Rare Earth Doping in Nitrides
Development of Rare-Earth Doped III-Nitride and Its Application for Optoelectronic Devices

Akihiro Wakahara and Hiroshi Okada
Dept. of Electrical & Electronic Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan

ABSTRACT

Eu doped AlGaN fabricated by ion-implantation method have been investigated for realizing an optoelectronic device in which a rare-earth doped layer is used as an active layer. Energy transfer efficiency is estimated from an integrated PL intensity ratio between Eu-related emissions and low-temperature integrated luminescence intensity in the range of 350-700nm at 15K. The estimated energy transfer efficiency from the host material to Eu is as high as 15%. Small-signal optical gain at 300K is ~70cm\(^{-1}\) for GaN, and ~130cm\(^{-1}\) for AlGaN with the AlN molar fraction around 0.2. We proposed and fabricated a three-terminal electroluminescent device in which Eu implanted active region is formed at the gate-edge of FET structure. The device shows excellent I-V characteristics as a transistor with gate control. By applying a drain bias of 20 V, red emission suggesting a luminescence from Eu ion is clearly observed. Applying a bias to the Schottky gate, the luminescence intensity can be controlled.

INTRODUCTION

Light emission from rare-earth ions (REIs) in a semiconductor has received much attention as a candidate of light source for signal indicator, display, optical telecommunication, and optoelectronic integrated circuits (OEICs), because the light emission caused by 4f inner-level transitions has narrow line width and less sensitivity for peak position on an environmental temperature[1]. In a viewpoint of light-source integrated with Si-CMOS based LSIs, materials for optical devices have to have compatibilities of a fabrication process, operating conditions, and also the wavelength range with Si-based systems. Recent progress in III-nitride leads to studies of REIs doped GaN, in which strong photoemission in visible range is available, and some research group demonstrated visible electroluminescent devices [2-4], and the lasing by optical pumping [5]. Moreover, III-nitrides have excellent thermal stability which is suitable for an optical source embedded in Si-LSIs, and thus REIs doped group-III nitrides are one of the candidate for an optical device in OEICs.

It has been reported that PL properties of REIs (Eu, Th, Tm, and Er) can be improved by using in Al\(_x\)Ga\(_{1-x}\)N host rather than GaN [6-11]. When the AlN molar fraction is increased, PL intensity related to REIs by the above band-gap excitation increases, and the thermal quenching is also improved. However, there are only a few reports on the effects of AlN molar fraction on the REIs related photoemission, and the mechanisms of energy-transfer and/or back-transfer processes in AlGaN are not deeply understood.

In a viewpoint of device application of REIs-doped III-nitrides, there are two-types of devices, i.e., conventional light-emitting diode (LED) based-on the energy transfer via injected electron-hole recombination, and electroluminescent (EL) device with impact ionization and/or hot-cattier excitation processes. Many researchers have been trying to realize LEDs with REIs-doped active layer, but it is hard to realize due to shortening the carrier diffusion length by high-
density traps related to REIs itself. Only a few reports have been published on LEDs with REIs doped active layer, such as GaAs:Er.O [12]. Concerning EL devices, these type devices are typically two-terminal devices. The operation bias is usually high, and thus high speed switching required for optical communication is hard to realize due to a high voltage swing for signal modulation.

In this paper, we report photoemission properties and optical modal gain of Eu-doped AlGaN using ion-implantation method. We also propose a novel luminescence device, in which Eu-ions are selectively introduced by ion implantation into the channel of high electron mobility transistor (HEMT) device to realize high-speed optical signal modulation.

