Vol. 90 (1996) *ACTA PHYSICA POLONICA A* No. 4

Proceedings of the XXV International School of Semiconducting Compounds, Jaszowiec 1996

ON GaN CRYSTALLIZATION BY AMMONOTHERMAL METHOD*

R. DWILIŃSKI, J.M. BARANOWSKI, M. KAMIŃSKA

Institute of Experimental Physics, Warsaw University
Hoża 69, 00-681 Warszawa, Poland

R. DORADZIŃSKI

Institute of Theoretical Physics, Warsaw University, Hoża 69, 00-681 Warszawa, Poland

J. GARCZYŃSKI AND L. SIERZPUTOWSKI

Dept. of Chemistry, Warsaw University of Technology
Pl. Politechniki 1, 00-661 Warszawa, Poland

GaN crystals are grown using ammonothermal method at pressures below 5 kbar and temperatures below 550°C. In this method, GaN is synthesised from high purity metallic gallium. The main role in the low temperature GaN crystallization is played by the chemically active and dense ammonia and dissolved mineralizer. Morphology of the obtained crystals as well as solubility experiments prove that gallium nitride is dissolved and crystallised from solution. Physical properties of GaN crystals obtained using ammonothermal method depend on the growth conditions and the type of mineralizer. All GaN samples reveal very intensive photoluminescence, also at room temperature. The spectra of crystals grown with lithium compound mineralizer are shifted towards higher energies in comparison to crystals grown with potassium based mineralizer. At helium temperatures, phosphorescence is also observed.

PACS numbers: 81.10.Dn

1. Introduction

The problem of optimal substrate for GaN epitaxy is still not solved. Commonly used sapphire causes high dislocation density. Use of better lattice matched SiC leads to the growth of silicon nitride rather than GaN layers. $NdGaO_3$, ZnO and other recent candidates for heteroepitaxial growth have not made the breakthrough in GaN growth, either. The reasons are the following: differences in the thermal expansion coefficient, big lattice mismatch and/or chemical instability.

*This work is supported by the Committee for Scientific Research grant no. 8 T11 B 033 10.

On the other hand, GaN bulk crystals grown in small diameter chambers by high nitrogen pressure (HNP) method [1] are still of too small dimensions for industrial applications. The main problem of HNP technique is the demand of both high pressure and high temperature, which strongly limits the dimensions of reaction chamber.

In ammonothermal method used by us the chemical reaction takes place in highly active supercritical medium [2]. This fact allows to expect that temperature and pressure demands for GaN crystallization by this method would be much lower than in HNP technique.

2. Experimental method

In ammonothermal method substrates are placed together into 10 cm^3 reaction chamber and heated for a few weeks with or without temperature gradient. High pressure autoclave of special construction is necessary in order to keep the supercritical ammonia. Filling the autoclave with ammonia and mineralizers is done using vacuum tensieudiometer and dry nitrogen glove-box. The processes are performed at temperatures up to 550°C and pressures up to 5 kbar. All experimental procedures and equipment are described in details in [3].

3. Results

Two kinds of phenomena were observed:

1. Spontaneous GaN crystallization in metallic gallium/ammonia/mineralizer system.
2. Dissolution of gallium nitride in supercritical ammonia with mineralizer.

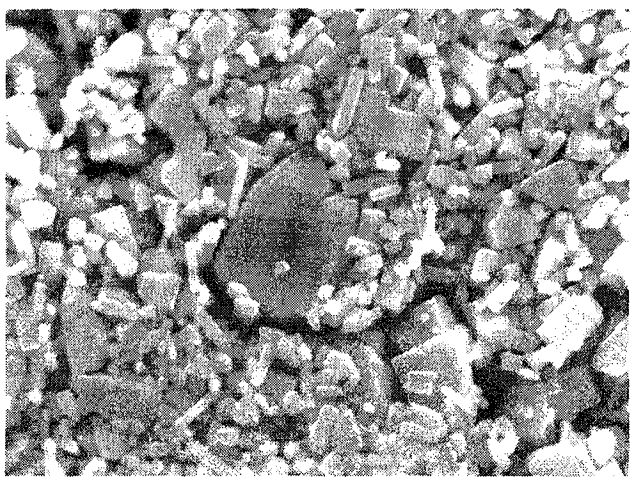

Fig. 1. GaN crystals obtained in synthesis process under the following conditions: $T = 550°C$, $p = 5$ kbar, Ga:$LiNH_2$:NH_3 = 1 : 2 : 20.

