Lanthanide ion incorporation in gallium nitride through a salt melt process

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Lanthanide ions have been doped in epitaxial gallium nitride material through a liquid phase salt melt process. The technique involves a brief photolytic etching of the sample surface followed by heating with a melt of a selected lanthanide halide under reducing conditions. In this work, hydrogen sulphide entrained in nitrogen gas was used to produce the reducing ambient. Europium-doped GaN pumped with above-gap UV radiation showed strong red emission. The temperature dependence of the intensity of this red emission is also described. Neodymium caused surface pitting and consequent enhancement of defect-generated yellow luminescence. Doping with cerium resulted in a diffuse broadband ultraviolet emission but no specific emission lines.

1. Introduction

The f-block Lanthanide elements are particularly attractive as substitutional impurities in light emitting semiconductors. Their presence can greatly modify the optoelectronic properties of host materials, making them useful for a variety of new applications. Appropriate lanthanide doping can be used for producing light emitters that are more efficient and have a broader range of emission wavelengths than devices made from host materials alone. Lanthanide dopants have a partially filled 4f shell shielded by completely filled outer 5s and 5p shells, resulting in very sharp optical emissions due to 4f-4f electron transitions with energies largely independent of the host material. By appropriate choice of the luminescent ion, the emission wavelength can be tuned from ultraviolet to the infrared [1]. In the past, several lanthanides have been incorporated in both zinc sulphide (ZnS) and gallium nitride (GaN) as well as in related alloys. These include Europium [2,3], Erbium [4-6], Thulium [7,8], Praseodymium [9,10] and Terbium [11,12]. Wide band gap semiconductors such as these are particularly suitable as host materials for such applications because their large band gap suppresses luminescence quenching at room temperatures [13]. Heterogeneous atomic or ionic substitutions can be performed by a variety of means. These include thermal diffusion doping from a gas phase, doping through contact with a suitable melt (as used in liquid phase epitaxy), spin-on glass doping, low and high energy ion implantation, in-melt dopant incorporation during crystal growth, dopant species incorporation during Molecular Beam Epitaxy (MBE) and during Metal Organic Chemical Vapour Deposition (MOCVD) processes. In the past, most lanthanide ion dopings in GaN and related compounds have been performed as either species incorporation during MOCVD growth of epilayers or through ion implantation techniques. The work presented here was undertaken to investigate liquid phase doping of MOCVD-grown GaN epilayers with three different lanthanides: Europium, Cerium and Neodymium.

2. Ion Incorporation Process

GaN epilayer samples were grown at U.K.'s Engineering and Physical Sciences Research Council (EPSRC) operated national III-V growth facility in Sheffield, England. The basic material was a low dislocation density 1.5 micron thick GaN epilayer grown on top of a several micron thick GaN buffer layer grown with the low temperature / high temperature growth technique that is usual for obtaining low dislocation density material. Transmission Electron Microscopy (TEM) studies showed this type of material to have dislocation densities in the range of 10^8 to 10^9 cm^{-2}. Square samples, 4 mm x 4 mm in size were diced from the as-grown wafer and cleaned by repeated ultrasonic cleaning in acetone, methanol, iso-propanol and deionised water. The chip samples were 600 microns in thickness. These chips were then etched in a dilute aqueous solution of potassium hydroxide (KOH) of 1.5 M strength. The etching was carried out while the samples were mildly agitated and illuminated with a 10 Watts ultraviolet lamp. The UV radiation provided spectral coverage in the 260 nm to 380 nm range. In this kind of photolytic etching process, UV radiation generates electron-hole pairs that etch a III-V semiconductor through a reaction in which holes oxidise gallium atoms, converting them into soluble ions whereas electrons reduce the group V component [14] (in this case converting it into gaseous nitrogen). GaN surface etching both removes environmental and handling damage at the surface, polishing it to a good surface finish

and exposes the end points of threading dislocations that originate at the substrate-buffer interface and propagate through the grown epilayers. The etch rate was found to be around 10 nm per minute at room temperature (23 °C).

