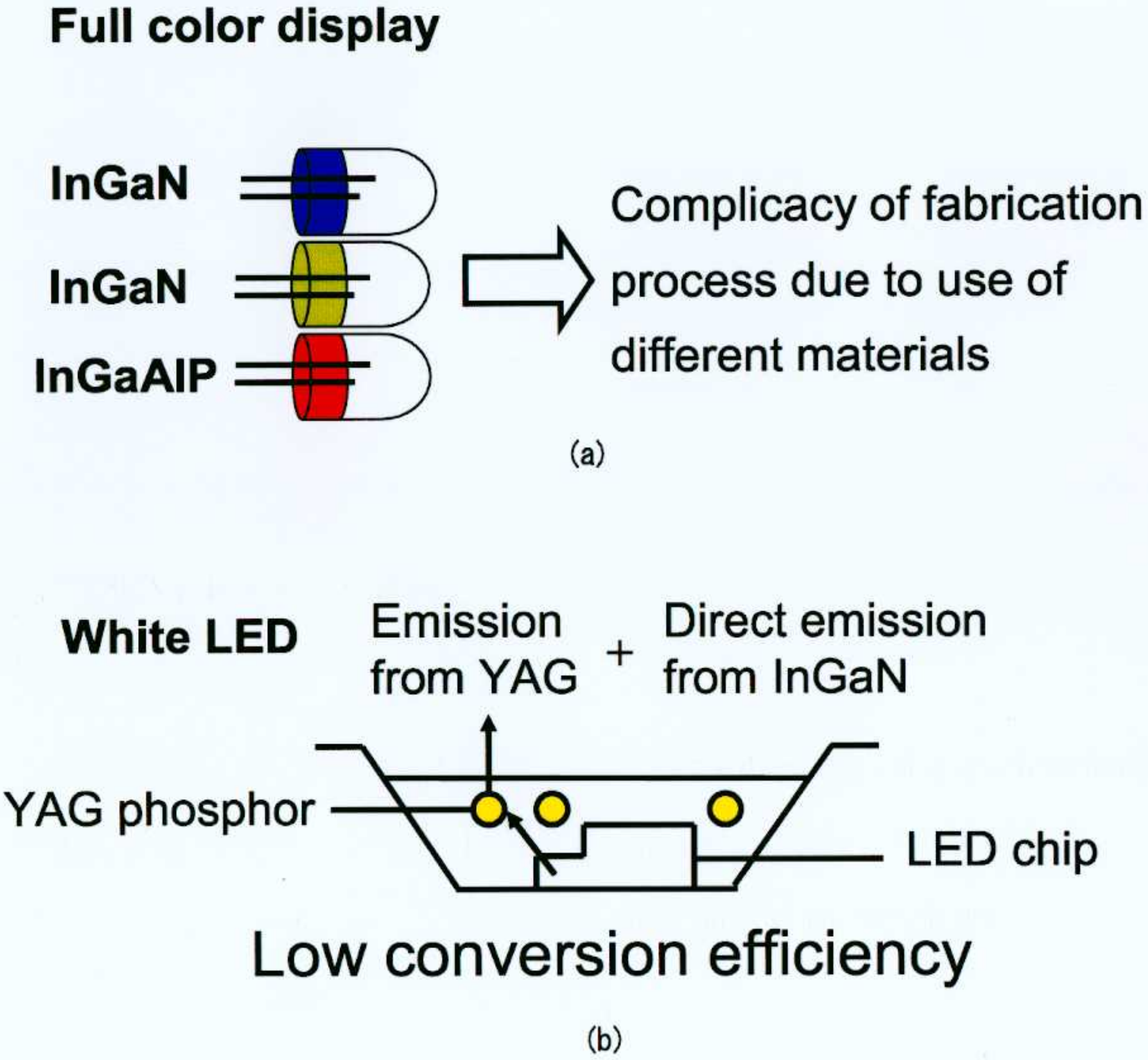


Figure 1-1: The structure of (a)full color display and (b)white LED that are currently commercialized.

sixth row of the periodic table stretching from lanthanum to ytterbium. From the name ‘RARE’, it is often misunderstood to be scarce. Actually, however, even thulium (Tm) that is known to be of the smallest storage among RE is stored several times more then silver (Ag) or platinum (Pt). RE is by no means really ‘rare’. The etymology may distribute to the difficulty of refining pure REs.

