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Intense red emission from an electron-beam excited GaN/Al_2O_3:Cr epitaxial sandwich structure

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We describe a two-step excitation process of a GaN/Al_2O_3:Cr specimen by a high energetic pulsed electron beam of 30 keV. Epitaxial GaN was grown on the (0001) faces of ruby by a metalorganic reaction of GaCl and NH_3 with He as a carrier gas. Spinel and ruby are frequently used as substrate materials for the epitaxial deposition of GaN. At the same time is ruby one of the most useful laser materials with a red emission line at ë = 694 nm. Due to its dielectric character, the pumping of ruby is performed usually subjecting it to the light of an intense flash lamp. Electron beam excitation, on the other hand, which could be more powerful, is impaired with electrical insulator material. This discrepancy can be overcome by a two-step excitation, where at first the semiconducting GaN-layer, epitaxially grown on a (0001)Al_2O_3:Cr (ruby) crystal is excited to emission radiation by an external electron beam. The following internal absorption process of the GaN luminescence radiation by the ruby crystal provides for the characteristic ^2E to $^4A_2$–transition at 1.786 eV. We found a strong and sharp emission line of that photon energy, which additionally displays polarization, typical for the anisotropic uniaxial ruby crystal. Such an indirect electron-beam excitation of ruby allows to generate almost monochromatic red light, and might point into a direction of interesting practical applications.

Keywords:

1. Introduction

Ever since the first preparation of thin films of GaN from metalorganic compounds several decades ago [1-3], research in group III-nitrides has proceeded during the last few years to a level, that GaN quantum wells, confined by (In_x or Al_x)$Ga_{1-x}N$ barriers, are now fabricated and used as active region in blue light-emitting diodes and lasers [4-6]. While MO-CVD was the method of choice during the last decades, high quality GaN as well as GaN/$Al_xGa_{1-x}N$ heterostructures and quantum wells, grown by MBE have been reported recently [7-11].

Gallium nitride is a large band-gap III-V compound semiconductor with a direct lowest fundamental energy gap situated at the Γ-point of the Brillouin zone with a value of 3.5 eV at room temperature. Having in mind the photon energy range of the visible light spectrum being about 1.6 eV … 3 eV, the luminescence radiation of this material stretches up to the uv light region. GaN crystallizes in the hexagonal wurtzite structure with a = 0.3182 nm and c = 0.5176 nm, but has shown dimorphism. Indeed it has been found that both hexagonal and cubic (a = 0.44 nm) GaN phases emerged from the beginning of growth on (111)spinel and (0001)Al_2O_3 substrates [12, 13].

The luminescence spectrum of not intentionally doped GaN shows in general typical near band-edge luminescence characterized by various transitions between 3.38 eV and 3.47 eV, beside a donor-acceptor pair transition radiation at 3.27 eV with phonon replicas shifted by about 90 meV [14] each. With impurities deliberately introduced, luminescence transitions appear within the 2-3 eV energy region [3, 4, 8, 15, 17]. The ruby crystals used here as substrates are in principle an α–corundum (α-Al_2O_3) with a small amount of Al^{3+}-ions substituted by paramagnetic Cr^{3+}-ions (aprox. $2{\cdot}10^{19}$ per cm^3). The radius of Cr^{3+}-ions is about 0.6 Å, that of isomorphic substituted Al^{3+}-ions about 0.5 Å. Due to the crystal field acting on the slightly displaced Cr^{3+}-ions, and unavoidable inhomogeneities present in the crystal, the energy levels $^4F_1$ and $^4F_2$ smear out into relatively broad bands (see Fig. 1), while ^2E, $^2F_1$ and $^2F_2$ are almost unaffected.