Fig. 2. GaN crystals grown in synthesis process at $T = 550°C$, $p = 5$ kbar, Ga:K:NH_3 = 1 : 2 : 20.

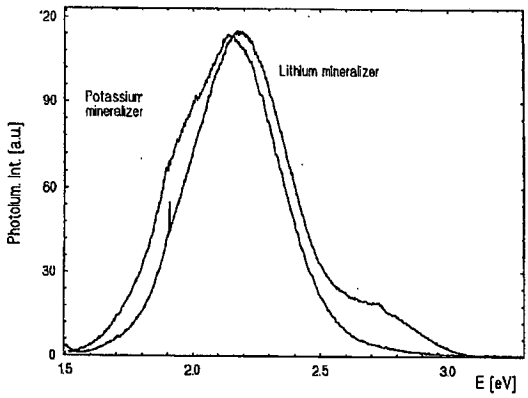

Fig. 3. Photoluminescence spectra (measured at 4.2 K) of GaN crystals obtained by ammonothermal method. The maximum of peak for the crystals grown in the presence of $LiNH_2$ is shifted towards higher energies in comparison to the crystals grown in the presence of KNH_2.

The first type of phenomena strongly depended on the kind of mineralizer and its contents in the solution. For small molar ratio of mineralizer ($LiNH_2$:NH_3 = 1:200) the kinetics of reaction was very slow, which resulted in polycrystalline GaN crust of irregular shapes. For higher mineralizer ratio (1:10) the reaction went faster and gallium nitride of regular, well shaped grains was obtained within a week (Figs. 1, 2). The kind of mineralizer was an important parameter for the crystallization process. Crystals grown in the presence of $LiNH_2$ had the form of regular grains of a few micrometers and created finely crystalline powder. The presence of

KNH_2 caused the growth of morphologically diversified, but very compact crystals of length up to 25 μm and the product was ceramic-like.

The second type of phenomena, dissolution of GaN in ammonothermal medium, was already visible by the morphology of synthesised crystals. This mechanism of crystallization was then affirmed directly: GaN needle of dimensions 0.5 × 0.5 × 3 mm (previously grown by HNP method [1]) was completely dissolved under ammonothermal conditions. In this process the mineralizers played also the crucial role: similar experiment performed in pure ammonia did not show GaN dissolution.

The influence of different mineralizers on optical properties of the obtained crystals was also observed. All crystals revealed very intensive photoluminescence, even at room temperature. It was found that the spectra of crystals grown in the presence of $LiNH_2$ were shifted towards higher energies in comparison to the ones grown in the presence of KNH_2 (Fig. 3). A helium temperature phosphorescence was also observed in some cases.

4. Summary

It is shown that using ammonothermal method GaN can be crystallised at temperatures not exceeding 550°C and pressures below 5 kbar. Solubility experiments prove that crystallization reaction takes place in the supercritical solvent. This fact is extremely important for further development of the method, namely GaN recrystallization in temperature gradient.

The obtained crystals revealed very intensive photoluminescence due to their high crystalline quality and purity.

Relatively low pressure and temperature demands and good quality of obtained crystals allow to recognise ammonothermal method as a potential method for industrial growth of GaN bulk crystals.

References

[1] S. Porowski, J. Jun, M. Boćkowski, M. Leszczyński, St. Krukowski, M. Wróblewski, B. Łucznik, I. Grzegory, *Proc. 8th Conf. on Semi-insulating III–V Materials, Warsaw 1994*, Ed. M. Godlewski, World Scientific, Singapore 1994, p. 61.

[2] R. Dwiliński, A. Wysmołek, J. Baranowski, M. Kamińska, R. Doradziński, J. Garczyński, L. Sierzputowski, H. Jacobs, *Acta Phys. Pol. A* **88**, 833 (1995).

[3] H. Jacobs, D. Schmidt, in: *Current Topics in Material Science*, Vol. 8, Ed. E. Kaldis, North-Holland, Amsterdam 1981, p. 381.