Synthesis of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and InN crystals under high pressures

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We have performed synthesis studies of various III-V nitrides crystals, key materials for optoelectronic and high-power/frequency devices, using a cubic-anvil-type large volume high-pressure apparatus combined with \textit{in situ} x-ray diffraction. Poly-crystalline polycrystallines of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys covering a composition range of $0 \leq x \leq 1$ were synthesized by a solid-phase reaction under high pressure. \textit{In situ} x-ray diffraction profiles were measured to observe the alloying process, which started at around 800°C under 6.0 GPa. Single crystal of $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$ was also successfully obtained by slow cooling of its melt from 2400°C at 6.5 GPa. For InN, its phase diagram was determined under high P-T conditions up to 20 GPa and 2000°C based on the \textit{in situ} observations, which demonstrates that 19 GPa and 1900°C are needed for its congruent melting.

Introduction

The Group-III nitride semiconductors, AlN, GaN, InN, have been used practically to realize short wavelength optoelectronic devices and have attracted the interest of many researchers (Pearton S. J., 1999). All these nitrides have the wurtzite structure and the band gap energy of AlN-GaN-InN system varies from 0.9 eV to 6.2 eV depending on their atomic composition, which corresponds to the visible and ultraviolet wavelength region.

High quality single crystals of these nitrides are desired both for basic science and industrial applications. However, it is impossible to grow their bulk single crystals from their melts by the well-known methods such as Czochralski or Bridgman growth because the nitrides decompose into nitrogen and group-III elements at high temperature before their melting points. High pressure is effective to synthesize the nitrides crystals and some attempts have been successfully made to grow GaN single crystals in high-pressure nitrogen gas (Porowski S., 1996, Porowski S., 1997). Recently, our group have found that applying high pressure above 6.0 GPa suppresses the decomposition of GaN perfectly and allowed its congruent melt at 2220°C (Utsumi W., 2004). High quality single crystals of GaN were obtained by slow cooling of the melt under high pressures. This method is rather simple and is expected to be applicable for other nitrides.

In this paper, we report our latest experimental results related to (1) synthesis of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) polycrystals by solid phase reaction under high pressure (Saitoh H., 2004), (2) single crystal growth of $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$ from its melt under high pressure (Saitoh H., 2004), and (3) phase relation of InN under high pressure and temperature based on the \textit{in situ} x-ray diffraction study.

Experimental Method

Experiments were performed using high-pressure apparatuses at SPring-8 in Harima Science Garden City, Japan. A cubic-anvil press installed on beamline BL14B1 and a two stage Kawai-type apparatus on BL04B1 were employed at pressures of less than 10 GPa and 10-20 GPa, respectively. Pressures were initially increased at room temperature and then temperature was increased under a constant applied load. In order to observe the variation of the specimens (phase transition, chemical reaction, melting, etc.) at high pressures and temperatures, \textit{in situ} powder x-ray diffraction profiles were acquired by the energy-dispersive method using the synchrotron radiation white x-rays.
For AlN-GaN experiments, the starting materials were fine powders of GaN (99.99%: Kojundo Chemical Laboratory, Saitama, Japan) and AlN (99.8%: Soekawa Chemicals, Tokyo, Japan), which were blended for suitable composition with a mortar. Fine powders of InN (99.5%: Soekawa Chemicals, Tokyo, Japan) were compacted into disk shape and used as starting materials. After high pressure and temperature experiments, the recovered specimens at ambient conditions were analyzed by a scanning electron microscope (JEOL, JSM-5310) and an x-ray microdiffractometer (Rigaku, R-Axis Rapid).

Result and Discussion

\(\text{Al}_x\text{Ga}_{1-x}\text{N}\)

Figure 1 shows a series of \textit{in situ} powder x-ray diffraction profiles at 6.0 GPa with increasing temperature. The starting material was a powdered mixture of \(x=0.6\). Peaks from both wurtzite GaN and AlN were observed at 600°C. As temperature was increased, the peak positions of GaN shifted to the higher energy, i.e., to the smaller lattice spacing. This peak shift was originated from an alloying between AlN and GaN by a solid-phase reaction. At 1400°C, the pairs of peaks from GaN and AlN with the same indexes observed at low temperature became single peaks, showing that the alloying process was completed and the sample became a single phase of the wurtzite structure. The same experiments were repeated using starting materials with other mixing ratio and similar alloying processes were observed.

Figure 2 shows the relationship between the nominal concentration and the lattice constant of recovered specimen at ambient conditions, which was determined using x-ray microdiffractometer. Each specimen was treated under the same conditions (6GPa, 1800°C). The errors in the lattice constants are smaller than the size of each symbol. Both lattice constants “\(a\)” and “\(c\)” continuously varied with the nominal composition, suggesting that the \(\text{Al}_x\text{Ga}_{1-x}\text{N}\) semiconducting alloy was formed over the entire composition range. All the data were plotted slightly above the straight line that connects the lattice constants of the end members, and expansion of the unit cells in the alloy relative to Vegard’s law was observed. We consider that this inconsistency from Vegard’s law was not intrinsic, but was caused by the minor localization of Al in the specimen due to the incomplete reaction.

\[\text{Fig. 1. A series of } \textit{in situ} \text{ x-ray diffraction profiles of a powdered mixture of AlN and GaN at 6.0 GPa. The dashed lines show peak shift of GaN.}\]
Single crystal of Al$_{0.1}$Ga$_{0.9}$N was successfully grown by slow cooling of its melt from 2400°C at 6.5GPa. Temperature was decreased with a constant speed of 3.33°C/min from 2400 to 2000°C, then cooled to room temperature for an hour. Figure 3 shows the SEM image of the recovered crystal along with the distribution maps of Al and Ga by the x-ray fluorescence analysis. Although small pieces of GaN are existed, both Al and Ga were almost uniformly distributed. The melting temperature of Al$_x$Ga$_{1-x}$N greatly increased as the Al content $x$ increased because the expected melting temperature of AlN is higher than 3000°C. Further technical development to achieve such high temperatures is required to synthesize more Al rich Al$_x$Ga$_{1-x}$N single crystals from their melts.
InN

The pressure-temperature diagram (Fig.4) summarizes the decomposition, structural transformation and melting behaviours of InN which are determined by in situ x-ray diffraction. Filled circles, open circles, open squares and filled squares represent the pressure-temperature conditions where the decomposition started, the wurtzite and rock salt phases coexisted, single rock salt phase was observed, and congruent melting occurred, respectively. Wurtzite structure InN transformed to high-pressure phase (rocksalt structure) at pressure around 10 GPa. The phase boundary between these phases had a slight negative slope. In the low-pressure phase region, InN decomposed into In and nitrogen at high temperature and InN melt was not obtained. The decomposition temperature increased with temperature and high-pressure phase of InN also decomposed at pressures lower than 19 GPa. The congruent melting of InN was observed at around 1900°C and 19 GPa, and reversible crystallization was confirmed by the diffraction profiles. Present results suggest that the single crystal of wurtzite phase is difficult to obtain but high pressure phase of InN is expected to be synthesized by slow cooling of its melt under high pressures greater than 19 GPa.

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References