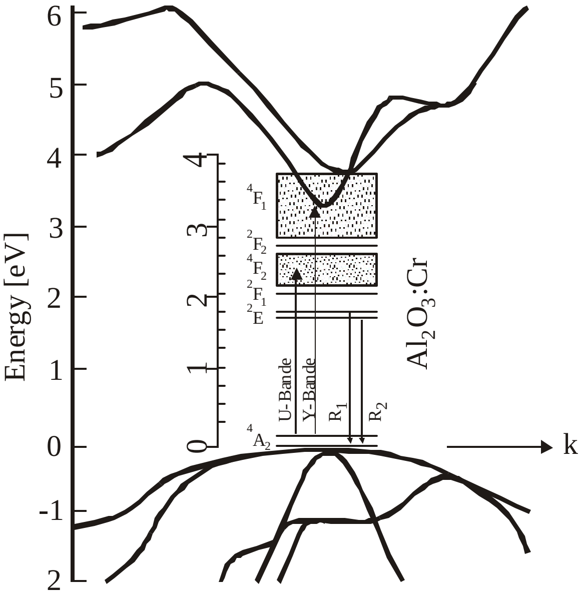

Figure 1. Energy band diagram of GaN shown without impurity levels [16], with the energy diagram of Cr^{3+}-ions in ruby inserted.

The luminescence spectrum of ruby is well known to display a sharp transition at 1.786 eV, which joins the splitted ^2E- and the $^4A_2$-levels [18]. Strong optical absorption corresponds to the up-transitions from $^4A_2$ to $^4F_2$ and $^4F_1$ in the energy range between 2-2.5 eV and 2.8-3.4 eV, respectively. The accordance of the luminescence radiation spectrum of GaN on the one hand, and the optical absorption bands of ruby on the other, make the here presented experimental study feasible. Indeed is the electron-beam excitation of any dielectric material, as ruby, impaired by the fact, that the initially impinging electrons build up a space charge strong enough as to avoid a further excitation.

2. Sample Preparation

We have used 10 to 25 µm thick epitaxial GaN layers, grown on a (0001) face of ruby as substrate, applying the vapor phase reaction of GaCl and NH_3 whith He as carrier gas, following a procedure given by Ilegems [2]. The substrate was placed in the mixing zone of the GaCl/He and NH_3 gas streams at a distance of about 15 to 20 mm downstream from the NH_3 outlet. Typical flow rates used are 45 l/h for He, 51 l/h for NH_3 and 0.03 l/h for GaCl. The chemical reactions leading to the formation of GaN, which make use of the ammonolysis of gallium monochloride, involve two steps; the formation of GaCl by the reaction of Ga with hydrogen chloride, and the reaction of gallium monochloride with ammonia in order to form GaN (l-liquid, g-gaseous, s-solid):

$$2\,Ga_{(l)} + 2\,HCl_{(g)} \rightarrow 2\,GaCl_{(g)} + H_{2\,(g)}$$
$$GaCl_{(g)} + NH_{3\,(g)} \rightarrow GaN_{(s)} + H_{2\,(g)}.$$

The two reactions occur in general at slightly different temperatures. While GaCl requires about 850 °C to form, the GaN epitaxy is realized at about 1000 °C. By use of a horizontal fused silica reaction tube, situated at a two-zone resistance-heated furnace, a corresponding temperature profile can be created (Fig. 2).

3. Electron Beam Excitation

The $GaN/Al_2O_3:Cr$ sample was placed on the cold finger of a custom-built multiple sample holder [19] in a cryostate MZK-1G, which is mounted on a focused electron beam stage, as shown in Fig. 3.

The samples are excited by a pulsed 30 keV electron beam of a few µA beam current, focused on a spot of about 100 µm in diameter at the GaN side. The luminescence spectra are registered by a common lock-in technique, using a Zeiss-monochromator SPM-2 as the dispersive and a photomultiplier as the detecting component.

4. Results and Discussion

A typical luminescence spectrum of the $GaN/Al_2O_3:Cr$ -specimen, taken at 80 K and 300 K, is shown in Fig. 4. While the donor-acceptor pair luminescence band at $E = 3.292$ eV $- n \cdot 90$ meV ($n = 0, 1, 2, 3$ phonon replicas) dominates the emission at T = 80 K, at room temperature only a near-gap GaN emission band at 3.41 eV appears. A further very sharp and intense line transition is manifest at 1.7786 eV, which is about 5 times stronger in peak intensity than the donor-acceptor pair peak.

