

SEMICONDUCTING III-V NITRIDES GROWN UNDER HIGH PRESSURE

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The experimental technique for phase diagrams determination at gas pressure up to 20 kbar and temperature up to 2000 °C is presented. Its application for study of III-V nitrides stability conditions is discussed. It is shown that AlN, GaN and InN crystals can be grown at N_2 pressure up to 20 kbar. The crystal characteristics are determined by X-ray, Raman scattering and optical absorption measurements.

1. Introduction. Binary nitrides belonging to III-V semiconductors, AlN, GaN and InN, are currently, considered as the most promising electronic materials. This is due to their physical properties, especially, large, direct energy gaps and thermal stability.

Besides the prospects for various applications it is interesting to include the nitrides into analysis of the chemical trends in physical properties of III-V compounds since they are of the highest ionicity and the smallest atomic volume.

Usually, the nitrides are deposited on the foreign substrates (i.e. sapphire or SiC) by the use of MBE or MOCVD methods of epitaxial growth [1,2]. Large lattice mismatch between the substrates and deposited nitrides lowers the quality and reproducibility of the layers.

Large substrate quality crystals of III-N compounds have not been obtained since their thermodynamical properties eliminate any standart method like Czochralski or Bridgman growth from the melt. Melting temperatures of considered nitrides [3-5] are very high and, moreover, GaN and InN have extremely high decomposition pressure.

In this paper, we present the experimental technique which is used to determine phase diagrams at hydrostatic pressure up to 20 kbar and temperatures up to 2000 °C. The conditions for crystal growth of III-V nitrides are derived from the experimental phase diagrams (Section III). In the last Section of the paper the physical properties of pressure grown crystals are presented.

II. Experimental technique for determination of phase diagrams at high gas pressure and high temperature. Pressure in the chamber with internal diameter of 30 mm is generated by the three stage gas compressor. The chamber is closed by plugs with gaskets and electrical bits-through. The set of thin Cu wires is passed through the plug in order to connect the pressure and temperature gauges working inside the chamber to the control and data aquisition systems. Four additional bits-through are arranged in the plug to heat the furnace while inserted into the chamber.

Furnaces with graphite or tungsten heating elements (with one, two or three zones) have been used for gas pressure experiments. Maximum temperature depends on the internal diameter of the furnace. In the case of i.d. of 10 mm, $T_{\max} = 2000\text{ °C}$ is possible whereas with 14 mm, $T_{\max} = 1550\text{ °C}$. For stable work of the furnace the crucial is the effective thermal insulation between the heater and the internal wall of the chamber.

The temperature in the system is controlled by a set of thermocouples arranged along the furnace and coupled with the input power control system. The parameters of high pressure experiments are measured with frequency up to 20 times per second and stored by a data aquisition system. The pressure is fully hydrostatic due to the gas pressure medium.

Precise and fast measurements of pressure, temperature and temperature gradients allows us to run not only the standard programs of annealing, heating or cooling with a given rate, but, also, to have "in situ" information about some phenomena occurring in the system. With the experimental setup just presented, any phenomena accompanied by a thermal effect (even very weak) can be registered. By the use of DTA configuration (Differential Thermal Analysis) one can observe the pressure dependence of phase transitions such as melting, solidification or solid-solid transformations. As an illustration the phase diagram of HgS [6], showing both the liquid-solid and the solid-solid transitions, is presented in Fig. 1.

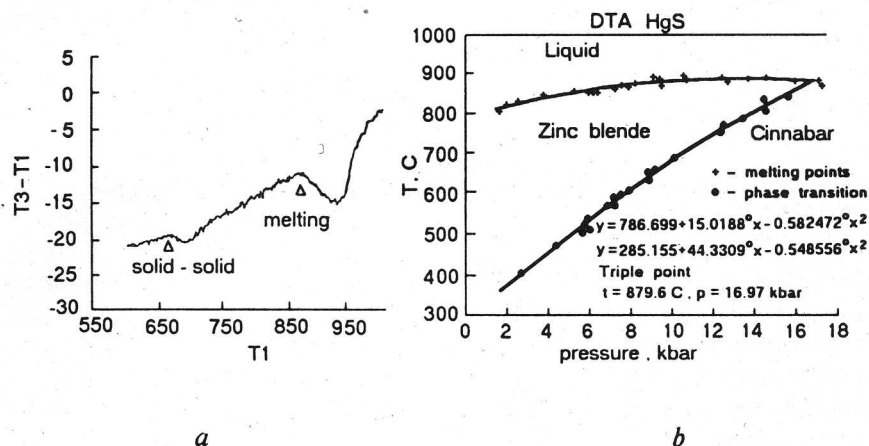


Fig. 1. *a* — DTA signals of melting and cinnabar \rightarrow zinc blende transition in HgS; *b* — phase diagram of HgS determined at high gas pressure by DTA [6]

DTA has been used for the measurements of decomposition temperature of InN [7]. Since the reported p - T stability data for this compound scatter by several orders of magnitude [8], we have verified the temperature of InN decomposition by the registration of thermal effect of this process at high N_2 pressure (Fig. 2).

