

Catalytic Effect of Metal Elements on the Growth of GaN and Mg-doped GaN Micro-Crystals

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Abstract—Catalytic effect of metal elements was observed in the growth of GaN and Mg-doped GaN micro-crystals. High quality GaN micro-crystals were synthesized by direct reaction of gallium and ammonia using a Ni-mesh catalyst. Mg-doped GaN micro-crystals were also grown by the same reaction scheme in the presence of MgCl_2 . The growth rate of GaN micro-crystals markedly increased in the presence of the catalyst. The average grain size of GaN micro-crystals synthesized in the presence of Ni and Mg metals was larger than that in the absence of the metals. The characterization of the catalytically grown GaN micro-crystals using transmission electron microscopy and X-ray and/or electron diffraction pattern showed the growth of dislocation free hexagonal GaN micro-crystals. Photoluminescence (PL) and Catholuminescence (CL) measurements also showed the growth of good quality n- and p-type GaN micro-crystals using Ni catalyst

Key words: GaN, Mg-doped, Micro-crystal, Vertical CVD Reactor, Metal Catalyst

INTRODUCTION

Owing to exceptional optical and electrical properties, III-nitride semiconductors have drawn great attention as important materials for optical and electrical devices [Akasaki and Amano, 1997]. GaN micro-crystal powders have been employed as a source to grow thick GaN films by using the sublimation method [Kurai et al., 1996; Ha et al., 2003]. The development of GaN substrate is still required to grow high quality GaN epilayer because the presently used sapphire substrate has big lattice-mismatch with -nitride materials [Nahm et al., 2000; Cho et al., 2003]. Micro/nano-scale GaN crystals are also an important material for the future optical applications. The preparation of nanoscale GaN crystals is important for the investigation of quantum confinement effect and for the significant improvement of the luminescent efficiency of GaN [Goodwin et al., 1997; Kibria et al., 2001]. Recent progress of field emission displays (FEDs) technologies activated the use of GaN micro-crystals for a blue phosphor with low electrical resistivity and high luminescence efficiency [Kataoka et al., 1999]. ZnS or (Zn, Cd)S system is currently used as low-voltage cathodoluminescent phosphors for vacuum fluorescent displays (VFDs) and FEDs. The easy degradation and toxicity of the materials demand the development of new substitutes such as ZnGa_2O_4 , $\text{SrTiO}_3\text{Pr}^{3+}$, and GaN. However, none of them have not satisfied the required luminescence and life-time characteristics for phosphorous application.

Micro/nanosized GaN crystals have lately been synthesized by various methods. Most GaN micro-crystals were synthesized by direct reaction of gallium with ammonia gas without metal catalysts [Porowski, 1996; Shibata et al., 1999; McMurran et al., 1998; Li et al., 1997], but the growth efficiency of the conventional methods was low. However, GaN nanowires and nanorods were commonly grown by using various transition catalysts [Chen et al., 2001;

Kim et al., 2002; Nahm et al., 2002]. On the other hand, little study on the growth of Mg-doped GaN micro-crystals has been reported so far though it is important to the realization of full color in phosphor application. Kanie et al. performed the synthesis of Zn doped GaN (and InGaN) micro-crystals and characterized their optical properties [Kanie et al., 2000; Kibria et al., 2001].

In this work, we report the growth of GaN micro-crystals using an Ni catalyst by a direct reaction of gallium and ammonia. In the presently employed growth system, the Ni catalyst is entirely dipped in a molten Ga which reacts with NH_3 . The catalytic activity is examined by measuring the growth rate, morphology, and crystallinity of the GaN crystal grains. The growth of Mg-doped GaN microcrystals has also been attempted by using magnesium chloride (MgCl_2) for Mg doping source. The grown GaN micro-crystals were characterized by various analytic techniques.