Other than the broad GaN emission, the line emission displays a polarization by about 20%. This latter finding is due to the anisotropic uniaxial ruby crystal, which shows considerable dichroism. While this is a clear prove, that the line emission arises from the ruby, the characteristic energy value of E = 1.786 eV confirms the ruby excitation by absorption of the electron-beam generated GaN luminescence radiation.

Conclusions

Once excited to luminescence, part of the emission radiation of GaN leaving the backside of the film, is reabsorbed by the Al_2O_3 crystal due to its broad $^4F_1$ absorption band and the ground state at $^4A_2$, given the coincidence of a corresponding density-of-states distribution in the band structure of GaN. Radiative electron transitions occur between the sharp energetic levels ^2E and $^4A_2$ of the Cr-ions in ruby, giving rise to the characteristic red emission at a photon energy of 1,786 eV.
Ruby as a dielectric material is here excited via a two-step process by an intense electron beam, stimulating first the GaN to luminescence radiation, and in the following the Cr-ions to reabsorption and emission of their own line spectrum with a high quantum yield.

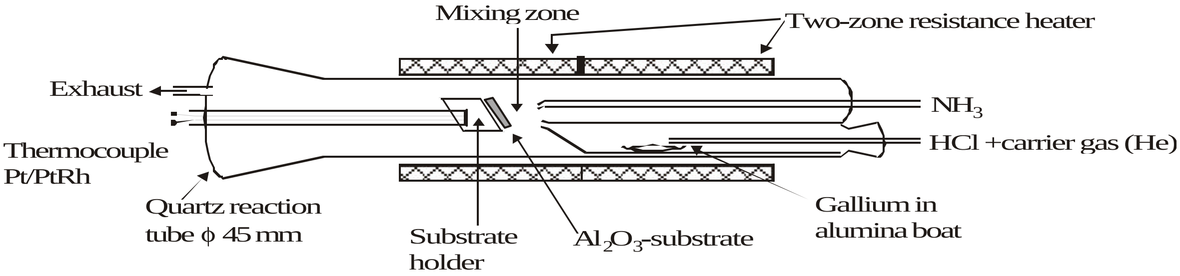

Figure 2. Schematic apparatus design for the growth of epitaxial GaN films on ruby. The formation of GaCl at 850 °C, and the epitaxial growth of GaN at 1000 °C is enabled by a two-zone resistance-heated furnace.