At low temperatures, a slow rate of decomposition can be expected. Therefore, DTA results should be confirmed by long term, direct decomposition experiments.

The equilibrium N_2 pressures over

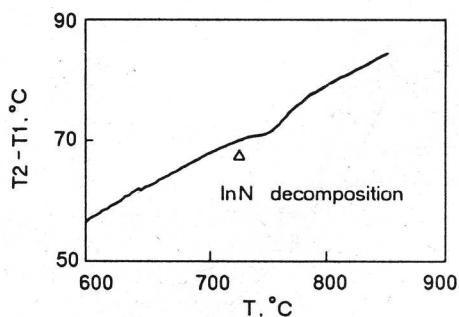


Fig. 2. DTA signal of InN decomposition at 10 kbar

AlN are relatively low [13]. It was reported that at 100 atm, the liquid phase occurs at 2800 $^\circ\text{C}$ [5]. We have investigated the behavior of the system consisting of bulk aluminium and N_2 under pressure up to 15 kbar [9]. During heating of Al sample DTA peak of Al melting was observed for all applied pressures. At higher pressures (> 5 kbar), a weak signal of opposite sign appeared indicating the formation of AlN layer on the Al surface. This is shown in Fig. 3, *a*.

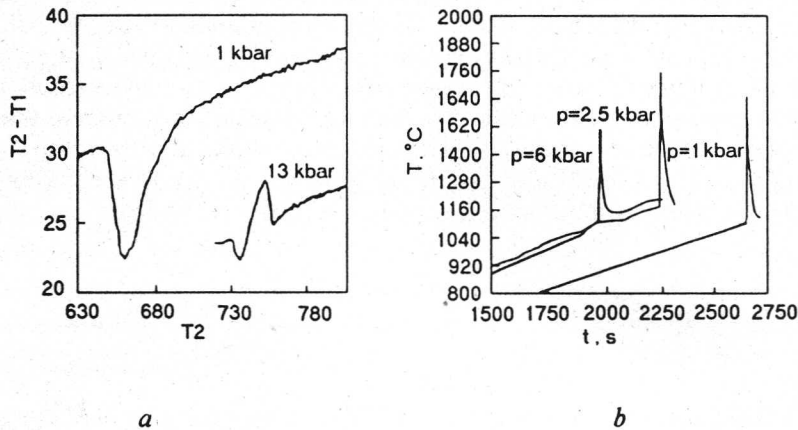


Fig. 3. *a* — DTA signals of Al melting and AlN surface layer formation during heating of Al bulk sample; *b* — DTA signals of AlN synthesis at high N_2 pressure

For a pressure range of 0.1–6.5 kbar very strong signals have been observed indicating highly exothermic reaction (Fig. 3, *b*) of bulk Al combustion leading to high degree conversion into AlN powder or ceramics. At higher pressures > 6.5 kbar, the combustion peak disappears and further heating of Al sample is possible. In the temperature range of 1600–1800 °C crystals of AlN have been grown.

The stability curve for GaN has been determined in large pressure and temperature range by Karpinski et al. [4], by direct decomposition and synthesis experiments at isothermal conditions. Additional annealing of GaN samples in a temperature gradient have been performed in order to estimate the kinetics of decomposition process (Fig. 4, *a*). It was found that the zone of partial decomposition narrows with increasing pressure (and corresponding equilibrium temperature). The observation has been explained by the proposed kinetic model of GaN decomposition (Fig. 4, *b*).

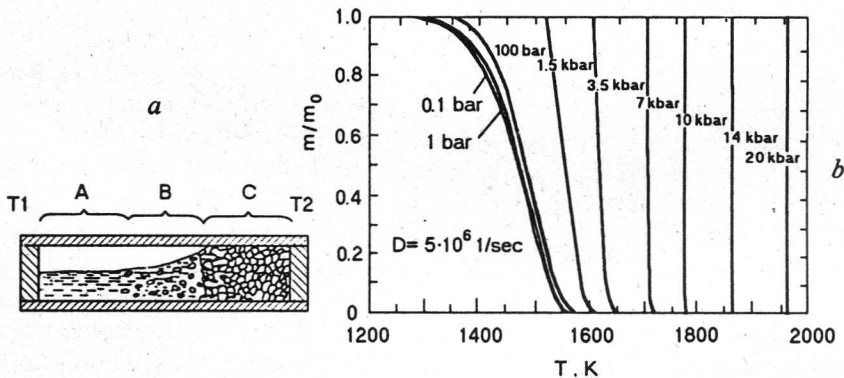


Fig. 4. *a* — GaN powder sample after annealing in the temperature gradient $T_1 > T_{eq} > T_2$ Zone A: liquid Ga, Zone B: Ga droplets, Zone C: undecomposed GaN powder; *b* — temperature dependence of GaN sample mass after 90 min annealing at different nitrogen pressure

