

AMMONO method of BN, AlN and GaN synthesis and crystal growth.

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Microcrystals of BN, AlN and GaN were obtained by the AMMONO method, in which nitridization of metal occurs in supercritical ammonia, at relatively low temperature and pressure conditions (below 550°C and 5 kbar). The reaction rate was regulated by the amount of mineralizers, i.e. alkali metal amides.

All crystals obtained by AMMONO method revealed intense and homogenous luminescence. Significant improvement of the optical properties was observed for crystals grown in the presence of Rare Earth elements. For such GaN crystals, helium temperature photoluminescence spectra were dominated by near-band-gap recombination. Exciton lines were extremely narrow, with full-width half-maximum (FWHM) as low as 1 meV. The concentration of uncompensated shallow donors in AMMONO GaN determined by electron paramagnetic resonance measurements was below $5 \times 10^{15} \text{ cm}^{-3}$.

1 Introduction

Gallium nitride and other nitride compounds have been attracting widespread interest for the last few years as suitable materials for various optoelectronic devices in the whole visible spectrum up to ultraviolet. Intensive technological efforts have resulted in commercially available GaN-based light emitting diodes (LEDs) of very good performance, and the achievement of lasing devices [1]. Parallel research on the nitrides' physical properties has been undertaken, but still, our understanding of these materials is far from satisfactory. The basic reason limiting both applications of the nitrides and studies of their properties comes from the difficulty of obtaining good quality crystals. None of the classical methods of bulk semiconductor crystal growth from the melt can be directly adopted to nitrides of the III group metals, as such compounds demand high temperatures and extremely large pressures in order to avoid their decomposition. Several methods studied up to now [2] [3] yielded some crystals used for research goals, but did not lead to manufacture of application grade crystals. On the other hand, heteroepitaxial layers, com-

monly grown on sapphire (of large lattice mismatch and substantial difference in thermal expansion coefficient in comparison to GaN), suffer from structural defects. Therefore, the development of growth methods still remains crucial for nitride applications. In this paper we present results of studies on the AMMONO method [4], originally invented for GaN, and now used also for AlN and BN growth.

2 Growth technology

The AMMONO method consists of GaN, AlN or BN crystallization by metal reaction with highly chemically active supercritical ammonia, at pressures in the range of 1 to 5 kbar and at temperatures up to 550°C. The growth processes are based on chemical reactions and therefore can be effective under relatively low temperature and pressure conditions. Prior to the growth, a special high-pressure autoclave [5] was loaded with III group metal and a mineralizer (lithium or potassium amide) in pure nitrogen atmosphere. The presence of such mineralizers effectively increases the reaction rate by increasing the amount of anions in the ammonia

solution. Without such mineralizers, reaction of the metals with ammonia at the studied pressure and temperature conditions was not possible. Rare earth elements in metallic form were also added in order to prevent oxygen contamination of GaN product. Then the autoclave was evacuated down to 10^{-2} mbar and filled with a precisely weighed amount of ammonia using a tensiometer (a vacuum apparatus of known volume with manometer and valves). The high pressure of ammonia resulted from heating of the loaded autoclave under constant-volume conditions in an ordinary tubular furnace. Processes lasted from 1 to 30 days, and then the autoclave was cooled inside the furnace. After that nitride crystals were separated from alkali metal amides by etching in aqua regia and rinsed in distilled water.

Among the group III metals we used for nitridization, the fastest reaction was noticed for gallium. This reaction, performed with a molar ratio of gallium to ammonia 1:10, was completed after 3 days at temperature 550°C and pressure 5 kbar. In the case of aluminum, completion of the reaction at similar conditions took 14 days. This unexpected result (aluminum seems to be much more chemically active than gallium) might be the consequence of various phenomena. The two phenomena we thought most important were the difference between the reactivity of liquid gallium and solid, bulk aluminum and/or the relatively good solubility of synthesized GaN in ammonia compared to AlN, leading to passivation of aluminum surface and slowing down the reaction. The lowest reaction rate we noticed for boron. It was applied in powder form in order to avoid surface passivation. Unfortunately, even after processing for 21 days, we found that the reaction was uncompleted, and metallic boron peaks were still visible in the powder X-ray diffraction spectrum of the AMMONO reaction products.

