Journal of Crystal Growth 312 (2010) 3161–3164

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Solubility of GaN in supercritical ammonia with ammonium chloride as a mineralizer

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ARTICLE INFO

Article history:
Received 6 May 2010
Received in revised form
9 July 2010
Accepted 12 July 2010
Communicated by P. Rudolph
Available online 16 July 2010

Keywords:
A1. Solubility
A1. Solvents
A2. Ammonothermal crystal growth
B1. Gallium nitride

ABSTRACT

The solubility of GaN in supercritical ammonia with ammonium chloride as a mineralizer was measured with a weight-loss method. Temperature-, pressure-, and mineralizer concentration-dependence of the solubility of GaN were investigated. The solubility increased with increase in temperature, and its pressure dependence was very low. The solubility behavior was quite different from the case of using the mineralizer KNH_2 as a basic mineralizer.

1. Introduction

GaN has attracted considerable attention as a component in materials used for the manufacture of high-power and high-frequency electronic devices. Therefore, high-quality and large-diameter bulk GaN is required. Many methods have been proposed and tested for the growth of GaN crystals [1–3]. The ammonothermal method (which is a solvothermal method) is one of the most promising techniques for achieving this purpose [2,4–6]. It may become a reliable process to synthesize bulk GaN crystals, which are the best substrates for GaN epitaxial growth. This method uses an autoclave containing two parts separated by a baffle that allows a temperature gradient between the upper and lower parts. One side is for dissolution and the other is for deposition. A solubility difference becomes the driving force in crystal growth by the ammonothermal method. Due to the limited dissolution of GaN in supercritical ammonia, a mineralizer must be added to the solution. To realize an ideal condition of supersaturation for the crystal growth of GaN in supercritical ammonia, it is essential to select a suitable mineralizer and to determine the ideal conditions of temperature and pressure.

The hydrothermal crystal growth method is an analogous process. An aqueous solution is held at high temperature and high pressure to dissolve a material in one part of the system. It is then transported to another part of the system to deposit it on a seed. This process is carried out in sealed vertical autoclaves with a temperature difference established between the top and bottom of the vessel. In general, the solubility of the material increases as the temperature increases. Therefore, the feedstock is placed in the lower, hotter part of the autoclave, and the seeds mounted in the cooler, upper part. Transport of the hot solution from the region containing the feedstock to the region containing the seeds is by convection. Once the solution reaches the growth region, it becomes supersaturated with respect to the seed materials and deposits on the seeds. The cooler, depleted solution then returns to the hotter zone by convection and dissolves more feedstock. To control the processes of crystal growth, the relationship between solubility and temperature is essential to evaluate the super-saturation degree in the autoclave. Large single crystals of SiO_2 and ZnO have been synthesized industrially by the hydrothermal crystal growth method [7]. In these cases, the feedstock was placed in the hotter, lower part of the autoclave and the seeds placed in the cooler, upper part. As for hydrothermal crystal growth systems, there have been many reports on the solubility of inorganic materials in supercritical water. However, limited information exists for the solubility of GaN under ammonothermal conditions. Wang et al. [5] and Dwiliński et al. [9] reported the negative temperature coefficient for the GaN solubility in a KNH_2–NH_3 basic system. Hashimoto et al. [8] also showed experimental data of the solubility of GaN in a $NaNH_2$–NH_3 system. These three cases are all basic ammonothermal systems.

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doi:10.1016/j.jcrysgro.2010.07.020

We previously prepared quick reports [10,11] on the solubility of GaN in supercritical ammonia with ammonium chloride as a mineralizer. The present contribution describes continuing work on the experimental determination of the solubility of GaN in supercritical ammonia using ammonium chloride as a mineralizer.

2. Experimental procedure

The GaN sample used was GaN crystals grown by hydride vapor phase epitaxy. The mineralizer was NH_4Cl, which had a minimum purity of 99.5% and was purchased from Wako Pure Chemical Industries. It was dried at 100 °C for 24 h before measurement. The NH_3 of 99.999% purity was supplied by Japan Fine Products Company Limited. The samples were used without further purification.

A solubility measurement apparatus of a flow type has been used in solubility measurement of the metal oxide in supercritical water [12]. This method can change measurement conditions continuously and many data are obtained for a short time. However, it is not very realistic with danger to flow supercritical ammonia continuously. Additionally, measurement accuracy of a flow type measurement apparatus is not good compared with a static method type measurement apparatus. Therefore, solubilities were measured with a weight-loss method. Although it takes a long time to measure solubility, the accuracy of measurement is good. A schematic outline of the experimental apparatus is shown in Fig. 1. The inconel-625 autoclave, without an inner lining made of platinum, was used in our rapid reports [10,11]. In the present study, the inconel-625 autoclave with a platinum inner lining was used to prevent corrosion. The inner volume was approximately 10 cm^3. The electrical furnace was divided into three parts, each of which was temperature-controllable. A pressure gage calibrated against a dead weight gage was used. Temperature and pressure values have an uncertainty of ± 1 °C and ± 1 MPa, respectively. The composition of the sample mixtures were determined by weighting. The uncertainty of the concentration of NH_4Cl was estimated to be less than 0.05 mol%. On the basis of the uncertainties of these properties, the uncertainty of the solubility data is estimated to be within ± 5%.