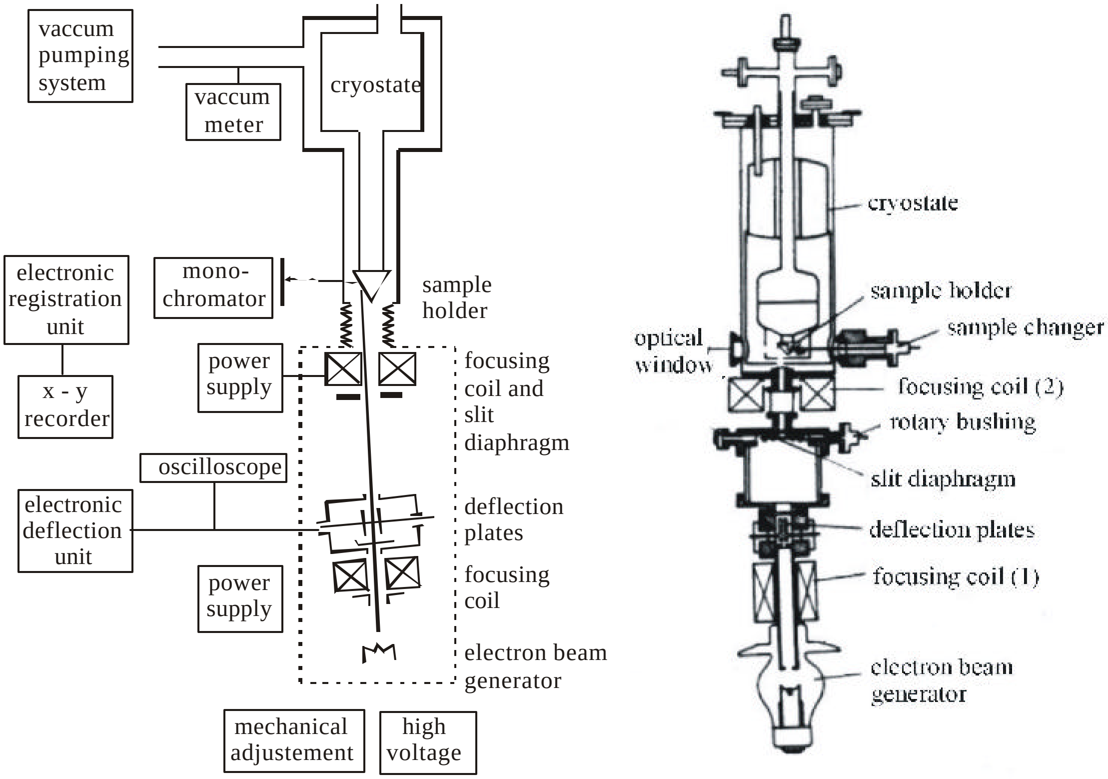

Figure 3. Cathodoluminescence equipment, and schematic diagram of the involved components. As electron-beam generator the cathode of a common X-ray tube was adapted to the cryostat.

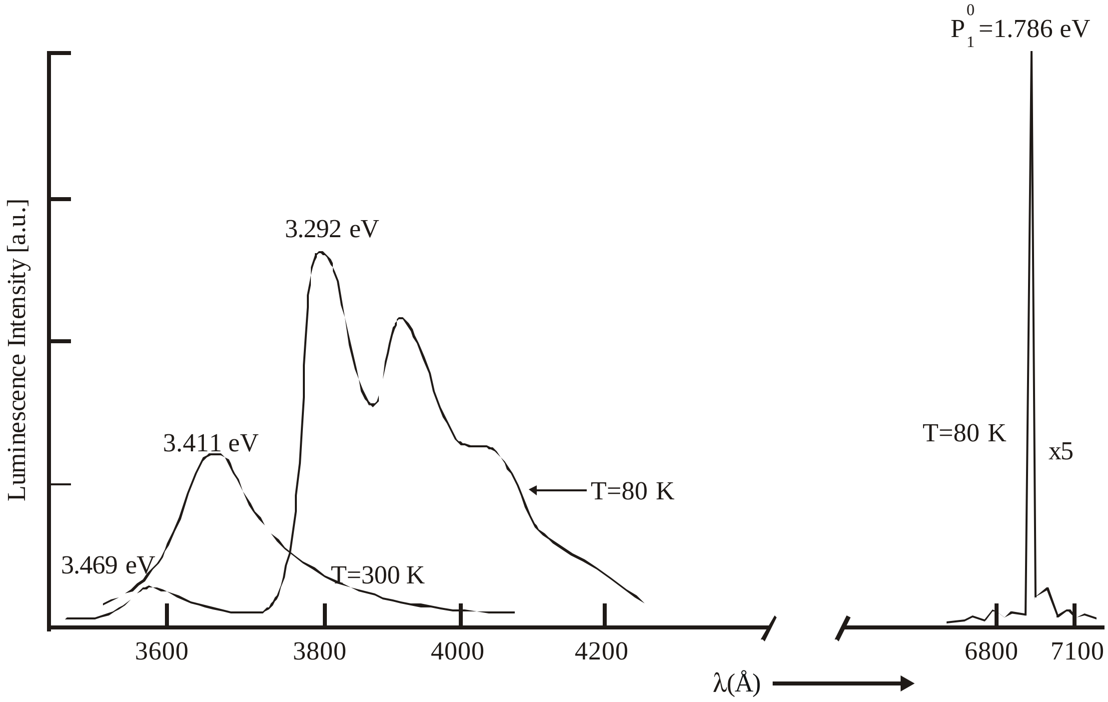

Figure 4. Measured luminescence intensity vs. emission wavelength of the specimen GaN/Al_2O_3:Cr at 80 K and 300 K, excited by a pulsed 30 keV electron beam on the GaN-layer side.

Such an indirect excitation of ruby allows to generate almost monochromatic red light, and opens up a field of new applications.

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