Suppression of concentration quenching of Er-related luminescence in Er-doped GaN

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Erbium-doped GaN with different doping concentrations were grown by ammonia-source molecular beam epitaxy. The intra-4*f*-shell transitions related green luminescence were observed by both photoluminescence (PL) and cathodoluminescence (CL) measurements. It was found that concentration quenching of Er-related luminescence was observed in PL measurements while not in CL measurements. The different excitation and relaxation processes are suggested as the cause of the concentration quenching characteristics between PL and CL. The strong Er-related CL intensity in highly doped GaN demonstrates that high energy excitation is a promising approach to suppress the concentration quenching in Er-doped GaN. © *2010 American Institute of Physics*. [doi:10.1063/1.3421535]

Benefiting from the intra-4*f*-shell transitions in rare earth (RE) ions, RE-doped semiconductors have great potential applications in optical devices.[1] Since the 1.54 μm emission from Er ions corresponds to the low-loss window in the absorption spectrum of silica optical fibers for optical communications,[2,3] Er has received attractive attention and been widely studied. Due to the predominance in the microelectronics industry, Si has been chosen for the primary host material. However, it was found that the intensity of Er-related luminescence in Er-doped Si decreases significantly with increasing temperature. This thermal quenching effect limited the application of Er-doped Si at elevated temperature. Fortunately, by systematic investigation of the dependence of the intensity of Er-related emission on the band gap of the host semiconductor as a function of sample temperature, Favennec *et al.*[4] reported that the thermal quenching effect can be suppressed by using wide band gap semiconductors. Therefore wide gap semiconductor such as GaN has received much attention.[5–8] However, another barrier called concentration quenching effect[9,10] hinders the developments. The concentration quenching effect means that the RE-related emission intensity increases with RE-concentration up to a certain concentration, and then decreases remarkably. The concentration quenching effect happens not only in Si and GaN, but also other host semiconductors, and the question how to overcome this phenomenon still remains open.

The luminescence properties of RE doped GaN are studied mainly by photoluminescence (PL).[5–10] In PL measurement, excitation source is photon, for device application however, electron excitation such as cathodoluminescence (CL) is more useful than photon excitation. However research reports on the optical properties of Er-doped GaN using CL are not so many as PL. In this letter, Er-doped GaN films with different doping concentrations prepared by molecular-beam-epitaxy (MBE) were characterized by PL and CL measurements. Obviously different concentration quenching characteristics were observed between PL and CL, and the optical process for PL and CL was discussed. The importance of the *d-f* configuration as the excited state was proposed and the transition through *d-f* configuration was suggested to be a useful way to suppress the concentration quenching in Er-doped GaN.

Er-doped GaN films were grown on sapphire (0001) substrates through ammonia gas source MBE at 700 °C with Ga cell temperature at 940 °C and ammonia flow rate at 2 SCCM (SCCM denotes cubic centimeter per minute at STP). Er was *in situ* doped and the concentration was controlled by varying the Er cell temperature from 1150 to 1250 °C. The main growth time is 2 h and the resulted film thickness was about 1 μm for all samples. Reflection high energy electron diffraction (RHEED) patterns were recorded during the crystal growth. Structural properties were studied by x-ray diffraction (XRD) measurements. Er doping concentrations were measured by Rutherford backscattering spectrometry. PL measurements were made at room temperature by using argon ion laser (488 nm) and He-Cd laser (325 nm) as excitation sources. Thermal field emission scanning electron microscope (Hitachi S4200) equipped with a CL system[11] was employed for CL characterization. The CL measurements were taken with 15 kV/1.2 nA condition at room temperature. For both PL and CL measurements, we mainly focused on the visible $^2H_{11/2}$ and $^4S_{3/2}$ to $^4I_{15/2}$ transition in this report.

Figures 1(a)–1(c) show the luminescence spectra of Er-doped GaN with different doping concentrations excited by He-Cd laser (325 nm, called above band-gap excitation), argon-ion laser (488 nm, called below band-gap excitation) and electron beam in CL system, respectively. Two characteristic green lines related to the intra-*f* electronic transition of Er^{3+} ions between the excited states of $^2H_{11/2}$ (537 nm), $^4S_{3/2}$ (558 nm), and the ground state of $^4I_{15/2}$ were observed in both PL and CL measurements.

