Decomposition Behavior of GaN Under Solid and Ambient N_2 Pressure

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Abstract

We investigated the decomposition behavior of GaN crystals under high N_2 and solid pressures using a belt-type high-pressure apparatus. The decomposition curve of GaN under solid pressure showed a considerably moderate increase compared to that under a N_2 pressure. Such difference was attributed to the N_2 dissolution in the Ga melt, where a high N_2 pressure creates a supersaturated GaN state, which effectively prevent its decomposition. Conversely,

under a solid pressure, the increase in the GaN decomposition temperature followed a common change in enthalpy, which is consistent with its typical thermodynamic behavior. The decomposition behavior of GaN under a solid pressure demonstrated its successful high-temperature annealing using a belt-type high-pressure apparatus. Therefore, this study provides valuable insights into the thermodynamic stability of GaN under different pressures, which is critical for optimizing high-performance GaN-based devices.

Keywords: GaN, Decomposition, High pressure, Nitrogen atmosphere

1. Introduction

GaN decomposition behavior has been investigated under various conditions, including vacuum [1], H_2 atmosphere [2–4], ammonia atmosphere [5,6], and high pressure [7]. Such research field is crucial considering the diverse processing conditions under which GaN devices are fabricated. In particular, studies have focused on the decomposition temperature under high pressure because high-pressure annealing can achieve p-type conduction in Mg-implanted GaN [8]. P-type conduction via Mg-ion implantation is crucial for developing high-performance vertical GaN-based transistors as it facilitates the manufacturing of guard-rings in transistors [9,10]. Annealing Mg ion-implanted GaN at temperatures above 1,300 ℃ under an ultrahigh N_2 pressure (1 GPa) has been demonstrated to achieve p-type conduction owing to the Mg activation. However, the size of the GaN samples treatable under 1 GPa N_2 under hot isostatic

pressing (HIP) is significantly limited. Although HIP can be used in treating samples larger than 2 inches under 1 GPa N_2 at the Japan Ultra-high Temperature Materials Research Institute, reconstructing such ultrahigh-pressure HIP systems is impractical because of strict safety regulations.

High-pressure annealing using solid pressures is preferable over HIP because a high-pressure apparatus can easily achieve ultrahigh pressures, exceeding several GPa [11,12]. However, understanding GaN under pressure remains difficult owing to the insufficient differentiation between solid and N_2 pressures. Utsumi et al. [7] reported congruent melting and subsequent single-crystal growth of GaN under 6 GPa with slow cooling. However, they did not clarify whether a solid or gaseous pressure was used nor whether equilibrium was maintained in a gas–liquid or solid–liquid state at 6 GPa. Although information on GaN decomposition under solid pressure has increased significantly through the research of Porowski et al. [13], phenomena under gas and solid pressures have not been demonstrated experimentally.

In this study, we created a detailed GaN decomposition curve under solid pressure using a belt-type high-pressure apparatus. Moreover, we compared our findings with previously reported data on the equilibrium state between N_2 gas and solid GaN.

2. Experimental Section

Figure 1 shows the experimental setup used to investigate the decomposition temperature

under a solid pressure. A 2 μm thick GaN film which was fabricated on a c-face sapphire substrate (4.5 mm × 4.5 mm, cut from a 2 inch wafer) at 1,200 ℃ using a metal-organic chemical vapor deposition method with trimethyl Ga and NH_3 as the sources. Subsequently, the film was placed in a high-pressure cell, which was then pressurized to a predetermined value and heated to a set temperature. The pressure and temperature were maintained for 10 min, followed by cooling to room temperature. After depressurization, the GaN film sample was analyzed by X-ray diffraction (XRD; Rigaku MiniFlex, Japan).

3. Results and discussion

Figure 2 depicts the XRD patterns after annealing under two different conditions: (top figure) 3.5 GPa and 1750 °C, and (bottom figure) 3.5 GPa and 1700 °C. The decomposition of the GaN film was indicated by the rapid disappearance of its XRD peaks.

