

Congruent Melting of GaN at High Pressures

Gallium nitride (GaN) is a very important material in optoelectronic devices for blue light-emitting diodes and lasers [1]. These devices are usually fabricated by epitaxial growth on sapphire (Al_2O_3) substrates because large GaN single crystals are unavailable. There is a large mismatch in the lattice constants of sapphire and GaN, which causes high-density dislocations in the deposited layer and is a major obstacle for improving device quality. Hence, the large single crystals of GaN suitable for substrates are strongly desired. However, such single crystals are difficult to grow because GaN usually decomposes into Ga and N_2 before melting at ambient pressure. Several studies, such as those involving hydride vapor phase epitaxy [2], Na flux method [3], and the absorption of high-pressure N_2 gas to a Ga melt [4], have attempted to alleviate this problem, but have all been unsuccessful in growing large single crystals suitable for the substrates of optoelectronic devices. If high pressure is effective in suppressing the

decomposition of GaN at high temperatures, a new method for the single crystal growth of GaN is expected to be developed. In order to clarify the decomposition and melting behaviors of GaN under high pressures and temperatures, *in situ* X-ray diffraction experiments were carried out. The congruent melting of GaN, which occurred above 6.0 GPa and 2215°C, was confirmed for the first time.

The experiments were performed using a multi-anvil high-pressure apparatus installed on beamline **BL14B1**. The pressure was initially increased at room temperature and then the temperature was increased under a constant applied load. The *in situ* powder X-ray diffraction profiles of GaN were obtained for each pressure/temperature condition by the energy dispersive method using a white synchrotron radiation beam.

Figure 1 shows the variations in the X-ray diffraction profiles as the temperature increased under high pressures [5]. At 2.0 GPa (a), GaN decomposed.

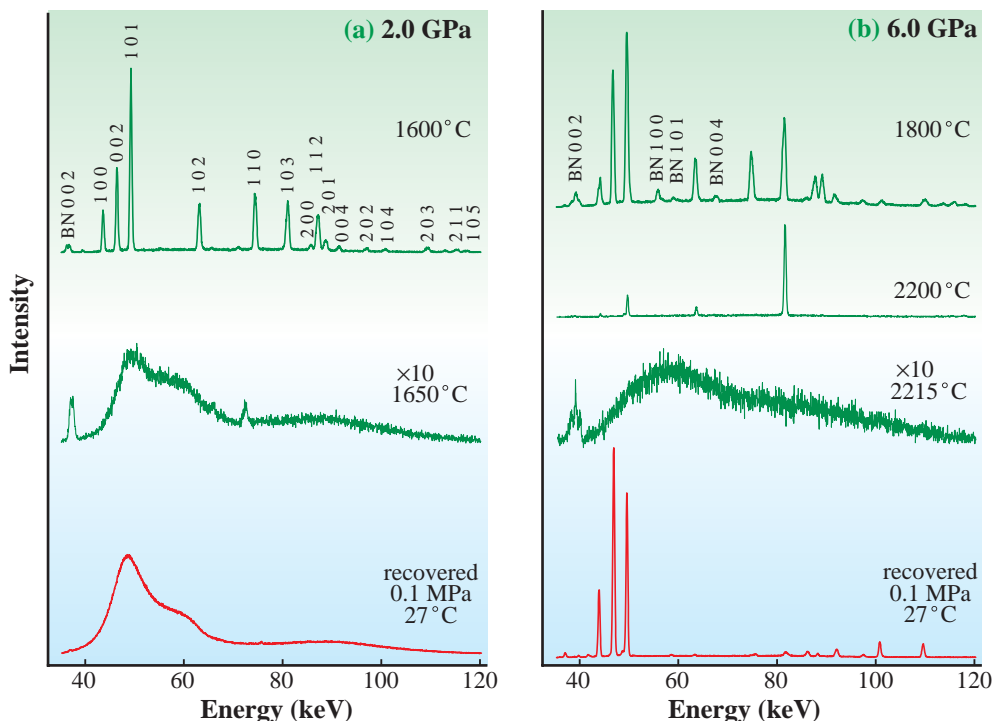


Fig. 1. A series of X-ray diffraction profiles of GaN as the temperature increased at 2.0 GPa (a) and 6.0 GPa (b). At 2.0 GPa, GaN decomposed and then Ga was formed at 1650°C. Ga metal was recovered under ambient conditions. In contrast, at 6.0 GPa, the sample melted congruently at 2215°C and it crystallized to the wurtzite GaN as the temperature decreased [5].