EXPERIMENTAL DETAILS

Photoemission properties of Eu-implanted AlGaN

Eu was implanted into AlₓGa₁₋ₓN epitaxial layers grown on a sapphire (0001) substrate with a 1 µm-thick AlN epitaxial template. The AlN molar fraction of AlGaN was in the range of 0.0-1.0. The ion implantation was carried out at room temperature with the acceleration energy of 200keV. The Eu dose was in the range of 1×10¹⁴–1×10¹⁵cm⁻². The projected range and the peak concentration of Eu estimated by SRIM2006 were 100nm and 3×10¹⁹–3×10²⁰cm⁻³, respectively. After the implantation, the samples were annealed by using rapid thermal annealing (RTA) technique to recover the implantation damage. In the present work, we used cap-less annealing in N₂+NH₃ mixture with NH₃ partial pressure of 0.33atm, in order to reduce the dissociation of the surface. The temperature and time for the annealing process were 1100°C and 120s, respectively. Reflection high-energy electron diffraction pattern reveals that the implantation damage was recovered by the annealing. From a scanning electron microscope image, the annealed samples showed mirror-like surface meaning no surface degradation by the annealing. Photoemission properties were investigated by photoluminescence (PL) and chathodoluminescence (CL) measurements. The PL was carried out at 300K using a He-Cd laser (λ=325nm) and/or ArF excimer laser (λ=193nm) as the excitation light source. The excitation power density and the pulse duration of ArF excimer laser were approximately 100W/cm²-pulse and 25ns, respectively.

Small signal optical gain was measured at 300K by using the variable stripe length (VSL) method [13,14], and the optical loss in AlGaN planar waveguide was evaluated by the shifting excitation spot technique(SES)[15] using ArF excimer laser as the excitation source. The excitation power density was about 83mJ/pulse-cm². The PL intensity detected at the edge of the samples.

Fabrication of three-terminal EL device

The device structure is similar to a conventional AlGaN/GaN high electron-mobility transistor (HEMT) excepting that Eu
was selectively implanted near the drain electrode edge, as shown in Fig.1. In the proposed device, luminescence due to the impact excitation of Eu by accelerated electron in two-dimensional electron gas (2DEG) is expected because the electrons in the transistor channel are accelerated by the high electric field at drain side of gate edge. Electric bias applied to the gate controls the current through the channel, i.e., direct modulation of the luminescence can be made.

Fabrication process of the device consists of standard photolithography and ion-implantation of Eu. A 25nm-thick Al0.25Ga0.75N on a 3μm-thick GaN heterostructure grown on sapphire substrate without no intentional doping was used as a starting material. The electrical properties of AlGaN/GaN HEMT wafers were evaluated by Hall effect measurement in van der Pauw configuration and a sheet electron density of $1.3 \times 10^{13}$ cm$^{-2}$ and the electron mobility of 1000 cm$^2$/V-s at room temperature (RT) were found. After the device isolation by inductively-coupled plasma reactive ion etching, a 600 nm-thick SiO$_2$ layer was deposited on AlGaN/GaN layer for a mask of selective area doping of Eu. The dimensions of SiO$_2$ window for Eu-implantation was 300μm in width (equal to the gate width) 3μm in geometrical length ($L_{GE}$). Eu ion implantation was carried out through the AlGaN layer to introduce the Eu in active 2DEG region by choosing the implantation energy. Eu doping was made at the acceleration energy of 200 keV at RT using the ion-implantation facility in JAEA. Eu dose was chosen as $5 \times 10^{13}$ cm$^{-2}$, then the samples were annealed for recovery of implantation damage and rare-earth activation. Ti/Al/Au Ohmic contact and Au Schottky gate were formed by e-beam evaporation and lift-off process. Dimensions of fabricated devices were source-drain distance of $L_{SD} = 20$ μm, gate length of $L_{G} = 7$ μm, and gate–drain distance of $L_{GD} = 7$ μm, respectively. Tracks of the Eu implanted region could not be seen by the microscope observation after the annealing for damage recovery. Eu implantation region is designed at the center of the gate-to-drain gap with lithographic alignment accuracy of about 2μm.