III. Conditions for crystal growth of III-N at high N_2 pressure. In Fig. 5, the stability curves for AlN, GaN and InN are shown together with the field available for gas pressure experimental technique described in Section II. Since either the decomposition pressure, at melting (GaN, InN) or melting temperatures (AlN, GaN) are outside this field, crystallization has to be carried out from the diluted solutions of N in the liquid metal. For successful crystal growth, some additional factors have to be considered. These factors are nitrogen solubility in the growth solution (i.e. liquid Al, Ga or In), the rate and mechanism of nitride synthesis and its dissolution in the liquid metal. Crystals of III-N grown under high N_2 pressure are shown in Fig. 6.

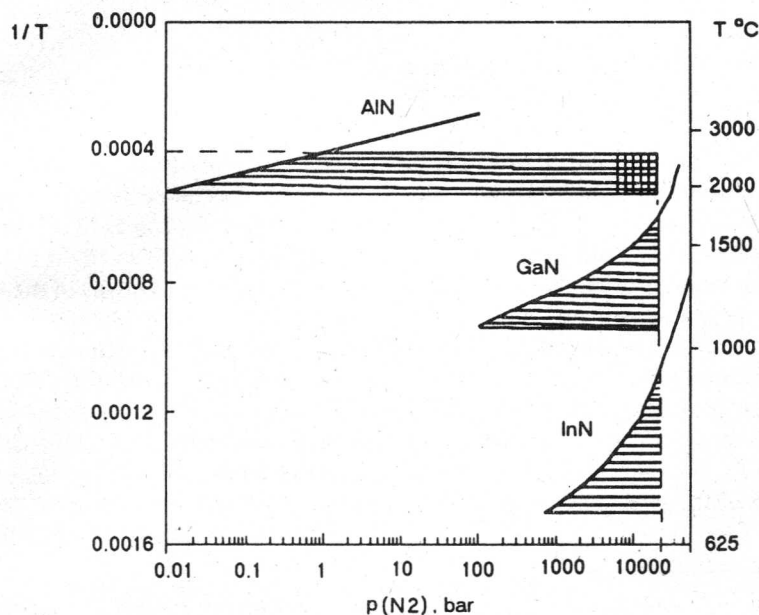


Fig. 5. Stability curves for III-N compounds: AlN-[13], GaN-[4], InN-[7], --- — experimental limits, shaded area — conditions for crystal growth

For GaN, it was shown that the solubility of nitrogen in the liquid Ga increases for three orders of magnitude when the temperature is increased from 1200 °C (10^{-5} mole fr.) to 1500 °C (10^{-2} mole fr.) [4]. GaN single crystals have been grown at N_2 pressure of 10–20 kbar in the temperature gradient during 5–12 h. processes [11,12].

AlN crystals were obtained at pressures exceeding the upper limit for combustion. The process was less effective than for the case of GaN. This result leads us to believe that solubility of nitrogen in the liquid Al is significantly lower than in the liquid Ga in the same temperature range. Increase of growth temperature is necessary for more efficient crystallization.

Small (10–50 μ m) InN crystals have been grown in temperature gradient, at pressure 18–20 kbar. It is suggested [7] that the rate limiting stage of the growth process is InN synthesis and its dissolution in the liquid In. The way to overcome this barrier could be the use of the InN powder as a source of nitrogen in the liquid phase.