EXPERIMENTAL

GaN and Mg-doped GaN micro-crystals were grown by a direct reaction of molten Ga and ammonia gas in a homemade quartz tubular reactor heated in a tubular furnace, which is pictured schematically in Fig. 1(a). Ga metal (99.99%) and NH_3 gas (99.99%) were used for Ga and N sources, respectively. Magnesium chloride (MgCl_2 , 99.99 %) was employed for Mg dopant source. The growth of the GaN crystals was carried out without Ni catalyst at various growth temperatures (1,000-1,100 °C). The growth temperature was monitored with an Rh/Pt thermocouple from the bottom of the reactor and controlled by a temperature controller. For the growth of GaN micro-crystals, cylindrical Ni-mesh catalyst (0.6 g) was placed between the delivery and inner reactor tubes and small pieces of solid Ga (8 g) were loaded in the inner quartz reactor. Meanwhile, Mg-doped GaN micro-crystals were grown at 1,000 °C with Ga (12 g) and MgCl_2 (0-1.7 wt%) under NH_3 atmosphere. The reactor was evacuated to 10^{-4} torr for 30 minutes and then purged with 100 sccm N_2 (9 N). This procedure was repeated more than five times

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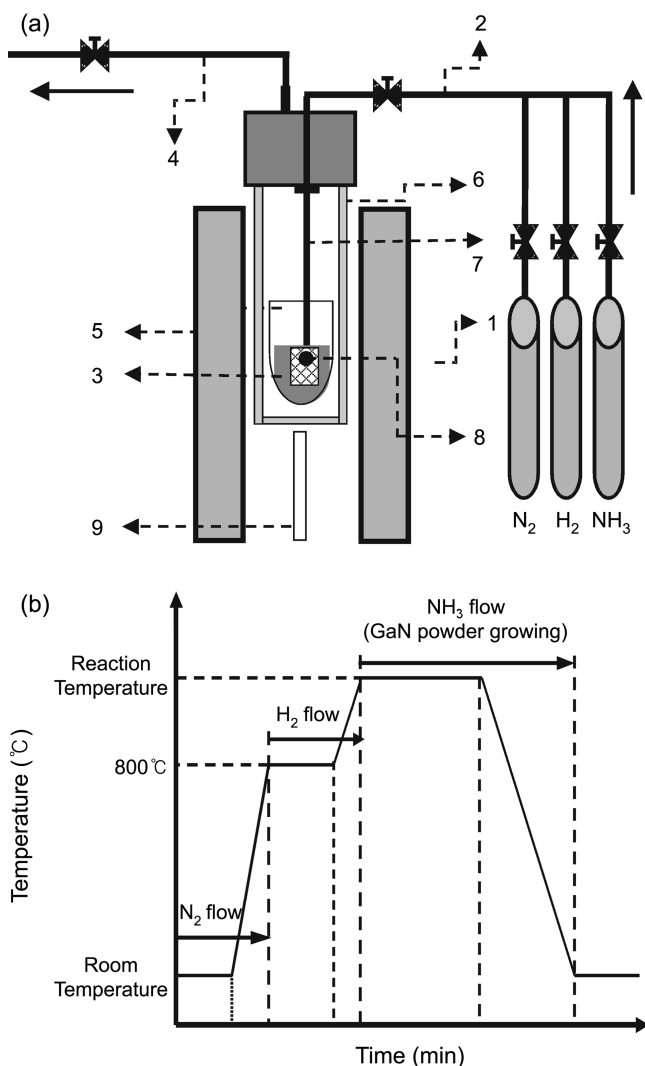


Fig. 1. (a) Schematic diagram of the growth reaction system for GaN micro-crystals and (b) a growth sequence of GaN micro-crystals.

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|--------------------------------|---------------------|
| 1. Vertical electrical furnace | 6. Outer reactor |
| 2. Input gas line | 7. Delivery tube |
| 3. Ga melt | 8. Ni-mesh catalyst |
| 4. Output gas line | 9. Thermocouple |
| 5. Inner reactor | |

to remove the residual impurities in the reactor. The reactor pressure was adjusted by using the N_2 to be one atmosphere. After the reactor temperature was elevated to $800^{\circ}C$ in the flow of N_2 gas, the N_2 flow was stopped, switched to 100 sccm H_2 gas (9 N), and the temperature maintained for 5 min to clean the Ni catalyst surface. The reactor temperature was again raised from $800^{\circ}C$ to the growth temperature and then the hydrogen gas was completely changed to 50 sccm NH_3 . All the gases were introduced into the reactor through the delivery tube and the Ni catalyst was completely dipped in the Ga melt during the growth. After the growth reaction, the temperature was slowly cooled to room temperature in the flow of NH_3 gas. The growth sequence of GaN and Mg-doped GaN micro-crystals is depicted in Fig. 1(b). The micro-crystals were removed from the as-grown mixture by dissolving unreacted Ga, Mg, and Ni