To compare the concentration dependence of the intensity of the Er-related green luminescence by using different

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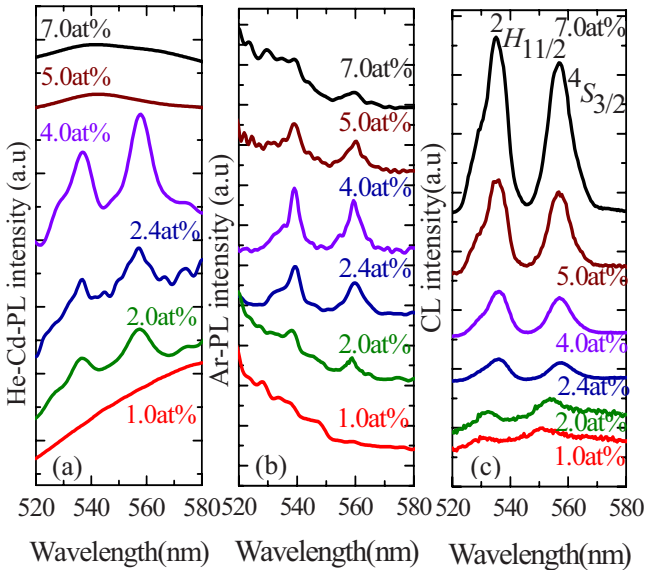

FIG. 1. (Color online) Luminescence spectra in visible region measured at room temperature of Er doped GaN with different doping concentrations excited by using 325 nm He-Cd laser (a), 488 nm argon-ion laser (b), and electron beam (c).

excitation methods, both the PL and the CL intensities as a function of Er doping concentration were plotted in Fig. 2. This figure clearly shows that for both above band-gap excitation (He-Cd laser, 325 nm) and below band-gap excitation (Ar-ion laser, 488 nm), the PL intensity increases with increasing the Er doping concentration up to 4 at. % and then decreases rapidly due to the concentration quenching effect. However, very interestingly, the CL intensity monotonically increases with Er concentration up to 7 at. %, namely, no concentration quenching of Er-related emission is observed in the CL measurements at least with Er concentration of 7 at. %. The CL spectra of the 7 at. % doped sample shown in the inset of Fig. 2 consists of strong emission peaks only from Er ions without other peaks from GaN or the defect-related luminescence, indicating that Er ions in the highly doped sample still act as luminescence center.

The excitation power density is around 5 $\mathrm{mW/mm^2}$ in PL and 7.2 $\mathrm{W/mm^2}$ in CL (15 kV × 1.2 nA/0.5 $\mu\mathrm{m}^2$). The

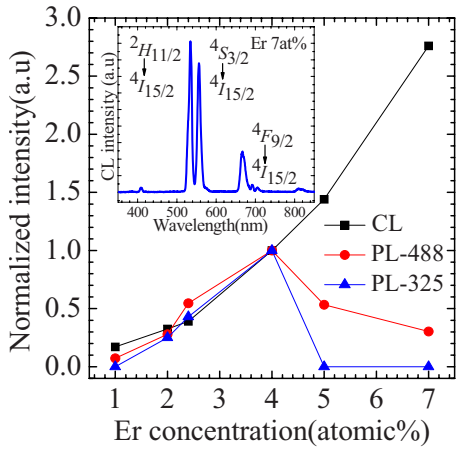

FIG. 2. (Color online) Luminescence intensity at 558 nm in PL and CL as a function of Er doping concentration measured at room temperature. The inset shows the CL spectra of Er-doped GaN with the Er concentration of 7 at. %.

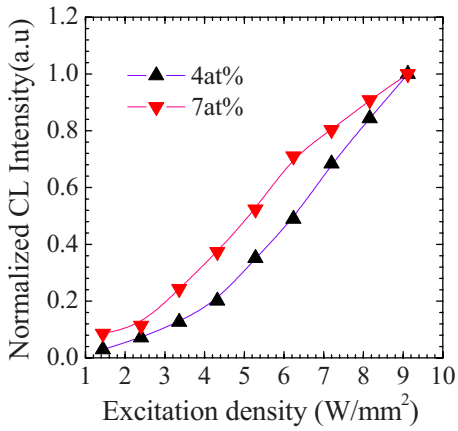

FIG. 3. (Color online) Normalized CL intensity of Er-doped GaN with 4 at. % and 7 at. % as a function of excitation density. The excitation density is varied by changing the acceleration voltage.

excitation density in CL is about three orders of magnitude larger than that in PL, however, it is generally accepted that the excitation probability by electron is less than that by photon. So the difference in the excitation density between PL and CL is less than three orders of magnitude. To rule out some unexpected effects which induce luminescence by high excitation power density in CL, excitation density dependence on the luminescence intensity was examined and the results are shown in Fig. 3. The intensity of CL from Er-doped GaN with the Er concentration of 4 at. % and 7 at. % increased proportionally with increasing excitation density in the range from 1.4 to 9.1 $\mathrm{W/mm^2}$. It may be possible to say that some unexpected effects induced by high excitation power density are negligibly small and that the remarkable difference in concentration quenching characteristics observed in PL and CL are due to the difference in transition process.

