Surface- and volume-related excitation of Eu-doped nanocrystalline GaN powders

A. Podhorodecki\textsuperscript{a,*}, R. Kudrawiec\textsuperscript{a}, M. Nyk\textsuperscript{a}, J. Misiewicz\textsuperscript{a}, W. Strek\textsuperscript{b}

\textsuperscript{a}Institute of Physics, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
\textsuperscript{b}Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wroclaw 2, Poland

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The influence of grain sizes on the excitation mechanism of Eu\textsuperscript{3+} ions doped into GaN powder has been investigated by photoluminescence and photoluminescence excitation spectroscopy. It has been found that depending on the grain sizes, different dopants excitation mechanisms can dominate. In the case of nanograins, where the europium related emission appears at \( \sim 612 \text{ nm} \), it has been concluded that the surface plays a very important role. In this case, the dominant excitation of Eu\textsuperscript{3+} ions is via the local charge transfer from the surrounding oxygen atoms adsorbed post growth at the GaN nanocrystals surface. This mechanism is not efficient for GaN micro grains, where the europium related emission appears at \( \sim 625 \text{ nm} \), due to small surface-to-volume ratio. In this case it has been concluded that the oxygen atoms at the GaN surface play a negligible role in the total Eu-related emission and the main contribution to Eu excitation comes from the energy transfer from the GaN matrix.

\* Corresponding author.
E-mail address: artur.p.podhorodecki@pwr.wroc.pl (A. Podhorodecki).

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This will depend on the amount of the surface defect states, alignment of the RE and NC energy levels, the electronic coupling between the europium and NC states, and the spatial localization of the states, particularly of the donor states which can be either localized surface states, or delocalized/localized core states.

In nanoparticles, most ions located at the surface are nonsaturated in coordination, thus can bind additional atoms from the ambient atmosphere, i.e. oxygen atoms. Moreover, in the case of nanoparticles, a different energy structure of the nanocrystals can be obtained, depending on the nanocrystals size. It gives the possibility of tuning the energy levels position to the energy levels of the acceptor (lanthanide ion). Also, the amount of surface states depends on the NC size.

In our previous work [18], it has been shown that an efficient energy transfer from nano-GaN grains to europium takes place. Thus, the aim of this work is to investigate the influence of the grain sizes of GaN:Eu⁺⁺ nanocrystalline powder on the excitation mechanism of europium ions.

2. Experimental details

A nanocrystalline GaN powder doped by Eu ions (−13%) has been obtained in the combustion method at 850 °C nitridation temperature. On the basis of our previous results [19–21] (i.e. TEM, SEM, XRD measurements together with the analysis by using Scherrer formula) it has been estimated that 850 °C nitridation temperature corresponds to GaN:Eu⁺⁺ grains with the average grain size of ~7 nm. By using a high energy electrons beam as a post-growth treatment, a micro grains have been obtained as it has been already discussed in our previous paper [21]. For total photoluminescence excitation (PLE) measurements a 450 W Xe arc lamp connected to a 0.18 m Jobin Yvon monochromator was used as the excitation source. A beam splitter redirects a portion of excitation light into power-meter to monitor the wavelength dependence of the Xe lamp output power. Thus, each obtained PL spectrum has been corrected by the excitation power. After recording the spectrum, the PL integrated intensity has been plotted versus excitation wavelength. The width of the excitation line was less than about ~8 nm, which gives the typical excitation powers of the order of 0.1 W/cm². The signal has been detected by using Ocean Optics HR4000 spectrometer.

3. Results and discussion

Fig. 1 shows the PL spectra obtained at 300 nm excitation wavelength for two different GaN:Eu⁺⁺ grain sizes. Fig. 1a presents results obtained for nanograins (~7 nm), where the strong, europium emission can be observed together with the surface states related broad emission band. Observed europium related emission bands are related to the $^5D_0 \rightarrow ^7F_2$ (612 nm), $^5D_0 \rightarrow ^7F_3$ (at ~650 nm), $^5D_0 \rightarrow ^7F_4$ (at ~700 nm) and $^5D_0 \rightarrow ^7F_1$ (at ~594 nm) $4f$–$4f$ europium transitions.

Fig. 1b shows results obtained for micro grains (μc-GaN:Eu⁺⁺). For μc-GaN:Eu⁺⁺, the surface states related band disappears and a band related to the GaN core appears at 384 nm. Additionally Fig. 1b has been supported by the emission band measured at the same setup for the freestanding GaN epilayer obtained by the hydride vapour phase epitaxy (HVPE). Observed emission band related to GaN band-to-band transition appear in this case at ~364 nm which value is typical for the most of GaN materials. Observed ~20 nm redshift is most probably due to Stark effect or strain which both can appear during the micro grains formation. Moreover, the changes in the signal related to nc-GaN core/surface states are due to the different surface-to-volume ratio and have been already discussed by us in Ref. [19]. Additionally, the lines related to europium ions split, and the dominant $^5D_0 \rightarrow ^7F_2$ band splits into two bands at 612 nm and 625 nm. The peak position at 612 nm is not characteristic of Eu⁺⁺ doped GaN materials, where it appears usually at about 622 nm [22,23]. Nevertheless, Hirata Flores [24] have observed Eu-related emission at ~611 nm for nano (~5–8 nm) grains same as Xu et al. [25] for GaN:Eu nanoneedles of diameters from 5 nm to 1 μm with a length of up to a few microns.