Experiments of another kind were performed to confirm directly the solubility of GaN in ammonia. In these processes we used HNP GaN bulk needles [2] and an ammonia/lithium amide solution. We noticed partial, and for longer times complete, dissolution of GaN needles, which suggested the possible existence of a recrystallization mechanism, analogous to the recrystallization under hydrothermal conditions commonly used for industrial growth of oxide crystals (like quartz SiO₂).

3 Crystal properties

The typical morphology of AMMONO crystals was shown in figure 1. Typically they have the form of regular grains, 2–3 μm in diameter, but small needles (70 nm thick and 0.5 μm long) and big needles (3 μm thick and 25 μm long) were also found. X-ray powder diffraction patterns showed that the phase of GaN, AlN and BN microcrystals was purely hexagonal (wurtzite structure).

The diffraction measurements were performed using Bragg-Brentano focusing conditions with a VEB Freiburger Präzisionsmechanik HZG-3 diffractometer and a copper lamp. Lattice parameters for GaN calculated using the Cohen method with extrapolation function $\cos^2\Theta/\sin\Theta$ were as follows: $a=3.1877\pm 0.0004$ Å and $c=5.183\pm 0.002$ Å.

The most outstanding features of AMMONO crystals were high purity and crystalline quality, resulting in excellent optical properties. Under ultraviolet light illumination, the microcrystalline grains shined homogeneously, very brightly in the case of GaN, and visibly well in the case of AlN and BN. The photoluminescence (PL) spectra of the nitrides, shown in fig. 2, contained the commonly known “yellow” band, and in the case of GaN, contained additional sharp exciton recombination lines in the ultraviolet range (magnified in figure 3). Unfortunately, we were not able to detect the near band gap transitions in the case of AlN and BN because of the wavelength (325 nm) of the HeCd laser light used for excitation, which was well below AlN and BN band gap. However, because of similar growth conditions, we expect similar quality of all nitrides.

The “yellow” band has been commonly ascribed to electron recombination at a deep level strongly coupled to the lattice [6]. The origin of this deep level has been connected to metallic vacancies or metallic vacancy based complexes [7]. This defect, constructed by four nitrogen atoms, should reveal similar properties for all III group nitrides, what is already visible in the similar “yellow” band of all the studied nitrides (fig. 2).

The PL spectrum of AMMONO GaN crystals, dominated by exciton recombination peaks (fig. 3), is very similar to the spectra observed for the best homoepitaxial GaN layers [8]. The FWHM of the exciton lines reached the values of 1 meV. The energy positions of the exciton lines were not sample dependent, in contrast to the changes always seen for hetero and homoepitaxial GaN layers and attributed to strain present in them. This experimental observation proves the strain-free structure of AMMONO GaN crystals. Therefore, the energy position of the donor bound exciton $E_{XD}=3.4719$ eV and acceptor bound exciton $E_{XA}=3.4668$ eV determined for them could be used as a reference data for GaN crystals grown by other techniques.

The intensity of the XA line was typically higher than the intensity of XD line in AMMONO GaN. This observation together with the narrow structure of exciton lines is evidence of low electron concentration in the GaN grains, this is also consistent with the EPR data presented below. The extremely small width of the excitonic lines allowed resolution of two donor bound excitons. Besides bound exciton lines there were free

exciton transitions seen in the ultraviolet luminescence spectra. Three free excitons, A, B, and C were observed (fig. 3). They are due to the split of GaN valence band into three subbands [9].

Electron Paramagnetic Resonance (EPR) measurements of AMMONO GaN revealed the donor line with $g=1.9494\pm 0.0005$, similar to the one observed by Carlos et al. [10]. A simultaneous measurement of AMMONO GaN and Si:P standard sample combined with precise weighing of these two samples enabled us to estimate the spin concentration due to uncompensated shallow donors in AMMONO GaN as about $5\times 10^{15}\text{ cm}^{-3}$. This is much lower than electron concentration in any undoped GaN grown by other techniques.