The REs are characterized by a unique structure that is a partially filled 4f shell that is shielded from external fields by $^5S_2$ and $^5P_6$ electrons. The energy levels of elements in this series are therefore largely insensitive to the environment in which they are placed. When incorporated in crystalline or amorphous hosts, the rare earths exist as 3+, or occasionally 2+, ions. The 3+ ions all exhibit intense narrow-band intra-4f luminescence in a wide variety of hosts, and the shielding provided by the $^5S_2$ and $^5P_6$ electrons means that rare-earth radiative transitions in solid hosts resembling those of the free ions and electron-phonon coupling is weak.

As a result of the shielding of the 4f electrons, the positions of rare-earth electronic levels are influenced much more by spin-orbit interactions than by the applied crystal field. The intra-4f transitions are parity forbidden and are made partially allowed by crystal field interactions mixing opposite parity wavefunctions. Luminescence lifetimes are therefore long (often in the millisecond range), and linewidths narrow. By careful selection of the appropriate ion, intense, sharp emission can be obtained across much of the visible region and into the near-infrared. And the emissions peak positions are known to be stable, and almost host independent. For these practical advantages, REs have been widely utilized in optical applications such as solid lasers and phosphor in color television.

Fig. 1-2 shows energy level diagrams for the isolated 3+ ions of each of the 13 lanthanides with partially filled 4f orbitals from cerium (Ce)(number of f electron=1) to ytterbium (Yb) (13)[1-25]. The most technologically important radiative transitions are labelled. Fig. 1-3 further illustrates the effect of spin-orbit and crystal field interactions on the energy levels of the erbium $(Er)^{3+}$ ion for example [1-26].

1.3 REs in GaN.

It has been reported that the thermal quenching of emission intensity was suppressed by increasing band gap of host materials[1-27]. From this point of view, GaN is one of the adequate materials to be REs doped for optical application. The wide gap of GaN is also advantageous to accommodate full color ranging from UV to infra-red which makes monolithic LED practicable. For example, europium (Eu) or samarium (Sm) ions, terbium (Tb) or Er ions and Tm ion can be chosen for emission center for the red (R), green (G), and blue (B) emission. Then, the RGB full-color-emitting-monolithic LED can be realized. If RGB emission achieved monolithically, the fabrication process of full color display based on GaN would become much simpler, and more efficient white light LED with adjustable mood coloring would be possible. Also, with conjunction of photo-detector such as Charge-Coupled Devices (CCD), an ultra-small-sized image processor will be applicable.