Figure 3 summarizes the experiments conducted at various temperatures and pressures. The red line indicates the decomposition curve of GaN under a solid pressure, whereas the blue line shows the curve under a N_2 gas pressure. The decomposition curve of GaN under solid pressure increases linearly, consistent with the reported calculation diagram [7] and scenarios with an increase in enthalpy due to the PV term.

The decomposition conditions of GaN under a high N_2 pressure can be determined from the reported data on single-crystal growth of GaN in molten Ga. The growth of GaN crystals in

molten Ga metal under a high N_2 gas pressure has been known as the “high pressure solution growth (HPSG) method.” In this method, a supersaturated state for GaN growth is generated by dissolving high-pressure N_2 gas in the Ga melt. The threshold condition for the GaN growth corresponds to the equilibrium point of its decomposition in N_2 atmosphere. We can create the decomposition curve of GaN by collecting the data of conditions that facilitate and inhibit GaN growth using the HPSG method.

Figure 3 summarizes the decomposition curve of GaN under different solid and N_2 pressures. The blue line in Figure 3 at the high-pressure region can be explained using Sieverts’ law, whereby diatomic gaseous molecules dissolve in a metal melt as follows:

$$W = kP^{1/2} \quad (1)$$

where W denotes the number of gaseous molecules dissolved in the metal melt, k is a constant, and P is the applied pressure. Sieverts’ law suggests that as the pressure increases, the amount of dissolved N_2 in the Ga melt increases sluggishly. In contrast, the required N_2 amount for GaN growth, which is equal to that needed to suppress GaN decomposition, increases exponentially with the temperature along with the solubility of GaN, resulting in a dramatic increase in the required pressure to suppress GaN decomposition at the high-temperature region. Hence, this explains the blue curve at the high-pressure region in the figure. This theory is elaborated in detail in a previous report [14].

As shown in Figure 3, the pressure needed to prevent GaN decomposition under a

solid pressure is higher than that under a N_2 atmosphere; however, achieving pressures in the GPa range is considerably simpler using a solid pressure compared to HIP. In particular, a pressure above 1.7 GPa, corresponding to the decomposition temperature of 1300 ℃, is required to activate Mg-implanted GaN without decomposition using solid pressure. Such can be attained using a belt-type high-pressure apparatus with a large treatment volume. In the future, we will work on high-pressure annealing using solid pressure to activate Mg-implanted GaN.

4. Conclusions

We successfully established a GaN decomposition curve under both solid pressure and N_2 ambient conditions. Our results indicate that the decomposition behavior of GaN under solid pressure significantly differed from that under a N_2 atmosphere. This discrepancy can be attributed to the dissolution of N_2 in the Ga metal. Maintaining solid-state GaN requires higher pressure under solid pressure conditions compared to ambient N_2, especially in the temperature range necessary to activate implanted Mg. However, activation is feasible using solid pressure because a belt-type high-pressure apparatus with a large treatment volume can conveniently achieve pressures of several GPa.

Declaration of Competing Interest

The authors declare that they have no competing financial interests or personal relationships that may have influenced the work reported in this study.

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Author Contributions

Fumio Kawamura: Conceptualization, Methodology Writing- Reviewing and Editing. **Hidenobu Murata.**: Data curation. **Naoomi Yamada**: Visualization, Investigation and Supervision.