4 Conclusions

GaN, AlN and BN in the form of microcrystalline powder of very high purity and excellent crystalline quality were obtained by AMMONO method. The growth was performed at relatively low temperature and pressure conditions. The microcrystals showed intense and homogenous luminescence. At helium temperature, the luminescence spectra of GaN samples consisted of narrow lines originating from bound and free exciton transitions. The FWHM of the lines ($\sim 1\text{meV}$) could be only compared with FWHM of the analogous lines seen for the best homoepitaxial GaN layers. The energy positions of the lines were not sample dependent. This showed that the crystals were strain free. A low shallow donor concentration, less than $5\times 10^{15}\text{ cm}^{-3}$ was estimated from EPR studies. These facts indicate AMMONO crystals to be unique, model materials for the determination of nitride parameters, and plenty of other applications. Such applications include calibration of analytical instruments (i.e. EDX), substrates for laser ablation, sources for sublimation/condensation growth techniques, indicators/phosphors stable at a wide temperature range (-273°C to $+750^{\circ}\text{C}$), and many others.

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REFERENCES

- [1] S. Nakamura, "InGaN/GaN/AlGaIn-based laser diodes with a lifetime of 10,000 hours", oral presentation at the 3rd European Gallium Nitride Workshop, Warsaw, Poland, June 1998.
- [2] S. Porowski, J. Jun, M. Bokowski, M. Leszczyński, S. Krukowski, M. Wróblewski, B. Uczeń, I. Grzegory, "III-V nitrides - conditions for crystal growth at high N_2 pressure", Proc. 8th Conference on Semi-insulating III-V Materials, ed. M. Godlewski, World Scientific Publishing Co. Singapore, 61 (1994)
- [3] CM Balkas, Z Sitar, T Zheleva, L Bergman, IK Shmagin, JF Muth, R Kolbas, R Nemanich, RF Davis, *Mater. Res. Soc. Symp. Proc.* **449**, 41-46 (1997).
- [4] R. Dwilinski, R. Doradziński, J. Garczyński, L. Sierzputowski, J. M. Baranowski, M. Kamińska, *Mater. Sci. Eng. B* **50**, 46 (1997).
- [5] H. Jacobs, D. Schmidt, "High-pressure ammonolysis in solid-state chemistry", in: *Current Topics in Materials Science*, ed. E. Kaldis, North-Holland, Amsterdam, 8, 381 (1981)
- [6] J Neugebauer, CG Van de Walle, *Appl. Phys. Lett.* **69**, 503-505 (1996).
- [7] S. Pacesova, L. Jastrabik, *Phys. Stat. Sol. B* **93**, K111 (1979).
- [8] J. M. Baranowski, S. Porowski, "GaN on GaN - Material for blue optoelectronics", Proc. 23rd Int. Conf. Phys. Semicond, ed. M. Scheffler, World Scientific Publishing Co. Singapore, 497 (1996)
- [9] R. Stepniowski, A. Wysmołek, *Acta Phys. Pol. A* **90**, 681 (1996).
- [10] W. E. Carlos, J. A. Freitas, Jr., M. Asif Khan, D. T. Olson, J. N. Kuznia, *Phys. Rev. B* **48**, 17878-17884 (1993).