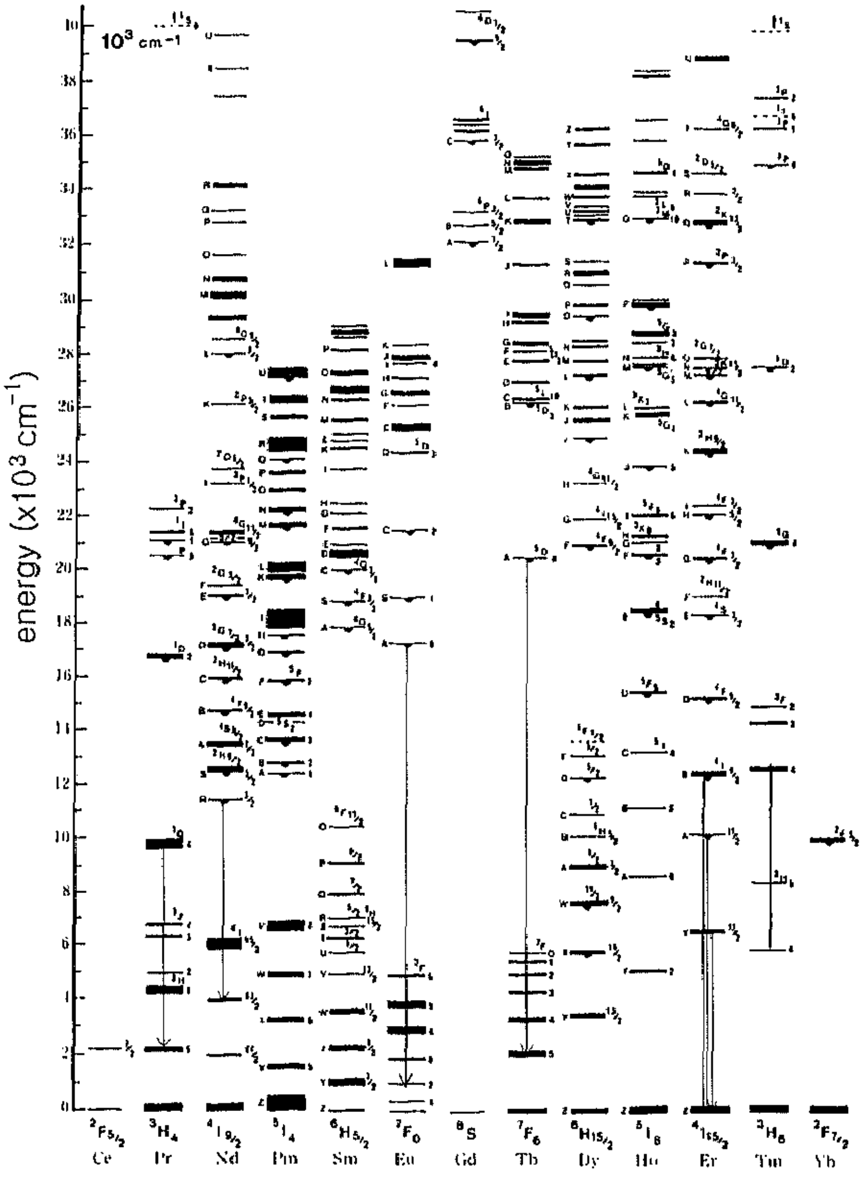


Figure 1-2: Energy levels of various RE^{3+} ions. Technologically important radiations are labelled[1-25].

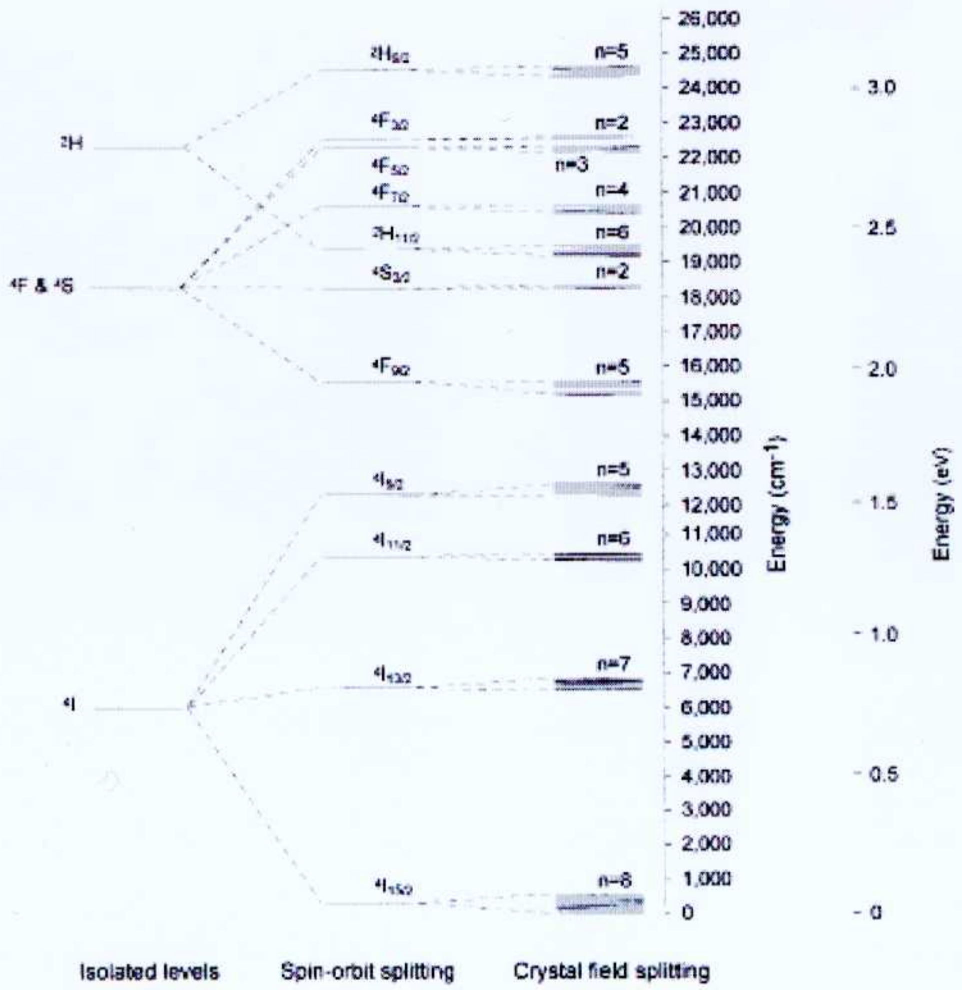
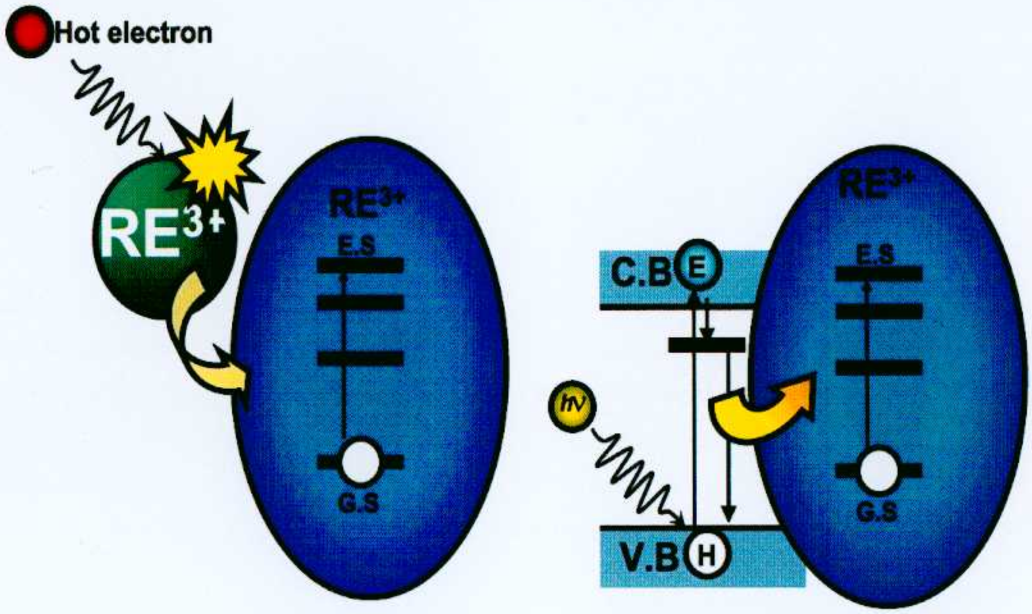