Fig.2. Dependence of AlN molar fraction ‘x’ on the photoemission properties measured at 300K
RESULTS AND DISCUSSION

Photoemission properties of Eu ions implanted into AlGaN

Figure 2 shows the dependence of AIN molar fraction on the Eu related PL properties measured at a planar configuration, meaning that the PL signal was taken from the normal direction of the sample surface. As can be seen in the figure, both PL and CL intensity attributed to Eu $^5D_0-^7F_2$ transition is dramatically increased with increasing the AIN content at low AIN content, and then reaches to the maximum around AIN content of $\sim$0.4. The line width also reaches to the maximum for $x$=0.4. On the contrary, the peak position decreases monotonically from 1.987eV (GaN:Eu) to 1.979eV (AlN:Eu). The broadening of the emission line width in AlGaN with the mid-range of AIN molar fraction is attributed to crystal field effect, as reported previously [11].

We used integrated PL intensity ratio between Eu inner shell transitions at various temperatures and the integrated PL intensity in the wavelength range of 350–700nm at 15K, to estimated energy transfer efficiency from AlGaN host to Eu$^{3+}$ ions. The intensity ratio, denoted as $\eta$ for the samples with AIN molar fraction of 0.13 was about 15% at 300K and did not depend on the Eu dose. At low temperatures, the value of $\eta$ increased as the Eu dose was decreased. For the Eu dose of $5\times10^{14}$cm$^{-2}$, it reached $\sim$30% below 100K. This result suggests that energy transfer efficiency is surprisingly large, because the implantation damages cannot remove completely by the post implantation annealing. We found that Eu-implanted GaN has a large radiation tolerance [16,17]. The Eu-related luminescence does not degrade until the density of radiation induced defect reaches the Eu concentration. In the viewpoint of less effect of defect density on the Eu-related luminescence properties, this high energy transfer efficiency could be expressed by high-density iso-electronic/hole traps caused by Eu ions.

In order to estimate the small signal optical gain, AIN epitaxial templates were used to confine the emitted light with in the AlGaN planar waveguide. ArF laser beam was focused by cylindrical lens to obtain a line shaped excitation pattern.

According to SES method, the optical loss in AlGaN:Eu/AlN sample at the wavelength of 620nm was lower than 10cm$^{-1}$ showing good optical guiding properties. Figure 3 (a) shows PL intensities of GaN:Eu and AlGaN:Eu as a function of the excitation length. It is clearly seen that the intensity increased super-linearly when the excitation length was short. Since the total amount of the introduced Eu was $<10^{14}$cm$^{-2}$, corresponding to peak concentration of $10^{20}$cm$^{-3}$, which is much smaller than the density of states for bulk, i.e., $\sim10^{23}$cm$^{-3}$, the PL intensity could be easy to saturate even though the excitation length was short. We estimate a small-signal optical gain using the excitation length in the range of 50-200|µm to eliminate a fringe effect at the spot edge [14]. The estimated value was $\sim70$cm$^{-1}$ for Eu-implanted GaN and $\sim130$cm$^{-1}$ for Al$_{0.13}$Ga$_{0.87}$N. The obtained small signal gain for Eu-implanted GaN was close to the reported value for MBE-grown GaN:Eu[5], though the Eu implanted samples contained a lot of residual implantation damages. The small signal gain increased with increasing the Al composition at the low Al composition region, and seems to reach the maximum value around the AIN fraction of $x$=0.2, at which PL intensity also reaches the maximum.

We also confirm the optical amplification by measuring the PL decay time at the different position from the edge, as can be seen in Fig. 3(b). When the excitation length was enough long for intensity saturation, the decay time was about 100µs, which is close to that obtained in planar
PL, i.e., typically a few hundred microsecond. While the PL decay time in the superlinear region was shorter than the saturated region. Since the saturation in PL intensity for longer excitation length is owing to the small amount of the excited Eu ions, the shortening of the PL decay time observed in the superlinear region is caused by stimulated emission. In order to confirm the stimulated emission in Eu-implanted AlGaN, further investigations for laser action by creating a cavity and the lasing properties are necessary.