For the actual lanthanide ion doping process, the samples were loaded into ceramic boats (runs were carried out with single samples) together with lanthanide halides. Half-a-gram to one gram of chloride salts were used for the doping experiments. The loaded boats were placed in the centre of a horizontal tube furnace capable of reaching temperatures in excess of 1200 °C. In order to avoid oxidation of the GaN surface and molten salts, reducing conditions were established inside the furnace tube. This was done by having pure nitrogen gas, mixed with small amounts of hydrogen sulphide, flow through the furnace tube during doping runs. Using a gas flow controller, the flow rate was consistently maintained at 4 standard cubic centimetres per minute (sccm). Small amounts of hydrogen sulphide were generated by placing a small boat of moist thioacetamide ($CS_3.CS.NH_2$) at the upstream end of the furnace tube. Thioacetamide hydrolyses to acetamide ($CH_3.CO.NH_2$) according to the following reaction and slowly releases hydrogen sulphide gas:

$$CH_3.CS.NH_2 + H_2O \rightarrow CH_3.CO.NH_2 + H_2S\uparrow$$
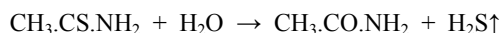
The hydrogen sulphide got entrained in the nitrogen stream and maintained non-oxidising conditions inside the furnace tube. This process also passivates the semiconductor surface [15], reducing non-radiative recombinations and thus boosting the overall fluorescence yield.

The three lanthanide ion dopings were carried out successively with Europium Chloride, Cerium Chloride and Neodymium Chloride. Their melting points are: 850 °C, 817 °C and 758 °C, respectively. In each case, the ceramic boat with GaN sample and the doping salt was heated from room temperature to 900 °C with nitrogen + H_2S stream flowing through the furnace tube all the time. The temperature ramp up rate was 1 °C per second. On reaching 900 °C the temperature was maintained for an hour before it was ramped down to room temperature over the period of several hours. During the time the sample was in contact with the salt melt consisting of dissociated lanthanide ions and chloride ions the former diffuse into the GaN lattice. The diffusion process is particularly efficient at the dislocation end points at the sample surface because these sites have an abundance of dangling bonds that can readily bond with foreign atoms. By enlarging such sites, prior wet etching facilitates the doping process. The diameter of these openings was around 100 nanometres and they were 1.5 microns long – equal to the thickness of the GaN epitaxial layer. Based on the volume of these dislocation cores and their aerial density as quoted earlier, it is estimated that the lanthanide doping density for each of the three elements reported in this work was about 2.4×10^{18} m^{-3}. Non-oxidising gas flow was maintained throughout this procedure. After furnace cool down, the samples were taken out of their ceramic boats and repeatedly cleaned with water and ethanol in an ultrasonic bath. The samples were carefully inspected under an optical microscope to make sure that no contamination from lanthanide salt was present.

3. Sample Characterization

The doped GaN samples were characterized by studying their photoluminescence spectra at different temperatures. Electrical resistance measurements showed all samples to have very high resistance both before and after doping. Visually, the samples had a clear, glass-like appearance except for the neodymium doped samples that had a milky white appearance.

3.1 Europium-doped GaN

GaN epilayer samples doped with Europium showed distinct and strong spectral lines attributable to Europium ions on the Ga sub-lattice of the zinc blend structure. As seen in the photoluminescence spectrum shown here in Fig. 1, these lines appear at 615 nm and 620 nm in the red region of the visible spectrum and come from the $^5D_0 \rightarrow$ $^7F_2$ transition of the Europium ion. These lines appear superimposed on a broad defect-generated background that is well known as GaN's yellow luminescence [16-21]. This broadband luminescence covers the region from approximately 475 nm to 675 nm; filling up most of the visible spectrum [22]. As a result of the mixing of the yellow defect luminescence and the red luminescence from incorporated Europium ions the sample emitted a diffuse orange colour when illuminated by a UV lamp. For clarity's sake, figure 1 has been plotted after subtracting the yellow background. Europium ion's red emission in GaN host has been observed by several researchers but the route for ion incorporation reported here is the easiest one described so far.
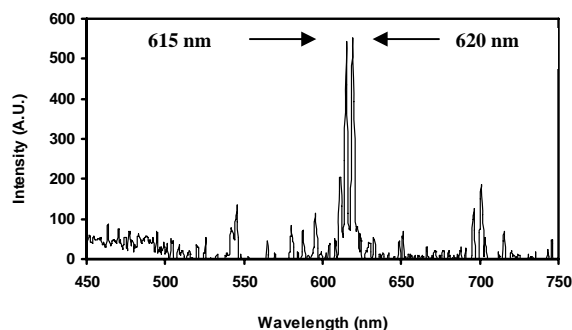

Fig. 1. Spectrum of the photoluminescence of europium-doped GaN at room temperature with the yellow background subtracted.

The temperature dependence of the red emission in the 30 °C to 400 °C range is shown in Fig. 2. The integrated intensity decreased gradually as the temperature

increased from room temperature. Conversely, the fluorescence was significantly stronger at liquid nitrogen temperature.
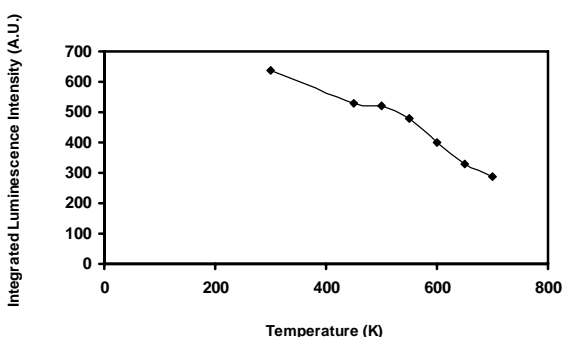

Fig. 2. Temperature dependence of the photoluminescence emission of europium ions hosted in a GaN matrix.

