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Photoluminescence enhancement from GaN by beryllium doping

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ABSTRACT

High quality Be-doped (Be = 0.19 at.%) GaN powder has been grown by reacting high purity Ga diluted alloys (Be-Ga) with ultra high purity ammonia in a horizontal quartz tube reactor at 1200 °C. An initial low-temperature treatment to dissolve ammonia into the Ga melt produced GaN powders with 100% reaction efficiency. Doping was achieved by dissolving beryllium into the gallium metal. The powders synthesized by this method regularly consist of two particle size distributions: large hollow columns with lengths between 5 and 10 μm and small platelets in a range of diameters among 1 and 3 μm. The GaN:Be powders present a high quality polycrystalline profile with preferential growth on the [10$\bar{1}$1] plane, observed by means of X-ray diffraction. The three characteristics growth planes of the GaN crystalline phase were found by using high resolution TEM microscopy. The optical enhancing of the emission in the GaN powder is attributed to defects created with the beryllium doping. The room temperature photoluminescence emission spectra of GaN:Be powders, revealed the presence of beryllium on a shoulder peak at 3.39 eV and an unusual Y_6 emission at 3.32eV related to surface donor-acceptor pairs. Also, a donor-acceptor-pair transition at 3.17 eV and a phonon replica transition at 3.1 eV were observed at low temperature (10 K). The well-known yellow luminescence band coming from defects was observed in both spectra at room and low temperature. Cathodoluminescence emission from GaN:Be powders presents two main peaks associated with an ultraviolet band emission and the yellow emission known from defects. To study the trapping levels related with the defects formed in the GaN:Be, thermoluminescence glow curves were obtained using UV and β radiation in the range of 50 and 150 °C.

1. Introduction

Gallium nitride (GaN) and its alloys have attracted much attention especially for the study of growth, and related structural, electronic and optical properties [1–4]. In the wurtzite form, pure GaN possess a direct band gap (E_g) of 3.45 eV at room temperature, which corresponds to ultraviolet radiation (~360 nm). The semiconductor GaN has been largely used in the areas of optoelectronics, microelectronics and power electronics [5–7]. For optical applications, GaN has been doped with Mg, Eu, Zn, Er and Be [8–12] to improve the luminescence and efficiency trough the incorporation of suitable impurities on the GaN lattice.

The gallium nitride doped with beryllium shows potential to obtain a shallow acceptor level for p-type GaN, exhibiting lower ionization energy and higher solubility in comparison with the Mg impurity [13]. Therefore, the impurities of beryllium on GaN have produced a shallower acceptor level due to their electronegativity and absence of electrons in d-shell. However, a self-compensation process may occur on GaN:Be due to the occupation of Be atoms on interstitial sites which produce a donor level [14,15]. In last reports, this phenomenon has been related to the migration of the Be atoms on a interstitial site to gallium vacancy and the formation of $(Be\text{-}Be)_{Ga}$ donors [16]. Therefore investigation of the Be doping effects is surely justified in relation to the presence of defects that may affect the GaN performance as optoelectronic device. Thermoluminescence (TL) is a very sensitive technique to study defects in the form of shallow and deep trapping levels. It may also provide information about the trapping and recombination mechanisms involved in the radiative recombination of charge carriers with recombination defects centers [17]. In the present work two distinctive deep trapping levels were identified by TL after

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exposure of the GaN:Be samples to UV and β-ray source.

Until now, most of the emphasis has been placed on the production of high quality epitaxial GaN doped Be layers by the methods of molecular beam epitaxy (MBE) and ion implantation [18,19]. Mostly reports, an emission line with an energy of 3.38 eV followed by two or more phonon replica has been observed in GaN:Be by means of photoluminescence, which are associated with the Be ions [20]. However, GaN polycrystalline and its alloys have demonstrated high potential in applications as phosphor components for solid-state lighting (SSL) and electroluminescent (EL) devices in the form of thin films and powder [21–24]. In particular, the GaN powder is a versatile material for optoelectronics applications due to their flexible form.

In the present work, bulk production of high quality Be-doped gallium nitride (GaN:Be) powders have been achieved by means of direct nitriding with ammonia. As main purpose, a close study of the luminescence properties using photoluminescence, cathodoluminescence and thermoluminescence techniques is development for the GaN:Be semiconductor. An optical enhancing with efficiency that exceeds those previously reported in undoped and doped (Si-Mg) GaN powders and their alloys [25–28] is analyzed. To study the trapping levels formed by the beryllium-defects, the TL curves using UV and beta radiation with varied doses are compared.