FIGURES

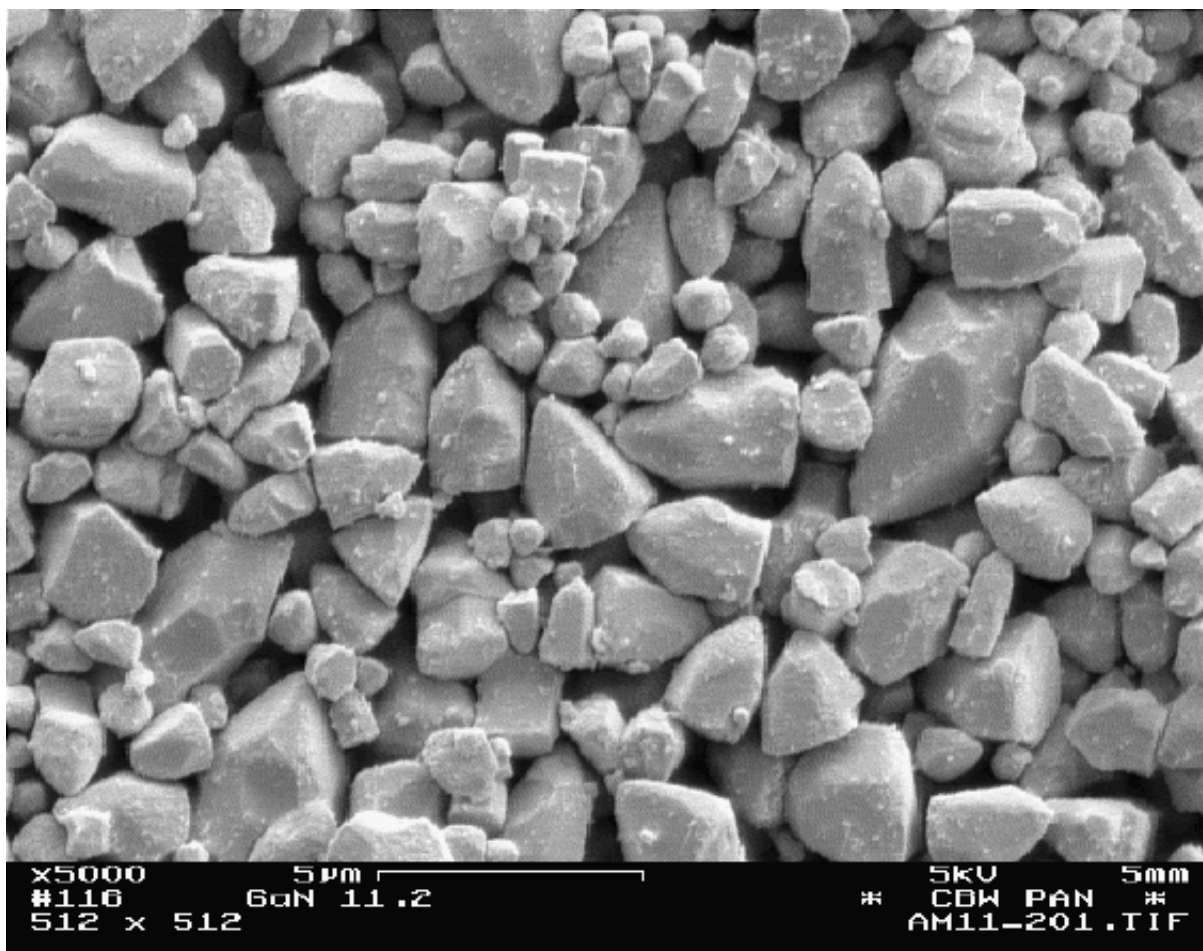


Figure 1. GaN crystals obtained in a synthesis process under the following conditions: T=550°C, p=5 kbar, Ga:LiNH₂:NH₃=1:2:20.

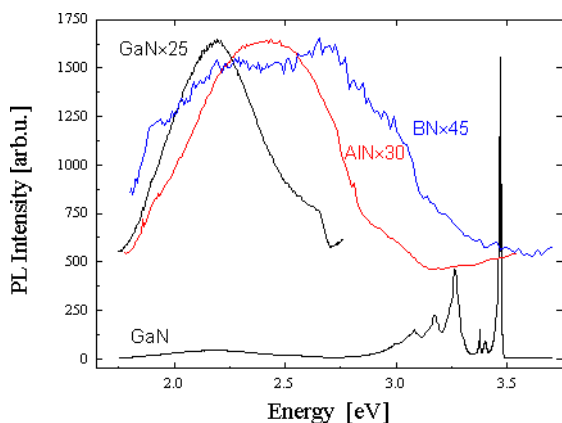


Figure 2. Photoluminescence spectra (measured at 4.2K) of GaN, AlN and BN crystals obtained by AMMONO method.

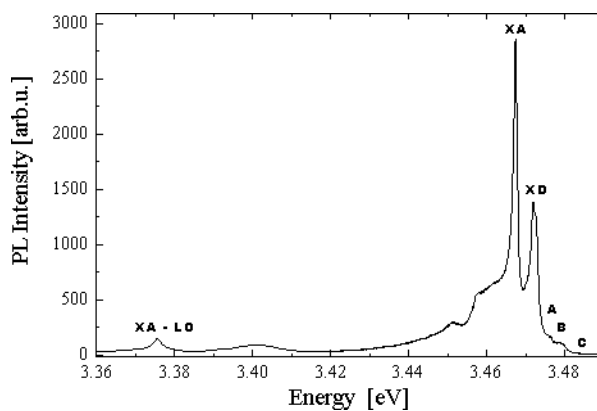


Figure 3. Near band-gap energy region of AMMONO GaN photoluminescence with very narrow exciton lines (FWHM~1meV).