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High pressure direct synthesis of III-V nitrides

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Abstract

The nitrides of group III metals: (AlN, GaN, InN) are very important materials due to their applications for short wavelength optoelectronics (light-emitting diodes and laser diodes). In this paper, the results of high-pressure direct synthesis of AlN, GaN and InN are presented. The conditions for the thermodynamical stability for AlN, GaN and InN are discussed. The influence of the kinetic barrier on the synthesis of InN, GaN and AlN is considered using the results of quantum mechanical calculations of the dissociative adsorption of N_2 on the liquid metal surface. It is shown that the kinetic barrier for InN synthesis is very high, preventing direct synthesis of this compound. This barrier is lower for GaN, which allows to grow GaN crystals from the solution of atomic nitrogen in liquid gallium. The lowest barrier is for AlN, which leads to the combustion reaction of liquid aluminum in nitrogen atmosphere, in the pressure range from 10 to 650 MPa. At higher pressure, the extinction of combustion synthesis takes place. \bigcirc 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Semiconducting III–V nitrides such as indium nitride (InN), gallium nitride (GaN) and aluminum nitride (AlN) are currently considered as the most promising optoelectronic materials in the green, blue and ultraviolet spectral region. This is due to their thermal stability and large direct energy gap [1]. The nitrides technology is developed to the point that commercial blue light-emitting diodes GaN/GaInN are commercially available [2]. On the other hand, from few years the ceramics of AlN are applied in electronics as heat sinks [3]. This is due to the excellent thermal conductivity of AlN, high electrical resistivity, and low thermal expansion coefficient, similar to that of silicon.

In this paper, we analyze the behavior of the systems consisting of Al, Ga and In metals and nitrogen under pressure up to 2 GPa, at high temperatures, from the point of view of direct synthesis of the corresponding nitrides.

2. Thermal stability of InN, GaN and AlN

The III–V nitrides are crystals with high bonding energies. The consequence of these are their high melting temperatures (see Table 1) and good thermal stability. On the other hand, the strong triple bond in nitrogen molecule lowers the thermodynamical

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Table 1 Melting conditions for III-N nitrides compounds

Nitride	Melting temperature (K)	Decomposition N_2 pressure at melting point
AlN	~ 3500 [4]	20 MPa [5]
GaN	~ 2800 [4]	4.5 GPa [6]
InN	~ 2200 [4,7]	6 GPa [7]



Fig. 1. Gibbs free energy change with temperature for GaN and its constituents for nitrogen pressure of 10^5 Pa and 1.1 GPa.

potential of the nitrides constituents: $Me + 1/2N_2$. Since the free energy of its constituents decreases with temperature faster than the free energy of the crystal, nitrides lose their stability at high temperature. At atmospheric pressure AlN is stable up 2500 K. GaN loses the stability at 1200 K. InN is stable only up to 600 K. On the other hand, the application of pressure allows to increase the free energy of nitrogen and therefore the free energy of its constituents. As a consequence, at high pressure the stability range is extended. This is clearly shown in Fig. 1. This figure presents the change in Gibbs free energy with temperature for GaN and its constituents for N₂ pressure of 10⁵ Pa and 1.1 GPa [8]. We can see that the stability region of GaN is extended at high nitrogen pressure. At pressure up to 2 GPa and temperature up to 2000 K (our experimental conditions), InN is thermodynamically stable up to 900 K which is very far from the melting point (see Table 1). On the contrary, GaN is stable up to 2000 K. AlN is stable to its melting point. In the case of this compound, high pressure is not necessary to extend its region of stability.

3. Kinetic aspect of direct synthesis of AlN, GaN and InN

The first stage of direct synthesis of nitrides is the dissolution of nitrogen in liquid metal. This process was analyzed by quantum mechanical calculations [9]. The nitrogen molecule approaching the metal surface is repelled by the metal that results in a potential barrier. If the molecule has enough energy to overcome the potential barrier, it gets closer to the metal and dissociates into two atoms forming new bonds with the metal. The potential barriers are lower than the bonding energy in the nitrogen molecule. However, their values are quite high (see Table 2), which suggests, that the dissociation process can be kinetically controlled even for relatively high temperatures. Such barrier is the lowest for Al and the highest for In. We can conclude that efficient N₂ dissociation requires higher temperatures for In than for Al.

Fig. 2 shows the rate of dissociation process estimated for nitrogen pressure of 2 GPa. The horizontal dotted line is the practical limit for the effective synthesis of nitrides. In this case it is 10 mg of nitride at 1 cm² during 100 h. It follows from Fig. 2 that the synthesis of InN at 2 GPa N₂ pressure is impossible. This synthesis, to be reasonably fast, requires at least 1800 K, which is quite far above the thermal stability limit for indium nitride at 2 GPa (900 K). In contrast to that, the synthesis of AlN at high pressure should be very fast already at temperatures slightly exceeding 1000 K. For GaN

Table 2

Potential barriers for N_2 adsorption on Al, Ga, In metal surface. The triple bond in the N_2 molecule is equal to 9.8 eV/molecule

Potential barrier (eV)
5.8
4.8
3.2



Fig. 2. Nitrogen dissociation rate on Al, Ga, In metal surface at 2 GPa.

the rate of dissociation is average. However, for the effective synthesis the temperature must be higher than 1500 K, which indicates that the application of high N_2 pressure allows direct synthesis of GaN.