**Three terminal EL device**

As shown in Fig.4, fabricated device showed excellent transistor operation with gate control. DC characteristics of the fabricated device agree with the conventional AlGaN/GaN HEMT having similar device dimensions [18]. Non-linear behavior in $I_D-V_{DS}$ characteristics around the $V_{DS}=0$ together with rather low channel conductance may come from a premature device fabrication process, because HEMT devices without Eu implantation also showed similar $I_D-V_{DS}$ characteristics with the same order of channel conductance. The results suggest that the formation of high resistive region around the Eu implanted region under the present condition does not lead to a dramatic degradation in the DC characteristics. By applying a drain bias of 20 V, a red emission was clearly seen in the fabricated device at the Eu-implanted region as shown in right hand side of Fig.4. Poor spatial uniformity of the emission could be come from the non-optimized fabrication process. The intensity of the red emission changed with the gate-bias condition, i.e., the emission intensity was decreased by applying a negative bias to the gate, which causes reduction of the drain current.

Figure 5 shows a spatial distribution of luminescence intensity across the source-drain region. A red emission was observed only on the drain edge, and the observed red emission is thought to be the inner-shell transitions of Eu-ions in GaN[19]. Now we briefly discuss a mechanism of observed luminescence in the present device. Under the cathodic excitation of Eu-implanted AlGaN, pure red luminescence was seen in CL chamber by naked eyes. Chen et al reported observation of electroluminescence from yellow luminescence -like defects in...
Fig.4. $I_D$–$V_{DS}$ characteristics of selectively Eu implanted HEMT. Photographs in right hand side of are photoemission from the Eu-implanted region at $V_{DS}=20V$ with various gate bias.

Fig.5. Special distribution of EL intensity across source-drain region.

conventional AlGaN/GaN HEMT[20]. We cannot wipe out that a superposition of yellowish luminescence from defects upon a Eu-related red luminescence in the present EL device. To obtain a red luminescence corresponding to $^5D_0 - ^1F_2$ transition in Eu$^{3+}$ ions, electron in the ground state $^7F_0$ should be excited to $^5D_0$ state of which energy difference is about 2 eV by energy transfer from host. Several excitation and de-excitation processes for luminescence centers are discussed by Buchal et al[21]. Among them, one can omit the excitation of Eu ions by electron-hole recombination as a major EL mechanism for the present study, because HEMT is a majority carrier device. According to the computer simulation by Hu et al, maximum electric field of ~ 60 kV/cm was expected for AlGaN/GaN HEMT with $L_G = 5 \mu m$ at $V_{DS} = 10 V$. This field is far low from the critical electric field of 34 MV/cm for impact ionization in GaN[22]. Therefore, hole generation by impact ionization is also not feasible for the present situation. In the present device, an impact excitation of Eu ions by hot electron under the high electric field seems major mechanism of the luminescence, because the device is in the drain current saturation region with $V_{DS} = 20 V$. Further study is required to clarify the EL mechanism, and is responsible for optimization of the proposed device. Anyway, present results suggest that the proposed device is promising for monolithically integrated light emitting FET having capabilities for multiband optical amplifier/modulator by changing REIs by ion-implantation.

CONCLUSIONS

Photoemission properties of Eu doped AlGaN using by ion-implantation method have been investigated. Energy transfer efficiency from the host material and thermal stabilities of photoemission properties are investigated. Energy transfer efficiency estimated from integrated PL intensity ratio between Eu-related emission and over all PL spectra at 15K was higher than 15%. Small signal optical gain at 300K measured by variable stripe length (VSL) method was ~70cm$^{-1}$ for GaN, and ~130cm$^{-1}$ for AlGaN with the AlN molar fraction around 0.2. As an example of device application, three-terminal electroluminescent device in which Eu implanted
active region was formed at the gate-edge of FET structure, was fabricated. Red emission suggesting a luminescence from Eu ion was clearly observed by applying a drain bias of 20 V and could control by a gate bias.

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