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Photoluminescence from (0 0 0 1) GaN grown by the acidic ammonothermal technique

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Abstract

We report the observation of two emissions from the (0 0 0 1) face of GaN grown by the acidic ammonothermal method, which appears rather unusual. Excitonic emission at 3.357 eV (called Y4) by photoluminescence was observed which is possibly due to an exciton bound to neutral donors related to structural defects of GaN. Deep level luminescence at 1.93 eV was also observed, which had two transition possibilities of a simple two-level transition and donor–acceptor pairs.

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1. Introduction

The ammonothermal growth of GaN might be a promising method for production of bulk GaN crystal in the future. This technology uses Ga or GaN as source for GaN and supercritical ammonia as solvent and transport fluid. A mineralizer serves to greatly enhance the solubility of GaN and is the key to establish significant crystal growth rates. Basic mineralizers were reported to obtain single-phase hexagonal GaN [1], which is used by some groups [1–3]. We reported already that the handling of acidic mineralizer is relatively simple and that growth can be performed under considerably lower pressure and temperature [4,5]. A study on the effect of the acidic mineralizer on GaN growth performance supports the use of acidic mineralizers and the growth yield can be tuned upon modifying the acidity [6]. For long-term growth, we focus on the acidic mineralizer NH_4Cl due to lower chemical activity than NH_4Br or NH_4I.

Since GaN crystals fabricated by the ammonothermal technique have been produced only recently, evaluations on the crystal quality of ammonothermal GaN are therefore sparsely reported yet. Recently, in-depth evaluation using photoluminescence method has been reported [7,8]. The optical quality of the GaN grown by the ammonothermal method with acidic mineralizer is almost the same as those for the crystals grown by the hydrogen vapor phase epitaxy (HVPE) as shown by sample A in Fig. 1. However, occasionally a different spectrum (hereafter called unusual spectrum) is observed, see sample B in Fig. 1. The origin of the different spectra suggests that the crystal quality has been improved. We focus here on this unusual spectrum and will discuss structural properties as the possible cause.

2. Experimental procedure

Ammonothermal GaN from NH_4Cl mineralizer was grown on (0 0 0 1) GaN seed crystals, which were fabricated by HVPE. A detailed description on the experimental routine has already been given elsewhere

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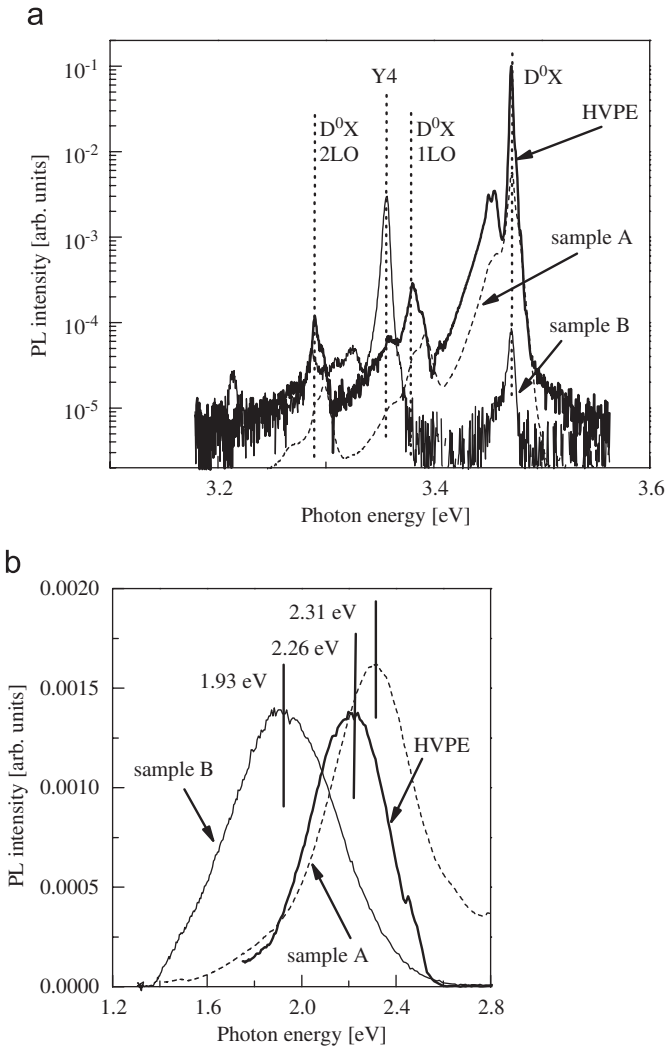

Fig. 1. The spectra of: (a) near band edge and (b) deep level emission of ammonothermal GaN crystal. The spectrum obtained from the HVPE-GaN is shown as reference. The spectra were measured from (0 0 0 1) Ga-face at 10 K. Note that intensity of sample A is not the same scale.