The sample maintained its original wurtzite structure up to 1600°C (additional peaks from the BN capsule are also shown). At 1650°C, all sharp peaks from GaN completely disappeared and a continuous broad diffraction profile was observed, which indicates that GaN completely decomposed and a Ga melt formed. On the other hand, GaN melted congruently at 6.0 GPa (b). Although an anomalous variation in the peak intensity occurred and some peaks were unobservable due to the grain growth, the crystal phase of GaN was maintained up to 2200°C. At 2215°C, all the sharp peaks disappeared and a broad diffraction profile appeared. In this profile, the shape and energy of the first sharp diffraction peak were significantly different from those of Ga melt, which suggests that GaN congruently melted at this temperature. After melting was confirmed, turning off the supplied power to the furnace rapidly decreased the temperature and then the pressure was released. The diffraction pattern of the recovered sample was obtained under ambient conditions and showed that the sample was a polycrystal with a wurtzite structure. This indicates that, unlike the case at 2.0 GPa, the melt formed at 6.0 GPa crystallized to the original structure when the temperature was decreased.

The pressure-temperature diagram (Fig. 2)

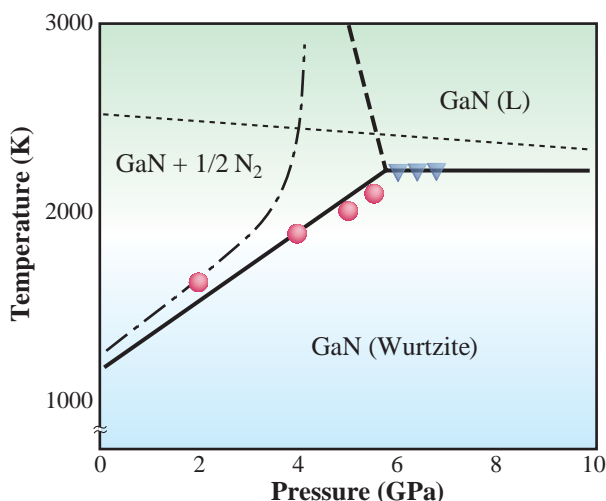


Fig. 2. The phase diagram of GaN under high pressure and temperature. Solid circles and triangles denote the pressure/temperature conditions under which GaN decomposed and congruent melting occurred, respectively. The dash line is a hypothetical phase boundary between Ga + 1/2N₂ and GaN (liquid) [5].

summarizes the decomposition and melting behaviors of GaN. At pressures less than 5.5 GPa, GaN decomposed into Ga and N₂ and the decomposition temperature almost linearly increased with pressure (solid circles). In contrast, at pressures higher than 6.0 GPa, congruent melting occurred at around 2220°C (solid triangles). This phase diagram clearly shows that the decomposition temperature rapidly increases with pressure, while the pressure dependence of the melting temperature is negligible. Consequently, the decomposition temperature exceeds the melting temperature at around 6.0 GPa and congruent melting occurs at higher pressures. Clausius-Clapeyron's equation, $dT/dP = \Delta V / \Delta S$, indicates that the volume change during melting or solidification must be very small because the slope of the melting line is almost negligible.

The present results have great potential in providing high-quality bulk single crystals of GaN by slow cooling of stoichiometric melt of GaN under high pressures. Single crystals of GaN with a diameter of 100 μm have already been obtained successfully by this method using a small high-pressure apparatus at SPring-8. By applying the established high-pressure diamond synthesis technology, the growth of much larger single crystals is expected.

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