In good agreement with the previous works,[9,10,12,13] we also have observed the formation of ErN phase and the degradation of GaN crystal quality by XRD and RHEED analysis in Er-doped GaN with the Er concentration of 7 at. %. It was suggested that, in higher concentration, due to the formation of defects and the shrinking of the distance between RE ions, ion-ion, or ion-defects cross-relaxation could cause the photoluminescence quenching.[9,10] The proposed excitation and relaxation processes of PL and CL are shown in Figs. 4(a) and 4(b), respectively. In PL, both excitation and relaxation are based on parity-forbidden intra *f*-*f* transitions. For above band-gap excitation, the *f* electrons will be excited to $^4G_{11/2}$ or $^2H_{9/2}$ by energy transfer from GaN through defect-trap levels such as V_N,[14,15] and the electrons at $^4G_{11/2}$ or $^2H_{9/2}$ level will then have two competing relaxation process; the first one is to relax to $^4S_{3/2}$ by multiphonon relaxation process followed by radiative transition from $^4S_{3/2}$ to the ground state $^4I_{15/2}$, and the second one is to relax via defect levels which may be correlated with $^4G_{11/2}$ and/or $^2H_{9/2}$ levels. The quenching of PL should be most possibly caused by the competing cross relaxation of *f* electrons from $^4G_{11/2}$ or $^2H_{9/2}$ to defects levels becoming much stronger than the multiphonon relaxation process relaxation to $^4S_{3/2}$. For below band-gap excitation, the *f* electrons are excited directly to the $^4F_{7/2}$ state by Ar ion laser with 488 nm, and the quenching in PL should be similarly caused by the non-

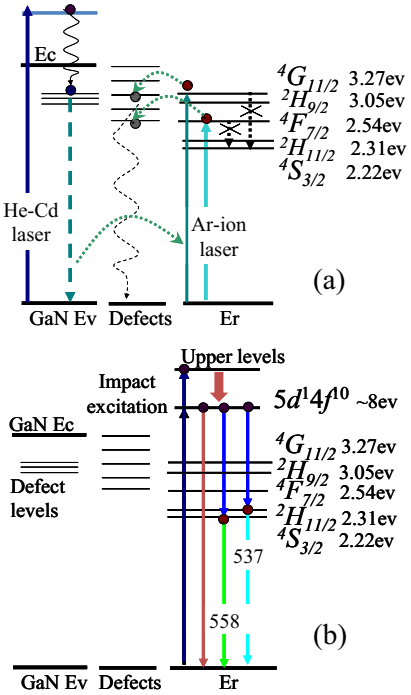

FIG. 4. (Color online) Proposed models of optical process for PL(a) and CL(b) in Er-doped GaN with higher doping concentration.

radiative cross relaxation of excited *f* electrons from $^4F_{7/2}$ to defects.

On the other hand, the direct impact excitation of Er ions by high energy electrons is dominant in CL. Electron beam with high energy can directly excite the 4*f* electrons into higher states like *d-f* configuration. The highest electronic state of $4f^{11}$ configuration situates around 6.7 eV (e.g., $^2F_{7/2}$) and the lowest $4f^{10}5d$ configuration situates at around 8 eV. In CL, the electron beam with high energy can excite easily into 5*d* levels. Due to the strong interaction of the energy levels of $4f^{10}5d$ configuration with the crystal lattice, the excited 5*d* electrons tend to relax via multiple-phonon-emission process to the lowest levels of the $4f^{10}5d$ configuration.[16] Since the transitions from $4f^{10}5d$ configuration to $4f^{11}$ configuration are parity allowed electric-dipole transition, and the transition rate greatly depends on the frequency of the radiation,[16] the transition probability from $4f^{10}5d$ configuration to $^4S_{3/2}$, and $^2H_{11/2}$ can be expected to be large. In fact, high transition probability from $4f^{10}5d$ to $^4S_{3/2}$ and $^2H_{11/2}$ was observed by synchrotron radiation excitation.[17,18] Therefore, the transition from $4f^{10}5d$ to $^4S_{3/2}$ in CL can avoid the participation of $^4G_{11/2}$, $^2H_{9/2}$, and $^4F_{7/2}$ levels which has correlation with defect levels and the cross-relaxation processes with defects which is observed in PL. The excited state of $4f^{10}5d$ may be a key state for reducing concentration quenching. The utilization of *d-f* transition is important to suppress the concentration quenching and to get high emission intensity from Er. The excitation to *d-f* configuration seems to be realized in electroluminescent devices where strong electric field is working. In such devices, it may be possible to get high intensity of luminescence from Er without concentration quenching.

In summary, green emission from Er-doped GaN films grown by ammonia source MBE has been observed in both PL and CL. Although the concentration quenching was observed in PL with the Er concentration of more than 4 at. %, the concentration quenching was not observed up to 7 at. % in CL. The excited state of $4f^{10}5d$ may play an important role in reducing the concentration quenching.

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