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Investigation of Microenvironment-Depended Photoluminescence in Eu^{3+}-Implantation of GaN

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Abstract: GaN thin films grown on sapphire were implanted by Eu^{3+} with three different fluences (5.0×10^{14}, 2.5×10^{15} and 5.0×10^{15} cm^{-2}). The photoluminescence (PL) spectra show that, after annealing, the samples exhibit strong emission at around 622.0 nm under 325 nm laser excitation. The intensity of this emission increases by one order of magnitude after annealing at from 600 ℃ to 900 ℃. Moreover, it increases less than 2 times when the fluence increases from 5×10^{14} cm^{-2} to 5×10^{15} cm^{-2} for the sample annealing at 900 ℃. The PL emission peaks around 622 nm of samples annealing at 900 ℃ can be well clarified by Gaussian fitting into 620.2, 622.0 and 625.0 nm, which are due to the Eu^{3+} related with defects, Eu^{3+} occupied at substitutional positions of Ga, and that located at interstitial sites, respectively. It shows that the different microenvironments and positions of Eu^{3+} are responsible for these peaks, and especially the defects introduced by implantation play an important role in the behavior of the PL because they set up an energy transmission bridge from exotic photons to Eu^{3+}.

Key words: ion implantation; photoluminescence; GaN; Eu^{3+}

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0 Introduction

The 3rd generation semiconductors (GaN, ZnO) by ion doping are the most attractive materials for optoelectronic devices[1-3]. Gallium nitride (GaN) becomes the most prevalent base material for ion doping because of its wide, direct band gap, high photon permeability and great thermal stability. GaN doping with several types of ions prepared by different doping methods have been achieved by many research groups[2-4], aiming to realize luminescence in the range of visible light.

Recently, it was found that rare-earth ions (REIs)[5-8], a kind of ions whose emission depends on its intra-4f transition, can act as the efficient luminescence centers in GaN, which have great emission intensity and narrow full width at half maximum (FWHM). The excited states of rare earth (RE) elements (e.g., Er, Tm, and Eu) lead to sharp emission lines from the ultraviolet (UV) through the visible to the infrared (IR). Therefore, RE doped GaN has different potential applications, such as IR emission at 1 540 nm by GaN:Er^{3+} used for optical fiber communication[5] or the visible blue emission by GaN:Tm^{3+} [6] and red emission by GaN:Eu^{3+} [7], both of which are probably applied to the visible light emitting devices. Recently, it was found that photoluminescence (PL) intensity of Er doped GaN at around 1 540 nm experiences no obvious thermal quenching from 14 K to 300 K [5]. Concentration quenching associated with this emission was also not found up to about 10^{21} cm^{-3}. However, this emission around 1 540 nm turns into several split peaks from low temperature to room tem-

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perature (RT).

Although there are lots of benefits of RE doped GaN for the potential future application in light emitting devices, thermal quenching, which leads to the low emission efficiency at RT, is the prime obstruction. For instance, green $^5D_4$ emission of Tb^{3+} doped GaN at low temperature has no obvious emission at RT[8]. However, several studies, from theory[9] and experiment[10,11], have proved that Eu^{3+} doped GaN has great red emission around 622 nm ($^5D_0$ - $^7F_2$) at RT, experiencing no obvious quenching. Thus, Eu^{3+} doped GaN has attracted large amounts of attention. Eu^{3+} doped GaN has been prepared by several methods, such as molecular beam epitaxy (MBE)[10], metal-organic chemical vapor deposition (MOCVD)[11], and ion implantation[12,13]. Compared with the other means, ion implantation serves as an ex-situ doping method that has the merit of convenient control of doping area and ion distribution. However, it will cause lattice damage and introduce defects into the base material [12,13]. Great controversy[12,14] exists in terms of whether the defects after thermal treatment at high temperature are eliminated or not although an agreement has been reached that the greater intensity of emission can be realized after thermal treatment at higher temperature. Defects play a very important role in below band gap excitation (BBGE) because they can provide energy levels situated in the forbidden band of GaN[15]. Understanding the defect-related photoluminescence properties in-depth will be beneficial to develop new-type LED.