4. Experimental procedure

Direct synthesis experiments were carried out in the high- pressure high-temperature equipment described elsewhere [10]. Inside the chamber hydrostatic N₂ pressure up to 2 GPa can be obtained. A one-, two-, or three-zone graphite furnace, capable of reaching temperatures up to 2000 K was used in order to heat the metal samples. The metal (Al, Ga, In) was placed into the crucible, in the furnace, and in the high-pressure chamber. The sample was heated with a constant rate to the given temperature and annealed at this temperature, at high nitrogen pressure. Then the sample was cooled down at a constant rate, the system was decompressed and the sample removed.

5. Results and discussion

5.1. AlN synthesis

During the heating of the Al sample at N_2 pressure, in the pressure range from 10 to 650 MPa, we

observe combustion synthesis of AlN [11]. This observation is in agreement with our theoretical considerations. Due to the low kinetic barrier for synthesis, the formation of AlN at high-pressure should be very fast. However, we observe low- and high-pressure limits for the combustion process. The lower limit can be simply explained by the access of nitrogen molecules into the reaction zone, which is pressure dependent. The synthesis rate is proportional to pressure [9]. Up to 100 MPa, increasing nitrogen pressure leads to the increase of nitrogen density and the amount of nitrogen gas at the reactional interface. However, at pressures higher than 100 MPa the combustion reaction begins to be controlled mainly by the thermal conductivity of nitrogen. Fig. 3 shows the typical time-temperature (t-T) profile measured during combustion synthesis. The analysis of the difference between the maximal temperature of combustion $(T_{\rm c})$ and ignition temperature $(T_{\rm ign})$ (see Fig. 3) as a function of pressure is presented in Fig. 4. As we can see this difference decreases for N2 pressure higher than 100 MPa [11]. At high pressure the thermal conductivity and the thermal capacity of nitrogen increase and the heat losses during reaction become significant. Therefore, one can observe the extinction of the combustion process [10,11]. This is an interesting agreement between this observation and a theoretical result obtained by Saur et al. [12] for a totally different reaction: combustion of methane in argon-oxygen mixture. Saur et al. have shown that the maximal combustion temperature can be reached at 100 MPa. For higher pressure, due to the high thermal conductivity and high thermal capacity of gas, the combustion temperature decreases and the extinction of combustion is to be expected.

As the result of AlN combustion synthesis, we have obtained very pure, low oxygen content, aluminum nitride powder. This powder was sintered to the ceramic form of high thermal conductivity-200 W/m K [13].

5.2. GaN synthesis

The heating of gallium sample does not lead to the combustion reaction. Annealing of gallium at high pressure and high temperature allows to grow



Fig. 3. Typical time-temperature (t-T) profile measured during combustion of aluminum in nitrogen gas.



Fig. 4. Difference between combustion temperature and temperature of ignition as a function of N_2 pressure.

quite big GaN crystals. Nitrogen molecules dissociate on gallium surface and dissolve in the metal. Therefore the crystals are grown from the solution of atomic nitrogen in liquid gallium. Supersaturation, that is the driving force for the crystallization process, is created by the application of temperature gradients along the gallium samples. Usually, the pressure of the experiments, 1.5–2 GPa, is higher than the equilibrium one for high temperature end of the solution. Therefore pressure and temperature in the whole sample correspond to gallium nitride stability range. Since the gallium is



Fig. 5. Typical GaN platelet.

in the temperature gradient, the nitrogen from the hot end of the sample is transported by convection and diffusion to the cooler part, where the solution becomes supersaturated and crystallisation of GaN is possible. The mechanism of GaN crystal growth is described in details elsewhere [14]. The GaN crystals are of wurzite structure, in the form of hexagonal platelets. Fig. 5 shows typical GaN platelet, grown with the rate of 0.1 mm/h into $\{10 - 10\}$ direction, perpendicular to the *c*-axis. The platelets are single crystals of perfect morphology suggesting stable layer by layer growth. Presently the maximum size of crystals exceeds 15 mm. The GaN pressure grown crystals are of the highest structural quality and the lowest dislocation density $(10^2 - 10^0)$ [15], ever reported for this material.

5.3. InN synthesis

After heating and annealing of indium at high nitrogen pressure (1-2 GPa) we have never observed the combustion of liquid indium or crystal growth of indium nitride. This is due to the high kinetic barrier for indium nitride synthesis at temperature where InN is stable at N₂ pressure of 2 GPa (only 900 K).

6. Conclusions

The main barrier preventing the direct synthesis of nitrides is the interface between nitrogen and

liquid metal. The rate of nitrogen dissociation on the liquid metal surface is kinetically controlled and it is proportional to N_2 pressure. For AlN the nitrogen pressure allows to control the mechanism of synthesis. By combustion of bulk Al, high purity AlN can be synthesised. For GaN, pressure allows to extend the stability range up to the temperature where effective crystallization is possible. Dislocation-free high-quality single crystals can be grown.

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