Figure 1-3: The effect of spin-orbit and crystal field splitting on the energy leves of the Er^{3+}[1-26].

On the one hand, Er ion emission band fortunately coincides with wavelength 1535nm[1-25] which is principal low-loss window in the absorption spectrum of silica optical fibers and waveguides. Bringing out such advantageous property, -stability on luminescence intensity with respect to temperature variation of surroundings-, of REs doped GaN, a smaller and simpler laser setup for light telecommunication without cooling system which is required in currently used system can be realized.

A number of excitation pathways are available for rare-earth luminescence in solid hosts. These can be broadly classified as either direct or indirect mechanisms(Fig. 1-4). Amongst the former are resonant optical excitation by the interaction of photons of appropriate wavelengths with specific rare-earth 4f absorption bands, cathode-luminescence, and electro luminescence in semiconductor hosts involving hot electron collision with rare-earth centers. Indirect mechanisms include carrier-mediated excitation transfer in semiconductors, and dipole-dipole Förster-Dexter coupling in insulators. Carrier-mediated excitation is of particular importance for the production of optoelectronic devices, and there has been much work directed at an understanding of such processes in a range of semiconductor hosts.



(a) Direct excitation **(b) Indirect excitation**

Figure 1-4: Excitation mechanism of RE ion in solids.

The purpose of this study is to examine the feasibility of rare earth doped GaN as a material for novel optical devices. Optimizations on growth conditions and explorations on material properties need to be preceded to practical device fabrication. In this dissertation, the introduction and backgrounds were mentioned in this chapter, and in chapter 2, the experimental tools used in this study will be described. Chapter 3 describes the optimizations on growth of Eu doped GaN through the studies on structural and optical properties. In chapter 4, Er or Tb doped GaN will be studied and compared with Eu doped GaN. Chapter 5 introduces the magnetic properties of RE doped GaN. Finally, general conclusions will be remarked in chapter 6.

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