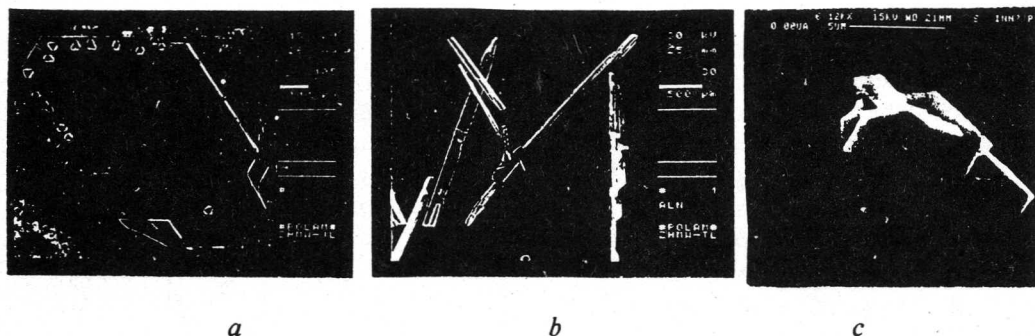


Fig. 6. Crystals of GaN (a), AlN (b) and InN (c) grown at high N_2 pressure

IV. Physical properties of pressure grown nitrides. High quality of GaN crystals has been confirmed by the measurements of double crystal rocking curves of the $CuK\alpha$ (004) reflection. In Fig. 7 we have shown a curve typical for GaN plates of 1–1.5 mm in size. The full width at half — maximum of the curves are usually 23–26 arc sec. (for heteroepitaxial MOCVD and MBE GaN layers the widths of the rocking curves are of few arc min. [14]).

Crystal-lattice stability of III-N crystals have been studied by Raman scattering and X-ray absorption spectroscopy in diamond anvil cell [15,16]. In Fig. 8, the Raman spectra of GaN and AlN single crystals are presented. In Table we have shown the values of transition pressures, at which the nitrides transform from the wurzite to the rock salt structure. The measured values are in good agreement with the results of first principles LMTO calculations [17].

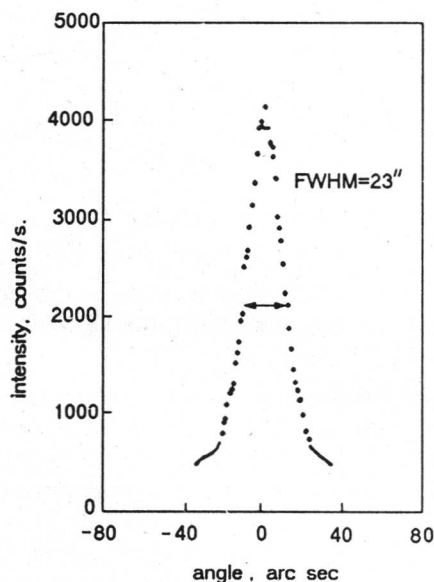


Fig. 7. Rocking curve for GaN crystal

Table. Transition pressure of III-N compounds

| Nitride | Ptr [kbar], calc | Ptr, [kbar], exp |
|---------|------------------|------------------|
| GaN | 650 | 470-500 |
| AlN | 166 | 165 |
| InN | 254 | 230 |

However, the results of Table do not agree with the prediction of Chelikowsky [18] that the transition pressures of tetrahedrally coordinated compounds into the rock salt changes linearly with Phillips ionicity for the same atomic volumes. According to this prediction, transition pressures for GaN and AlN should be very close, what is not confirmed by the

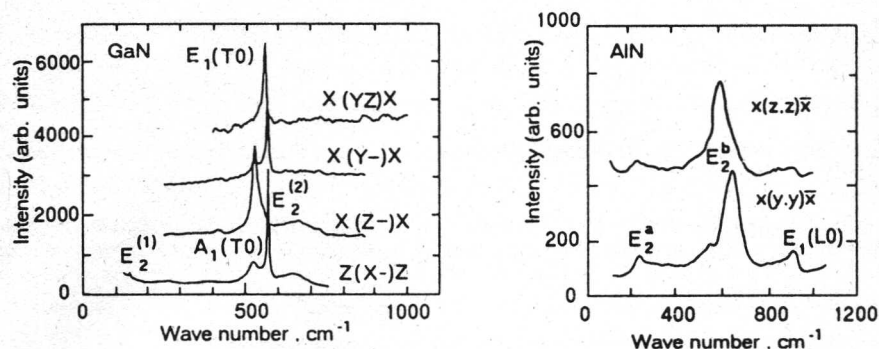


Fig. 8. Raman spectra of GaN and AlN single crystals grown at high pressure

experiment. It was shown [19] that ionicity scale, proposed by Majewski and Vogl [20] based on atomic terms of anions and cations, is more appropriate for analysis of structural stability of nitrides.

The pressure coefficients of the absorption edge have been measured for GaN and InN [7,16]. The experimental and theoretically predicted values [17] were in good agreement.

V. Summary. Gas pressure experimental techniques allow the determination of the thermodynamic properties of the systems containing important electronic materials like III-V nitrides. Results obtained so far show that high quality crystals of semiconductors can be grown. However, to obtain the crystals of substrate dimensions large technical effort is still necessary.

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