In this work, in order to make clear the role the defects play in the transportation of carriers and transmission of energy, thermal treatments at comparatively moderate temperatures are processed. In general, Eu^{3+} responsible for effective emission is located at several different positions, such as substitutional positions of Ga, the interstitial sites and regions related to defects. Although several works [10,11] are focusing on microenvironments and positions of Eu^{3+}, it remains unclear and opaque about these issues. In this work the PL spectra of $^5D_0$ - $^7F_2$ of Eu^{3+} (615-630 nm) are investigated by Gaussian fitting, making clarification about the origins of these emission peaks and the role of the defects playing in the luminescence.

1 Experimental

Three samples of 3-μm-thick undoped GaN grown on sapphire were implanted by Eu^{3+} ions to different fluences, 5.0×10^{14}, 2.5×10^{15}, and 5.0×10^{15} cm^{-2}, named as samples 1, 2, and 3, respectively. In order to avoid channeling effect, the samples were tilted for 7° to the perpendicular direction of the ion beam. The acceleration energy of implantation is 200 keV so that the Eu^{3+} are distributed within the depth less than 100 nm from the surface as simulated by SRIM2010. The peak concentration of Eu^{3+} of the sample 3 is 1.6% roughly 40 nm from the surface. X-ray diffraction (XRD) measurement was carried out by a Bruker D8 advance X-ray diffractometer with monochromatized Cu Kα radiation (λ = 0.154 18 nm). Subsequently three samples were annealed at 600, 750, and 900 ℃, respectively, for 60 min in the atmosphere of nitrogen. A single-mode He-Cr laser at 325 nm with output power of 30 mW was used as excitation source. The PL signals from the samples were clarified using a 32 cm monochromator and then detected by a photomultiplier. Especially the PL spectra of 3 samples after annealing at 900 ℃ were analyzed by multi-peak Gaussian fitting and detailed discussion and analysis of these peaks were processed.

2 Results and Discussion

The overall quality and crystalline structure of the samples maintain well after implantation. XRD results show that the FWHM of GaN (0002) peak of all the samples does not change very much, remaining around 0.14 degree. Simulation results provided by SRIM2010 show that the ions are distributed within a thin layer around 100 nm next to the surface, a narrow area in comparison with 3 μm GaN grown on sapphire. Therefore, the damage of this area introduced by implantation would not influence the structural quality of the whole GaN layer, which is in accordance with our XRD results.

Figure 1 shows the PL spectra of 3 samples under He-Cd laser excitation (325 nm) at RT after annealing at 900 ℃. The peaks at 601 nm, 622 nm and 665 nm are attributed to the $^5D_0$ - $^7F_1$, $^5D_0$ - $^7F_2$, and $^5D_0$ - $^7F_3$ intra-4f transition of Eu^{3+} [7]. Above band gap excitation (ABGE) with He-Cd laser results in strong red emission due to a dominating peak at 622 nm, which can be observed by our naked eyes for all the three samples. Remarkably, the intensity of emission at 622 nm increased by less than 2 times in consideration of the fact that the fluence of ions enlarges by 10 times from sample 1 to sample 3. Less proportion of Eu^{3+} can serve as the active centers as the increase of fluence. This phenomenon is due to more lattice damage and defects were introduced under higher implantation fluence.

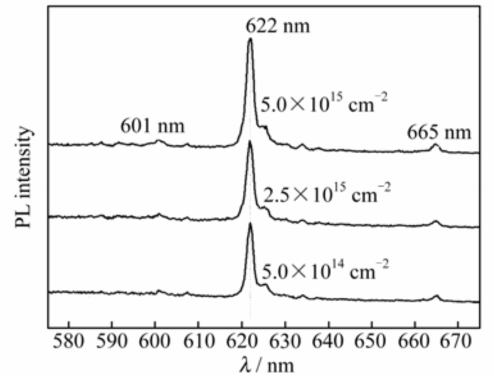

Fig. 1 PL spectra (RT) under 325-nm laser excitation of 3 samples with fleunce of 5.0×10^{14}, 2.5×10^{15}, and 5.0×10^{15} cm^{-2} after annealing at 900 ℃

Figure 2 reveals the PL spectra of sample 3 under He-Cd laser excitation (325 nm) at RT after annealing at different temperatures, 600, 750, and 900 ℃, respectively. It shows that annealing temperature plays a significant role in optical performance of GaN:Eu^{3+}. The intensity of the Eu^{3+} emission at 622 nm increases by one order of magnitude between 600 ℃ and 900 ℃. However, unlike annealing at high temperature that changes the displacement of Eu^{3+} from perfect substitutional sites of Ga and dramatically improves the optical performance of samples[12], annealing at moderate temperature eliminates more defects and drives a larger fraction of Eu^{3+} to occupy at substitutional positions of Ga, and accordingly increasing the intensity of Eu^{3+} emission.