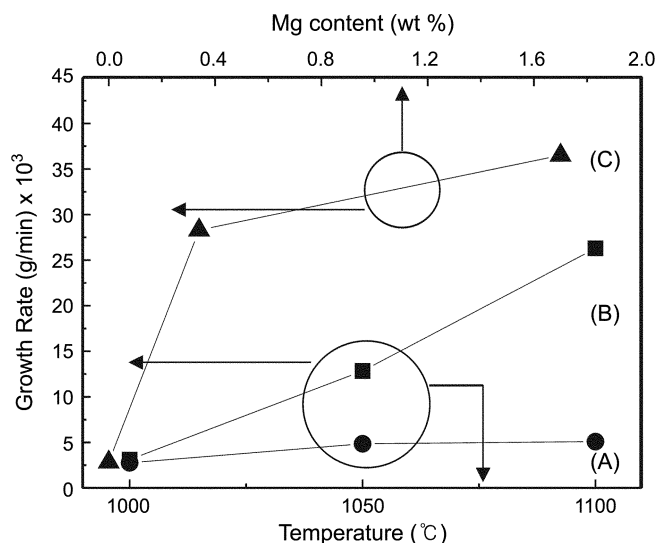


Fig. 2. The growth rate of GaN micro-crystals vs. growth temperature [(a) with Ni-mesh catalyst and (b) without Ni-mesh catalyst] and (c) Mg-doped GaN micro-crystals vs. Mg content. The GaN micro-crystals were grown at 1 atm with 50 sccm NH_3 .

catalyst in HCl solution. The separated micro-crystals were washed with distilled water and dried in a vacuum oven.

The structure of the synthesized GaN and Mg-doped GaN micro-crystals was investigated by using scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Optical properties of the crystals were characterized by photoluminescence (PL) and cathodoluminescence (CL) measurements at room temperature.

RESULTS AND DISCUSSION

Fig. 2 shows the growth rate of GaN micro-crystals as a function of growth temperature in the absence and presence of Ni-mesh catalyst. Samples A and B refer to the GaN micro-crystals grown without and with the Ni catalyst, respectively, and sample C is Mg-doped GaN micro-crystals. The growth rate of the GaN crystals increases as the reaction temperature rises from 1,000 to 1,100 $^{\circ}C$ and the dependency of the growth rate on the temperature is much more significant in the presence of Ni catalyst. For 1,100 $^{\circ}C$, the growth rate of sample B is almost ten times higher than that of sample A. This result demonstrates that Ni-metal acts as an active catalyst in the growth of the GaN crystal. It is thought that the Ni-mesh catalyst enhances the decomposition of NH_3 gas into chemically active nitrogen species and speeds up the reaction of gallium with NH_3 , resulting in the increase of the GaN crystal growth rate. The decomposition of NH_3 on Ni surfaces has been widely investigated by many research groups using various analytic techniques for the fundamental understanding of catalytic processes in the Haber synthesis of ammonia [Klauber et al., 1985; Bassignana et al., 1986; Chrysostomou et al., 1999]. The decomposition mechanism revealed that $NH_{3,ads}$ undergoes decomposition into $NH_{2,ads}$, NH_{ads} , N_{ads} , and H_{ads} intermediates at the Ni surface through a series of thermally-induced dissociation reactions [Klauber et al., 1985; Bassignana et

al., 1986]. This reactive nitrogen species vigorously reacts with atomic Ga around Ni catalyst to produce GaN. In general, it was reported that the decomposition of NH_3 is the reaction rate controlling step of the GaN. To enhance NH_3 cracking, some researchers installed metal crackers over the GaN growth zone in molecular beam epitaxy (MBE) growth system and observed the significant increase of the GaN growth rate [Ban, 1972; Liu and Stevenson, 1978; Kamp et al., 1997].