2. Experimental

Be-doped GaN powders were produced using a Ga-Be-NH_3 diluted alloy (Be = 0.19 at.%). Using ultra-high purity (UHP) precursors (Ga and Be 99.9995 wt% and ammonia 99.9995 wt%) and highly controlled parameters (temperature, pressure, gas-flow and time) high quality GaN:Be polycrystalline powders were produced in two stages. First, an initial heat treatment for the Ga-Be alloy is realized to form Ga-Be-NH_3 diluted alloy. According to the binary alloy phase diagram, Be is soluble in Ga until 19 atomic percent and can form liquid solutions in all proportions at temperatures above 580 °C [29]. To prepare Ga-Be alloy, desirable amounts of UHP Ga and Be in an aluminum oxide crucible were placed inside a stainless steel vessel that was fitted to a mechanical shaker (see Fig. 1A). The vessel was tightly closed and heated under vacuum (~10^{-3} Torr) from room temperature to 600 °C. Then the vessel was filled with high purity ammonia and shaken for several hours (~5 h) in order to produce a highly homogeneous gas-liquid solution. The solution was then poured into an aluminum oxide boat and then placed inside of quartz tube reactor positioned horizontally (see Fig. 1B). The growth method using that horizontal reactor has been previously described in Ref. [24].

For the second stage, the method of doping with beryllium on the gallium nitride is based on the following reaction:

$$2Ga\text{-}Be_{(l)} + 2NH_{3(g)} \rightarrow 2GaN{:}Be_{(s)} + 3H_{2(g)} \quad (1)$$

The quartz tube reactor was evacuated at 10^{-3} Torr using a mechanical pump. Then, a flux of ultra high purity N_2 was introduced into the quartz tube and the aluminum oxide boat was placed at the entrance of the reactor (<200 °C). When the central part of the reactor reached 1200 °C, in about 1 h, the vacuum system was closed and a flow of UHP ammonia (~350 sccm) was introduced through the reactor. Once the steady-state conditions were achieved (~30 min), the boat containing the solution was rapidly moved to the middle of the reactor (hot zone, 1200 °C) using a magnetic manipulator. The complete reaction of the GaN:Be powders was achieved after 5 h. Subsequently, the aluminum oxide container with the product, a light gray powder (GaN:Be), was moved to the coldest part of the reactor (room temperature) using a magnetic manipulator. Then the ammonia flow was closed and N_2 was flowed through the quartz tube. After the product was cooled, the boat was taken out of the reactor. Finally, the GaN:Be powder was ground in a mortar and stored in a vial for further analysis.

The crystalline structure of GaN:Be powders was determinated by X-ray diffraction using a X'pert Philips powder diffractometer with CuK_α radiation and 2theta scan from 20° to 90°. The morphology of the surface of GaN:Be powders was obtained by a JEOL 5300 electron scanning microscope. High resolution image of the beryllium doped gallium nitride powder was recorded trough a JEOL JEM-2010F transmission electron microscope. The PL measurements were performed by means of a 74 Series Omnichrome He-Cd laser as excitation source, slit width of 100 μm and 1 order of magnitude filter. The PL characterization of the GaN samples was performed at room temperature and low-temperature. The CL spectra were obtained in a JEOL 6300 SEM, operated at an acceleration voltage of 5 kV and a beam current of 300 pA at room temperature. The thermoluminescence curves were acquired in a Risø TL-OSL-DA-15 equipment with a ^{90}Sr-^{90}Y beta radiation source with a dose rate of 0.05 Gy^{-1}. Also, TL curves were obtained using an UV excitation in the range of wavelengths from 200 to 400 nm, which is provided by a Xenon lamp. The TL characterization was performed from 30 to 400 °C at a heating rate of 2 °Cs^{-1} and exposure doses from 100 to 800 Gy. The glow curves were detected by a photomultiplier tube (9235B ET enterprises) over a wavelength range between 290 nm and 630 nm.

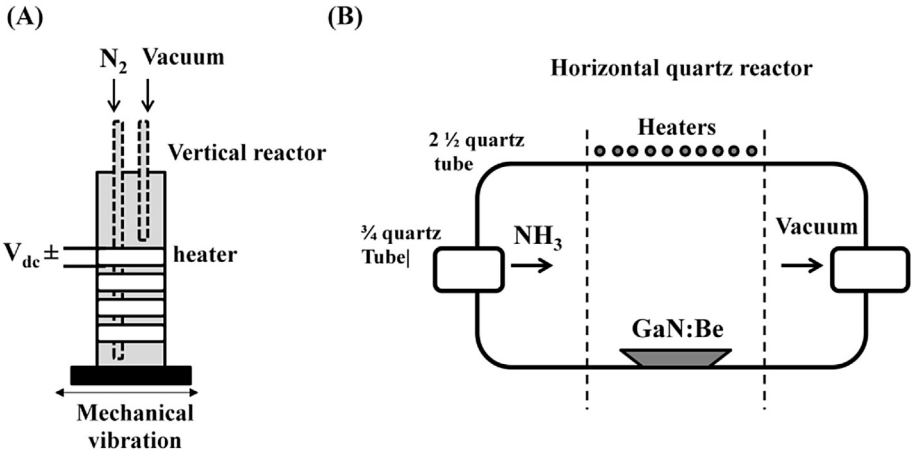

Fig. 1. Schematic diagrams of the two heating systems of GaN:Be powders growth. A) Small reactor utilized to form the Ga-Be melt and B) Horizontal furnace used to synthesize the GaN:Be powder.