The band gap of GaN is 3.4 eV which corresponds to radiation of 365 nm wavelength. When illuminated with below band gap radiation at 390 nm, the europium-doped sample didn't emit its characteristic red emission. This was verified to be independent of the intensity of illumination and exposure to intense UV radiation from a frequency doubled Ti:Sapphire laser at wavelengths longer than 365 nm also didn't produce the red luminescence. This supports the idea that it is electron-hole generation in GaN followed by recombination at a europium ion site that is responsible for the emission of red light. Thus the red europium luminescence is essentially caused by radiative intra-gap recombination at europium ion-decorated dislocation sites as well as at sites of europium ions in bulk un-dislocated regions. This observation is in accord with findings from europium-doped electroluminescent devices which seem to work at high bias voltages from carrier-impact mediated processes that likely generate electron-hole pairs [23]. It is likely that if suitable band-engineered structures are developed with europium ion doped active regions then such devices could be made to work at much lower voltages. Our findings are, therefore, important for enlarging the set of emission colours possible from GaN-based electroluminescent pn-junction diodes. Furthermore, with interest in zinc oxide (ZnO) as a possible future supplement to GaN increasing [24], similar techniques could potentially be used with that material as well.

3.2 Cerium-doped GaN

Cerium is an important luminescent ion is several host materials ranging from laser crystals to scintillators and phosphors for white LEDs [25-28]. In GaN, on the other hand, cerium ions doped through the liquid phase diffusion process described here didn't produce any sharp and distinct photoluminescent lines. Instead, cerium-doped samples showed a broad low intensity UV band, as shown

in Fig. 3 here. This occupied a 75 nm wide band with an FWHM of 23 nm and appeared just short of the strong GaN band edge luminescence at 365 nm. The data shown here were taken at room temperature with a UV excitation in the 260 nm to 380 nm band. The origin of the broad line-like features seen in the spectrum is not known. The broadband luminescence implies a strong phonon coupling for Ce^{3+} ions when GaN is used as a host. Vibronic smearing could broaden a sharp transition to an extended non-homogenously broadened band.
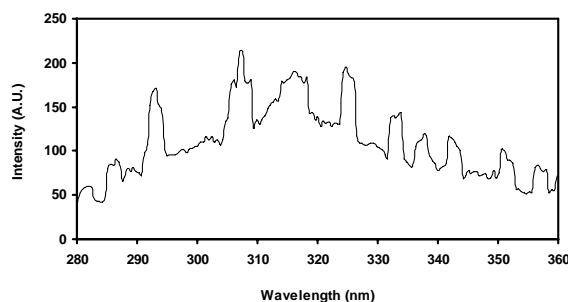

Fig. 3. UV spectrum of photoluminescence from cerium-doped GaN at room temperature.
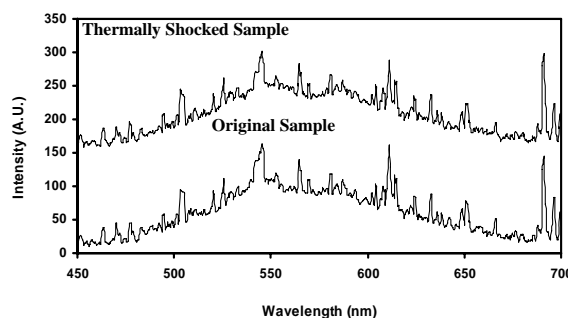

Fig. 4. UV fluorescence spectra of a GaN chip before and after thermal shock from a ~1200 °C butane-oxygen flame (duration 10 seconds).

A separate experiment was also done to verify that elevated temperature thermal processing itself doesn't alter the spectral emission characteristics of GaN. In this experiment the UV fluorescence of a GaN chip was measured before and after holding it at an elevated temperature. Thermal shock was administered by heating the chip to around 1200 °C for 10 seconds in a butane-oxygen gas flame. The spectra before and after this treatment, for the same chip, are shown in figure 4 where these have been vertically separated for clarity. All the spectral features appear unchanged after thermal shock and this proves that high temperature treatment by itself doesn't cause any lasting change to GaN.