The growth rate of Mg-doped GaN micro-crystals was also measured as a function of Mg content. The growth rate increases with the amount of Mg doped. It seems that the presence of MgCl_2 enhances the growth rate and size of the GaN micro-crystals and promotes the formation of hexagonal crystals. It is suggested that this

might be attributed to Mg or Cl species included in the MOCVD growth of GaN [Lachab et al., 2000]. Mg has the lattice parameters ($a=0.32$ nm and $c=0.52$ nm) very close to those of GaN ($a=0.318$ nm and $c=0.517$ nm). It is likely that magnesium inflicts some positive effects on the growing surface, which induces the structural stabilization, leading to the increase of the growth rate and size of the GaN micro-crystals. It was reported that the existence of Mg impurity in the GaN growth slightly accelerates the growth in c -direction [Porowski, 1998]. Meanwhile, it has also been reported that extremely high growth rate ($3 \mu\text{m/h}$) and high-quality of GaN were attained in a halide vapor pressure epitaxy (HVPE) process [Aujol, 2001]. The flow of hydrogen chloride over metallic gallium escalates the transport of Ga by forming GaCl_3 vapor, which then reacts with NH_3 gas to form GaN, resulting in the increase of the growth rate and crystal size [Lee and Harris, 1996]. Besides, the introduction of chlorine species generates various chemical reactions in the growth process, which influences the crystal quality and the growth rate of GaN [Cadoret, 1999].

Shown in Fig. 3(a), (b), and (c) are SEM images for samples A, B and C, respectively. The GaN crystals were grown at $1,000^\circ\text{C}$ and 1 atm with 50 sccm NH_3 . The average grain size of sample B ($2\text{--}8 \mu\text{m}$) is larger than that of sample A ($1\text{--}3 \mu\text{m}$). The catalyst induces the increase of the GaN crystal size. The increase in the crystal size might be one reason why the GaN growth rate increases in the presence of the Ni-catalyst. For the Mg-doped GaN, however, GaN lumps are formed with various sizes and shapes, which are formed mainly by the aggregation of many hexagonal-shaped GaN micro-crystals. The size of the Mg-doped GaN crystals is larger than that of the undoped GaN micro-crystals (sample A) and increases with the amount of Mg. The Mg-doped GaN crystal also forms a hexagonal structure.

Fig. 4(a), (b) and (c) show XRD spectra for samples A, B, and

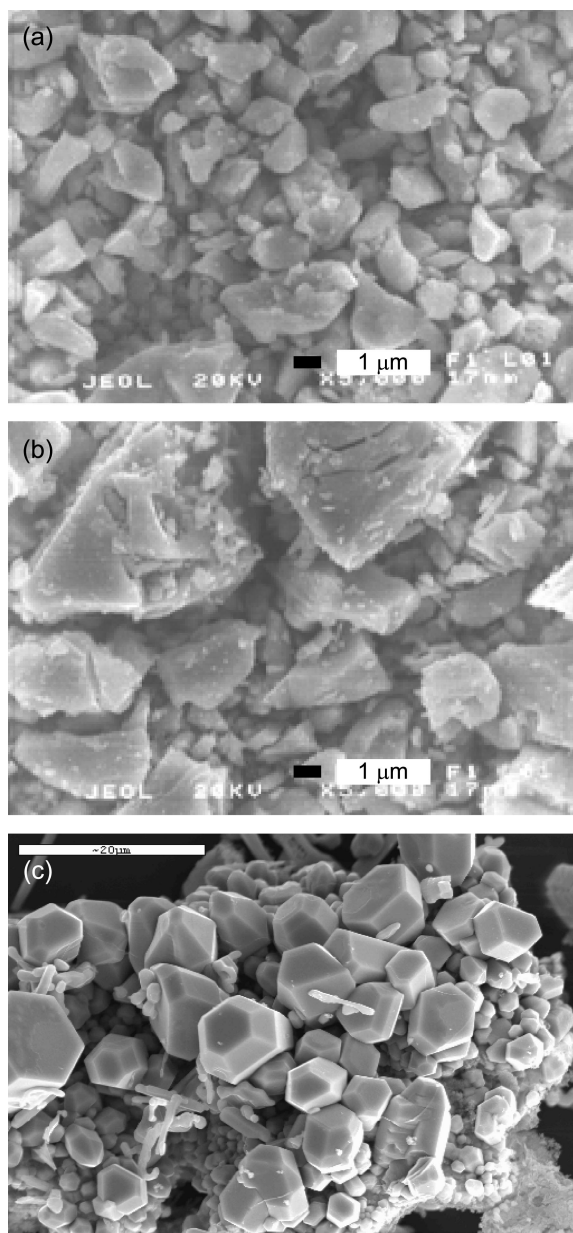


Fig. 3. SEM images for GaN and Mg-doped GaN micro-crystals; (a) sample A and (b) sample B, (c) sample C (Mg=0.34 wt%). The growth was carried out at $1,000^\circ\text{C}$ and 1 atm with 50 sccm NH_3 .