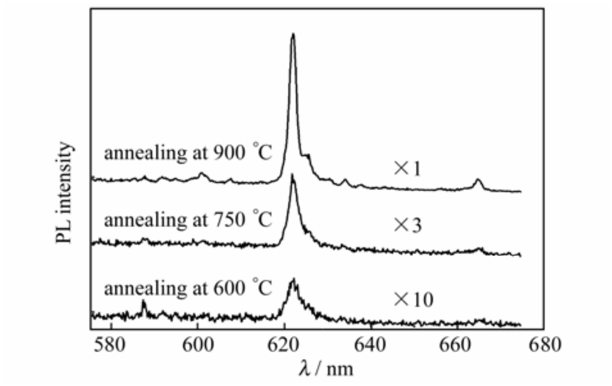

Fig. 2 PL spectra (RT) of the sample 3 under different annealing temperatures of 600, 750, and 900 ℃

The notations of ×1, ×3, and ×10 denote the intensities of the corresponding PL spectra are magnified by 1, 3, 10 times, respectively

Figure 3 shows the detailed PL spectra from 615 nm to 630 nm of 3 samples after annealing at 900 ℃. By Gaussian fittings of the PL spectra, 3 peaks are obtained, which are centered at 620.2, 622.0, 625.0 nm, named as peak 1, peak 2, and peak 3, respectively. All these peaks stem from emission of $^5D_0$ - $^7F_2$ transition of Eu^{3+} posited at different microenvironments and lattice positions [14,15].

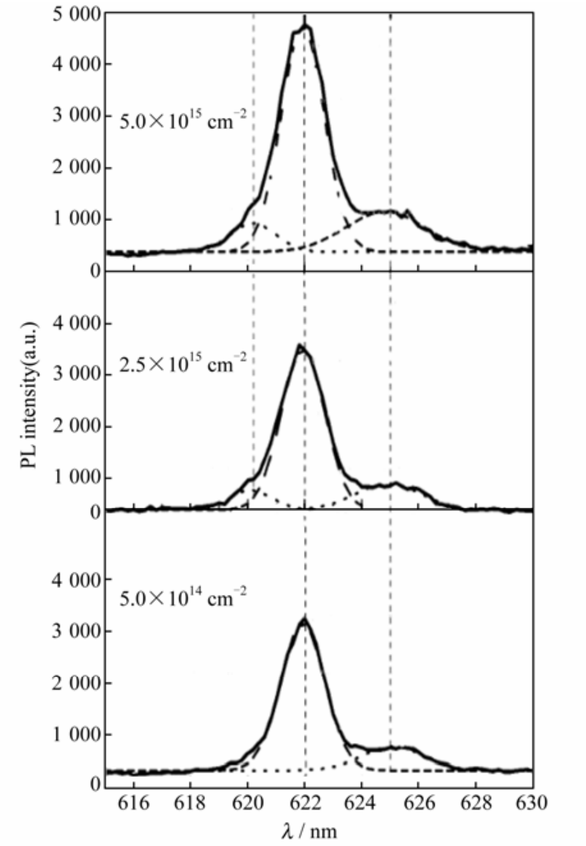

Fig. 3 Gaussian fitting result of the PL spectra (RT) of $^5D_0$ - $^7F_2$ of Eu^{3+} (615-630 nm) of 3 samples with fluence of 5.0×10^{14}, 2.5×10^{15}, and 5.0×10^{15} cm^{-2}