3.3 Neodymium-doped GaN

Attempts to dope GaN with Neodymium, using the technique described in this paper, produced an interesting result. Instead of a physical diffusion inside the GaN epilayer crystal, the melt of neodymium chloride attacked the surface of the sample. The resulting corrosion was easily seen on the surface of the chips as a mottled appearance. The exact chemical reaction involved is not known. Previously, other workers have reported characteristic emission lines, in the near-infrared region, from Nd^{3+} ions hosted in GaN [29]. As Neodymium ions require efficient host-mediated level mixing in order to generate luminescence so it appears that GaN as a host doesn't couple very strongly with incorporated Neodymium ions. However, it was found that the corroded surface had a much higher luminescence efficiency for crystal defect-generated yellow luminescence than a comparable surface not treated with the melt of neodymium chloride. Fig. 5 shows an undoped GaN chip (left) and a neodymium-doped GaN chip (right) under UV illumination. The enhancement of yellow emission is clearly seen. Furthermore, this effect was confined to a thin layer at the surface and, therefore, this was not a bulk effect. The distribution of photoluminescence intensity at room temperature is shown in Fig. 6 here.
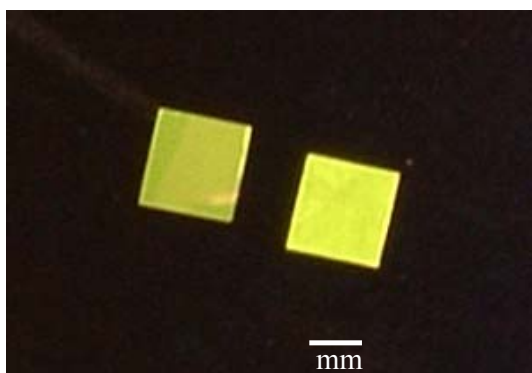

Fig. 5. Yellow light emission from two similar GaN chips – one without Nd doping (left) and the other with Nd doping (right).
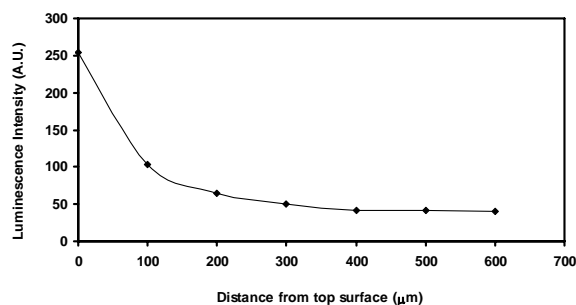

Fig. 6. The vertical spatial distribution of photoluminescence intensity from a neodymium salt melt-treated GaN chip at room temperature.
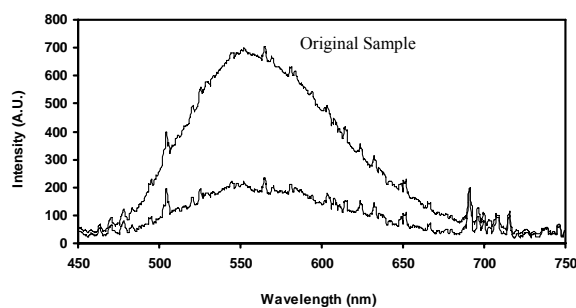

Fig. 7. Spectrum of broadband photoluminescence emission from a neodymium-treated GaN sample (upper curve). The lower curve is emission from an untreated GaN sample for comparison. Both data sets were taken at room temperature.

Notice that most of the emission comes from a near-surface layer. The high temperature doping process likely plays a role here because with high temperature annealing, ion implanted erbium in GaN films is known to preferentially move up to the surface [30] and it is likely that the same happens with neodymium ions. A spectrum of neodymium-treated GaN sample illuminated with 310 nm radiation is shown in Fig. 7. For comparison the spectrum of background luminescence from an untreated GaN sample is also shown (lower curve). It is clear that neodymium treatment enhances the broadband defect luminescence from GaN samples without introducing any further spectral lines that could be identified with transitions in neodymium ions. Note that the small spikes in the spectrum that constitute a kind of finger print of the material and its growth are preserved in the two spectra shown which are otherwise from separate chips. Neodymium treatment enhanced the central portion of luminescence between the wavelengths of 480 nm and 689 nm as indicated in the figure. The most likely explanation is a severe increase in the defect volume in the top layer of the sample.

4. Conclusions

In conclusion, GaN samples were treated with molten salts of three different lanthanides at 900 ºC. This treatment modified the luminescent properties of the samples in different ways. Europium-doped samples exhibited strong red lines in their fluorescence spectra which could be attributed to 4f to 4f transitions in Eu^{3+} ions on the GaN lattice. Cerium-doped samples showed a weak diffuse emission in the near-UV portion of the spectrum. Neodymium treated samples were seen to become very efficient yellow emitters under above-gap UV irradiation.

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