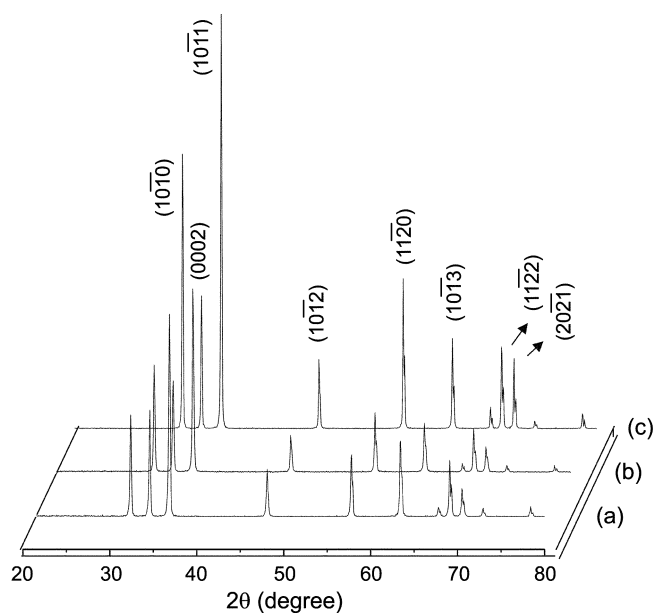


Fig. 4. Typical X-ray diffraction patterns of GaN and Mg-doped GaN micro-crystals; (a) sample A and (b) sample B, (c) sample C (Mg=0.34 wt%). The growth was carried out at $1,000^\circ\text{C}$ and 1 atm with 50 sccm NH_3 .

C, respectively. There is no big difference in the three XRD spectra. The XRD patterns are very consistent with characteristic peaks of a hexagonal GaN structure reported in the X-ray powder data file of JCPDS as well as other previous works [Li et al., 1997; Roh et al., 2002; Park et al., 1998]. The Miller indices are indicated on each diffracted peak.

Crystalline quality of samples A, B, and C was investigated by transmission electron microscopy (TEM). Fig. 5(a) shows the dark-field micrograph and the corresponding selected area diffraction pattern (SADP) along the electron beam direction $B=[01\bar{1}0]$ with the reflection vectors $g=0002$. It should be noted that the crystal is