In order to search for the origins of these three peaks, the relation between the integral intensity of these peaks and the fluence of Eu^{3+} is shown in Fig. 4. In general, the integral intensity of these peaks increase as the increase in fluence of Eu^{3+}. However, the increasing trends are different between these peaks. The integral intensity of peak 2 is much larger than the other 2 peaks. Since the dominant luminescence lines are attributed to isolated, substitutional Eu^{3+} occupying at Ga positions [16], peak 2 stems from this group of Eu^{3+}. The intensity of peak 3 increases faster after the fluence reaches the point of 2.5×10^{15} cm^{-2}. On the other hand, the trend of fluctuation of peak 1 is opposite. In consideration of the fact that peak concentration of Eu^{3+} in sample 3 reaches 1.6%, very close to the critical value of 2% that leads to the change of structure of GaN from single crystal to polycrystal [17], it is reasonable to deduce that there exist large amounts of Eu^{3+} posited at the interstitial sites of crystal. As the fluence increases over 2.5×10^{15} cm^{-2} which sample 2 possesses, Eu^{3+} will occupy mainly at the interstitial sites, leading to a fast enhancement of PL intensity of these Eu^{3+}, the same trend as that of peak 3. Therefore, peak 3 stems from a group of Eu^{3+} posited at the interstitial sites of the crystal. Peak 1 emerges after the fluence reaches 2.5×10^{15} cm^{-2}, which leads to the peak concentration of Eu^{3+} obtaining almost 1%. Large amounts of defects and phases of GaEu and EuN are created by this high concentration of doping ions[17]. There exists no peak 1 in PL spectrum of sample 1, which possesses a much lower fluence and peak concentration compared with the other two samples. Therefore, peak 1 is tentatively attributed to a fraction of Eu^{3+} related with defects. The defects in the crystal can provide energy levels situated in the band gap, creating a pathway to realize below-gap excitation.

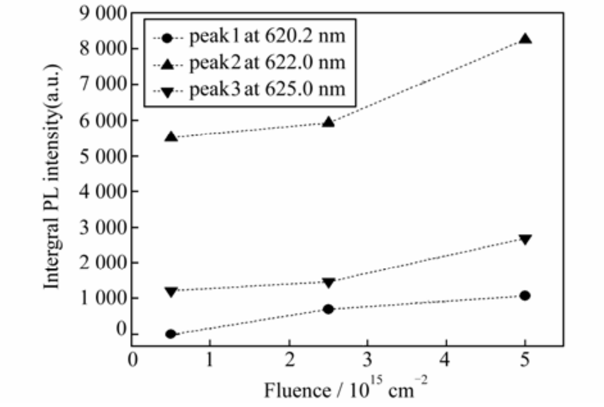

Fig. 4 Integral PL intensity of peak 1, peak 2, and peak 3 as a function of fluence

As reported previously[15], photoluminescence excitation (PLE) of Eu^{3+} doped GaN has a broad excitation spectrum from 360 nm to 400 nm belonging to BBGE. Defects play a dominant role in this kind of excitation because they can provide energy levels posited in the forbidden gap of GaN. Electrons are excited from valence band (VB) to these energy levels and accordingly left holes in VB. Energy released by recombination of these electrons and holes is delivered to the Eu^{3+}, driving these cations to arrive at excited energy levels. However, our study also shows that defects have their own contribution to the PL under ABGE. It was believed that after formation of excitons and pairs of electrons and holes after absorbing photons, the energy released by recombination of these particles will transmit to Eu^{3+} directly without participation of others. In fact, defects play the same role in the process of PL as under BBGE. The only difference is that under ABGE these defects will absorb energy from exotic photons in an indirect way, that is absorbing energy by recombination of excitons and pairs of electrons and holes. In fact, conduction band has a higher absorbing efficiency of exotic photons compared with defects so that Eu^{3+} doped GaN has a higher emission efficiency under ABGE.

3 Conclusion

PL spectra of GaN:Eu^{3+} by ion implantation with several different fluences under annealing at moderate temperature were studied. Annealing temperature plays a significant role in intensity of PL peaks, increases rapidly as the enhancement of annealing temperature. Gaussian fittings of the PL spectra of $^5D_0$ - $^7F_2$ of Eu^{3+} show that they consist of 3 main peaks centered at 620.2 nm, 622.0 nm, and 625.0 nm, respectively. The changing trend of intensity of these peaks demonstrates that they stem from Eu^{3+} placed in different microenvironments and positions. These peaks are attributed to Eu^{3+} posited at the interstitial sites, substitutional positions of Ga, and around defects. Defects play an important role in the behavior of the PL because they set up an energy transmission bridge from exotic photons to Eu^{3+}.

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