This disagreement between the experimental data and expected for Eu in GaN emission wavelength can be understood if we realize that this measured value is very similar to the position of the emission band of Eu⁺⁺ ions in the oxide matrices which appears at about 610 nm [26]. This suggests that some of the Eu ions have oxygen neighbors and most probably are placed at the oxidized grains surface.

On the other hand, Shi et al. [27] have observed Eu-related emission at 622 nm in GaN:Eu powder (~3 μm diameter) whose value is very similar to value of 621 nm observed by Wu et al. [28] also for ~3 μm GaN:Eu particles. These results suggest that emission at longer wavelengths is also possible to achieve from Eu⁺⁺ ions doped into nanostructured GaN but when the GaN size is of order of microns rather nano meters.

Thus, in μc-GaN:Eu⁺⁺ there are probably various environments of the Eu⁺⁺ ions and the obtained emission signal is a superposition of the emission from different emission centers – one related to Ga interstitials of Eu⁺⁺ surrounded by N atoms (at ~625 nm) and the other related to Eu⁺⁺ ions with oxygen neighbors (at ~612 nm). We attribute the latter sites to europium ions surrounded by the oxygen atoms at the nanocrystalline surface, since the XRD results [21] do not show any additional Ga, N-oxide phase but only pure GaN crystalline phase. On the other hand, it is not expected that oxygen atoms, which are absorbed on the NC surface, are strongly manifested in XRD spectra. To verify this scenario, excitation properties for a different GaN:Eu⁺⁺ grain sizes have been investigated by using TPLE experiment.

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Fig. 2 shows the TPLE spectra obtained for $^5D_0\rightarrow^7F_2$ transition of the Eu$^{3+}$ ion for two kinds of powder: (i) nanocrystalline (~7 nm in diameter) GaN:Eu$^{3+}$ grains, and (ii) μc-GaN:Eu$^{3+}$ grains. The origin of the TPLE signal, in the case of nanograins, has been discussed already in our previous work [18]. One of the conclusions presented there was that the TPLE peak at 4.4 eV could be associated with the excitation of Eu$^{3+}$ ions through the charge transfer from the oxygen atoms. Approximately at this energy, the CT is very strong for Eu$^{3+}$ ions in oxide-based hosts [10]. In the case of nitrogen, according to some theoretical considerations (Jörgensen formula) [29] and recent work of Dorenbos and van der Kolk [30], the CT of Eu$^{3+}$ ions in GaN material is also expected at ~3.0–4.5 eV. However, rare earth doped nitride matrix was investigated very rarely thus no clear experimental evidence for CT in nitrides due to nitrogen is reported so far.

Fig. 2b shows the same results as Fig. 2a, but obtained for μc-GaN:Eu$^{3+}$ grains. Recently, similar excitation spectra have been also obtained for Eu$^{3+}$ ions doped into epitaxial GaN host [31]. As it can be seen, the same features can be observed in both spectra (for nano and micro grains), the main difference is only in the relative TPLE peaks intensities. The different relative intensities for nano and micro grains can be explained by different contributions of the excitation mechanisms of Eu ions: (i) charge transfer from the oxygen atoms, and (ii) energy transfer from the GaN host. In the case of nanograins, the dominant peak, related previously to CT, is centered at 4.4 eV, where in the case of micro grains the highest intensity has a peak associated with the excitation related to the GaN host it has a similar intensity as the peak related to CT.

The explanation of this result is as follows. Despite the fact that no oxygen phase is present in the powder, the surface of the nanocrystalline powder could be oxidized post growth. Thus, in the case of nanograins, most of the ions are bound to the NC surface with the oxygen neighbors. In this case, a significant excitation channel, related to CT from oxygen to europium ions bound at the surface, will be open, since Eu$^{2+}$ is a more favorable state than Eu$^{4+}$. Also, other excitation processes, due to energy transfer from the GaN host, are present in this case, which indicates that some of Eu$^{3+}$ ions could be incorporated also into the nanocrystalline core. This can be also confirmed by the energy position of the nc-GaN:Eu$^{3+}$ absorption edge shown in Fig. 2a, whose energy corresponds to the europium excitation edge (at ~3.4 eV) taken from TPLE spectrum. Nevertheless, it is worth to notice here, that the energy position of this excitation band, for the micro grains is slightly redshifted in comparison with the energy position of the excitation band obtained for nanograins. This result is in agreement with the discussion given previously and the experimental data obtained from PL. Moreover, as it can be seen in Fig. 2a, the absorption spectrum shows much less details since this technique is not as selective as TPLE on the europium excitation properties and gives only the absorption response of the matrix.

On the other hand, in the case of μc-GaN:Eu$^{3+}$ agglomerates, much more ions sit inside NC core in GaN host surrounding. In this case, the excitation channel through the GaN host increases and the total signal related to excitation of europium ions changes. Nevertheless, there are still some grains (micro and/or nano) in the powder with europium ions at the oxygen rich surface, which emits light at 612 nm and gives the contribution to the total excitation signal.

4. Conclusions

In conclusion, the dependence of the excitation mechanisms of Eu$^{3+}$ ions doped into GaN nanocrystalline powder on their grain sizes have been discussed. It has been shown that in the case of nanograins, dominant excitation mechanism is through the local charge transfer from the oxygen atoms to europium ions and Eu-related emission appears at 612 nm. Both facts indicates that probably most of the ions are placed at the grains surface in the oxygen surrounding. In the case of micro grains, the dominant excitation is via the GaN matrix and Eu-related emission appears at 625 nm.

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References