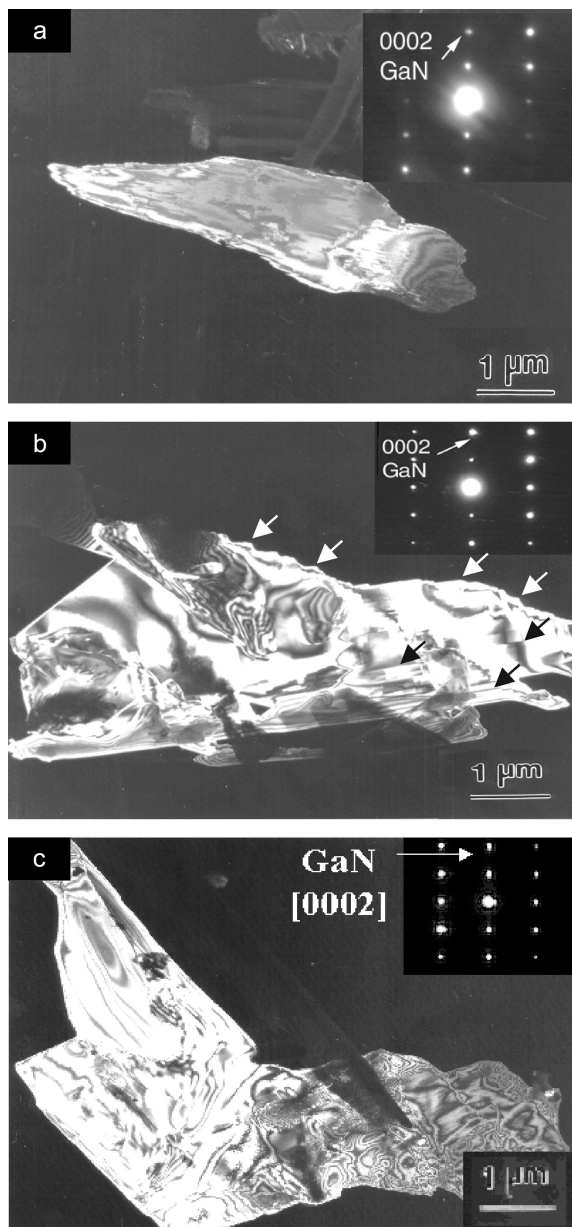


Fig. 5. The dark-field micrographs and the corresponding selected area diffraction pattern (SADP) along the electron beam direction $B=[01\bar{1}0]$ with the reflection vectors $g=0002$; (a) sample A and (b) sample B, (c) sample C (Mg=0.34 wt%). The growth was carried out at 1,000 °C and 1 atm with 50 sccm NH_3 .

about 3 μm long and 1 μm wide in size, which is in agreement with the SEM result shown in Fig. 3(a). All the GaN crystals observed in the present study by SADP are identified to have the 2H hexagonal structure with rod crystal, i.e., the crystal's length and width correspond to the c- and a-axis of hexagonal structure, respectively. Dark field micrographs show that the crystal consists of a single crystal without any grain boundary, although some fringes, due to differences of crystal thickness, are observed. Dislocations identified as the major defect in epitaxial GaN films [Cherns et al., 1997] grown on various substrates having the Burgers vectors $b=1/3[2\bar{1}10]$, $b=[0001]$ and $b=1/3[2\bar{1}13]$ are not observed from our grown GaN crystals. If such dislocations were found in the present GaN crystal, they should appear with the reflection vector either $g=0002$ or $g=\bar{2}110$. However, this is not the case in the present TEM micrographs. Thus, it can be concluded that most of the GaN crystals exhibit a dislocation free structure, which indicates they experience no strain during the growth process. The dark-field micrographs and the corresponding SADP for sample B were observed as shown in Fig. 5(b). It should be noted that the crystal size is greatly increased compared to sample A, i.e., about 6 μm long and 2 μm wide. Dislocations and other defects are not observed when imaged with either $g=0002$ or $g=\bar{2}110$ as in the crystal observed in Fig. 5(a). Fig. 5(c) shows the dark-field micrographs and the corresponding SADP for sample C. The TED pattern also shows both the undoped and Mg-doped GaN micro-crystals are identified to have high quality 2H hexagonal structure.

Shown in Fig. 6 are PL spectra for samples A, B, and C. PL measurements were carried out to characterize the optical properties of GaN and Mg-doped GaN micro-crystals using a 325-nm line He-Cd laser with 15-mW output power. No big difference was observed in the PL spectra of samples A and B. Samples A and B emit a strong band edge emission, possibly shallow donor-acceptor recombination, at 3.38 eV, whereas sample C, Mg-doped GaN micro-crystals, shows a broad peak centered at ~2.7 eV, corresponding to the band emission of heavily doped MOCVD material. A sharp peak at 3.02 eV is not induced by the sample but by the measurement system and should be neglected. With increasing the amount of Mg

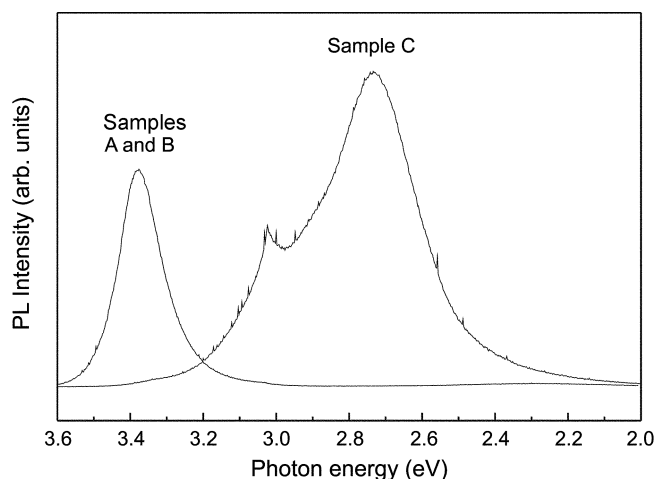


Fig. 6. Photoluminescence spectrums for samples A, B, and C (Mg =0.34 wt%) at room temperature. The growth was carried out at 1,000 °C and 1 atm with 50 sccm NH_3 .