[4,6]. An autoclave with a Pt inner liner to prevent from corrosion was used for the growth. Source material and mineralizer were placed on the bottom of the autoclave and successively up to 4 HVPE seeds were charged. Temperature and pressure inside the autoclave were kept at 500 °C and about 135 MPa. The temperature for the lower part of the autoclave was kept higher than that for the growth zone to establish a proper temperature gradient to build up a supersaturation. Growth was typically performed for the duration of 4–10 days at constant temperature.

The thickness of the ammonothermal GaN sample to be investigated here was approximately 8 μm for both (0 0 0 1) Ga- and (0 0 0 $\bar{1}$) N-face. The GaN grown by HVPE was used as a reference sample. The PL measurements were performed using a He–Cd laser (Omnichrome 3056-M-A01: $\lambda = 325.0$ nm, $P_{out} = 10$ mW, Kinmon IK5351R-D: $\lambda = 441.5$ nm, $P_{out} = 25$ mW: only for the excitation energy dependence) for excitation and a cryostat (Daikin UV202CL) for temperature control. The spectra were obtained by a photomultiplier using a monochromator (Jobin–Yvon Spex HR320: 1200 lines/mm gratings, 320 mm focal length).

3. Results and discussion

3.1. Near band edge emission

The unusual spectrum of the near band edge emission is shown as sample B in Fig. 1a and is clearly different from the spectra obtained from sample A and the HVPE-GaN. This spectrum was observed only from the Ga-face of a specific sample. A detailed discussion of the spectrum has already been given elsewhere [7]. The exciton bound to neutral donors (D^0X) line of the hexagonal structure (3.472 eV) was observed from sample A and HVPE-GaN [9]. The intensity of the typical D^0X emission from sample B was weaker than that from the HVPE-GaN, and an additional excitonic peak at 3.357 eV was found in sample B. In addition, the peak intensity of the emission at 3.357 eV varied over the surface. This 3.357 eV peak was previously assigned as Y4 line, and was related to some structural defects [9].

The temperature dependence of the peak position and the intensity of the Y4 line are similar to the D^0X line of HVPE-GaN as shown in Fig. 2. Both D^0X and Y4 peaks

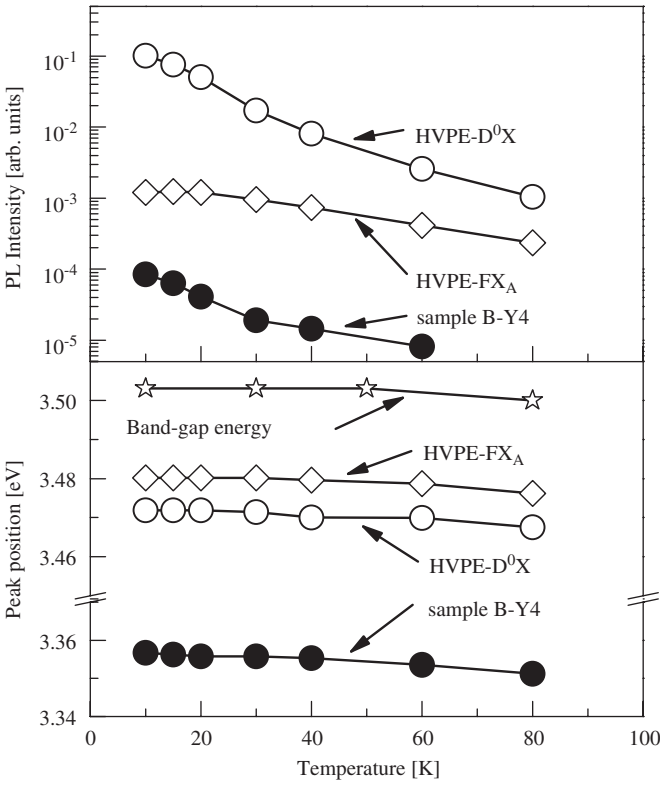

Fig. 2. Temperature dependence of peak position and intensity of the Y4 line of ammonothermal GaN (sample B) and D^0X and FX_A lines of HVPE-GaN. The spectra were measured from the (0 0 0 1) Ga-face. Band-gap energy is also shown in the lower graph which data is taken from Ref. [10].