The measurement procedure was as follows. First, a weighed amount of the mineralizer and three or four pieces of polycrystalline GaN were charged in the autoclave. The valve and transducer were attached to the autoclave. After degassing for about 5 min, NH_3 was introduced into the autoclave with a plunger pump. The amount of NH_3 charged in the cell was determined by weighing the autoclave with an electric balance (accurate to within 0.01 g) before and after loading NH_3. After introducing NH_3 and weighing the autoclave, the autoclave was set into the electric furnace. The autoclave was heated for 100 h at a predefined temperature to establish the dissolution equilibrium and subsequently allowed to stand to cool down. Then NH_3 was released and the autoclave opened. All solid polycrystalline GaN was recovered, washed with water, dried, and weighed. GaN dissolved in supercritical ammonia deposited on the inside wall surface of autoclave, not on the GaN polycrystalline. Therefore, the solubility of GaN in supercritical ammonia can be determined by weighing GaN polycrystalline with the electrical balance, accurate to within 0.0001 g, before and after measurement. The solubility was determined using the following formula:

$$\text{solubility}[\text{mol\%}] = \frac{\text{feed GaN[mol]} - \text{recovered GaN[mol]}}{\text{feed } NH_3\text{[mol]}} \times 100.$$

We confirmed that in the case of the experimental time between 100 and 180 h agree with within experimental uncertainty.

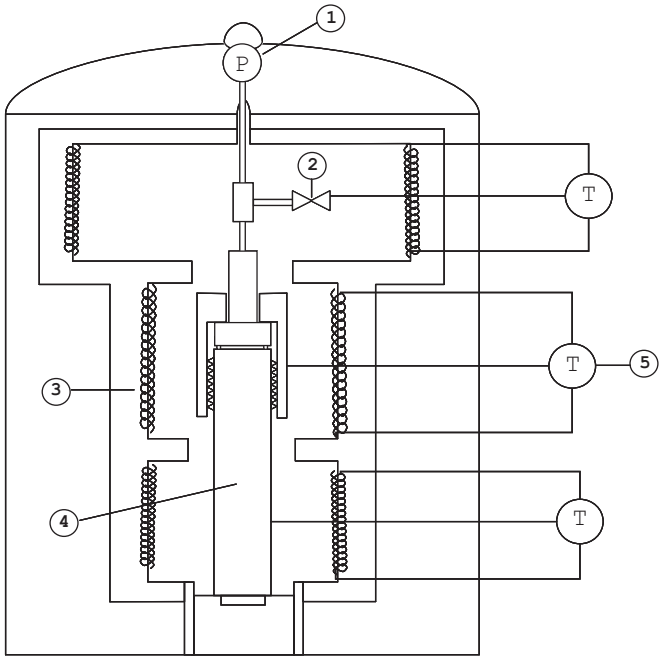

Fig. 1. Schematic outline of experimental apparatus: 1: pressure gage; 2: valve; 3: electrical furnace; 4: autoclave; 5: thermocouple.

Table 1
Solubility of GaN in supercritical ammonia with NH_4Cl as a mineralizer.

Temperature (°C)	Pressure (MPa)	Concentration of NH_4Cl (mol%)	Solubility (mol%)
420	100	3.2	0.79
470	55	3.1	0.81
470	83	3.1	1.07
470	100	3.0	1.01
470	150	3.1	1.04
490	100	0	0.04
490	100	1.6	1.18
490	100	9.1	3.30
490	100	15.5	5.47
520	100	3.2	1.22
530	100	3.1	1.26
575	100	3.1	1.35
600	100	3.2	1.40

3. Results and discussion

The experimental results of the solubility of GaN in supercritical ammonia with NH_4Cl as a mineralizer are given in Table 1. The solubility data with the inconel-625 autoclave without a platinum inner lining are shown in Table 2 for reference. Fig. 2 shows the temperature dependence of the solubility of GaN in supercritical ammonia with NH_4Cl as a mineralizer. The solubility increased with increase in temperature. Up to near 530 °C, it increased linearly and there was a tendency for the slope to increase gradually above 530 °C. For comparison, the solubility of GaN in supercritical ammonia with KNH_2 is shown in Fig. 2. The temperature dependence of the solubility of GaN in supercritical ammonia differed between acidic mineralizers and basic mineralizers. With acidic mineralizers, the temperature dependence showed the same tendency as SiO_2 [13] or ZnO [14] in supercritical water. The residues in autoclave after solubility measurement were confirmed to be h-GaN, c-GaN, and NH_4Cl by XRD. Dissolution species cannot be confirmed because it is not stable at room temperature and normal pressure.