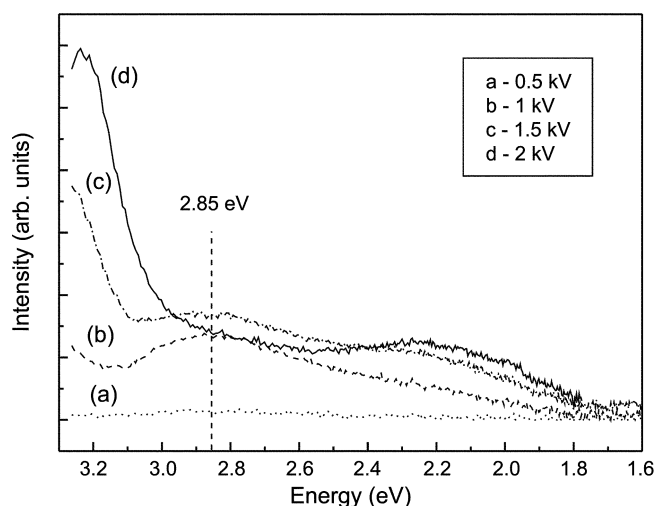


Fig. 7. Cathodoluminescence spectra measured at room temperature for Mg-doped GaN micro-crystals (Mg=0.34 wt%) as a function of the accelerating voltages.

doped, the intensity of the near band edge emission peak at 3.38 eV decreased, while that of the peak at 2.7 eV increased.

Fig. 7. shows cathodoluminescence spectra measured at different accelerating voltages (0.5-2 kV) for Mg-doped GaN micro-crystals. It is seen that blue emission (2.85 eV) begins to be detected at ~0.5 kV and the emission shifts toward green color as the accelerator voltage increases. At accelerating voltages above 1 kV, GaN host wide band peak starts to appear at ~3.25 eV and grows in the intensity with increasing the accelerating voltage. These lines are commonly observed in room temperature PL and CL measurements of Mg-doped GaN. The ~3.25 eV line is widely attributed to a free electron-Mg acceptor transition and the broad emission at 2.85 eV could be assigned to a deep Mg-related complex [Smith et al., 1996; Gross et al., 1999; Jeong et al., 2002].

CONCLUSION

We reported the growth of GaN micro-crystals using an Ni catalyst by a direct reaction of gallium and ammonia. The growth of Mg-doped GaN micro-crystals has been attempted using magnesium chloride (MgCl_2) for Mg doping source. The grown GaN micro-crystals were characterized by using various analytic techniques. The growth rate of the GaN crystals increased with the reaction temperature. The dependency of the growth rate on the temperature is much more significant in the presence of Ni catalyst. At 1,100 °C, the growth rate in the presence of Ni catalyst is almost ten times higher than that in the absence of the catalyst. The growth rate of Mg-doped GaN micro-crystals was the highest and increased with the amount of Mg. The presence of MgCl_2 was assumed to enhance the growth rate and size of the GaN micro-crystals. All the GaN micro-crystals grown in this work had the 2H hexagonal structure, and dislocations and other defects were not observed from presently grown GaN micro-crystals. GaN micro-crystals emitted a strong band edge emission at 3.38 eV, whereas Mg-doped GaN micro-crystals showed a broad peak centered at ~2.7 eV. It is confirmed that the presence of metals in the reaction of Ga with NH_3 gas enhances the growth rate and size of the GaN micro-crystals. How-

ever, the catalytic growth mechanism is still unclear. Although not clearly presented in this paper, it is assumed that Ni and Mg metals act as active catalysts in the growth of GaN micro-crystals. We believe that further experimental investigation will be necessary in future to prove the catalytic role of the metals in the GaN crystal growth.

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