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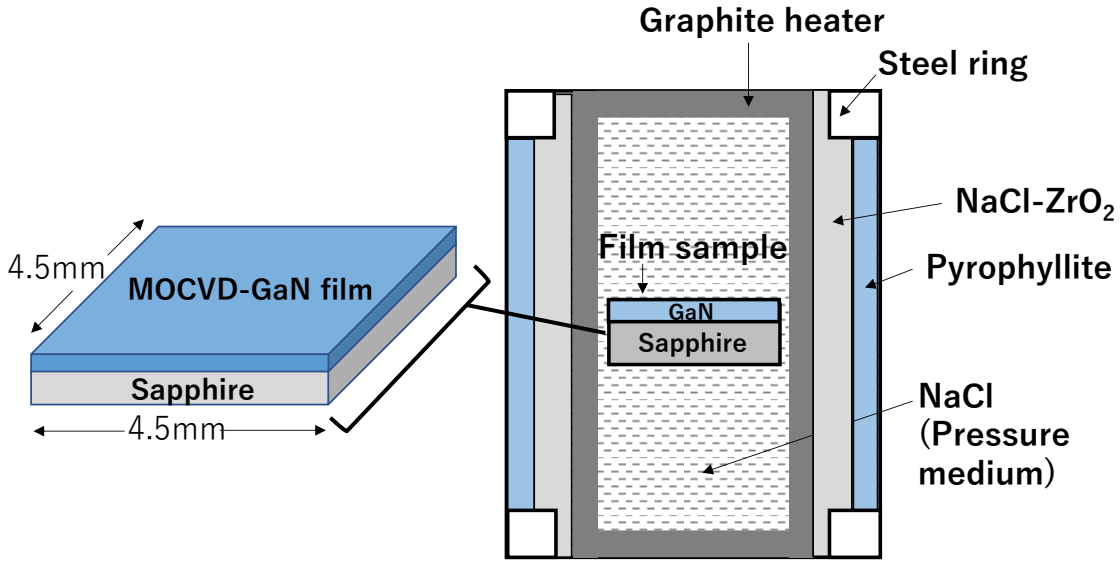
Graphite heater
Steel ring
NaCl-ZrO2
Pyrophyllite
Film sample
GaN
Sapphire
NaCl
(Pressure
medium)
4.5mm
MOCVD-GaN film
Sapphire
4.5mm

Figure 1.

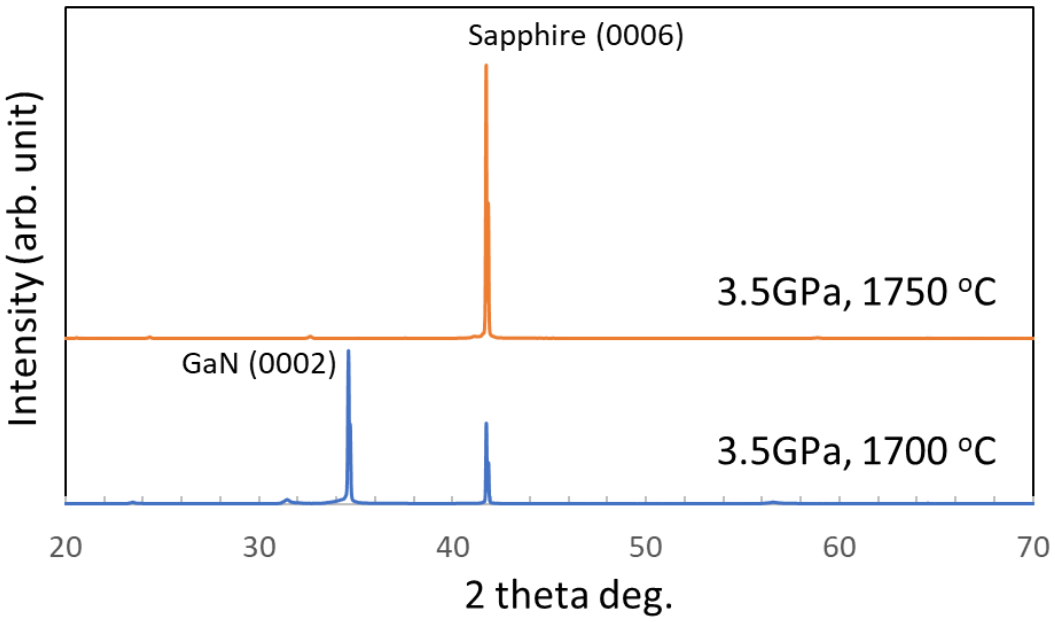
Sapphire (0006)
3.5GPa, 1750 °C
GaN (0002)
3.5GPa, 1700 °C
Intensity (arb. unit)
20
30
40
50
60
70
2 theta deg.

Figure 2.

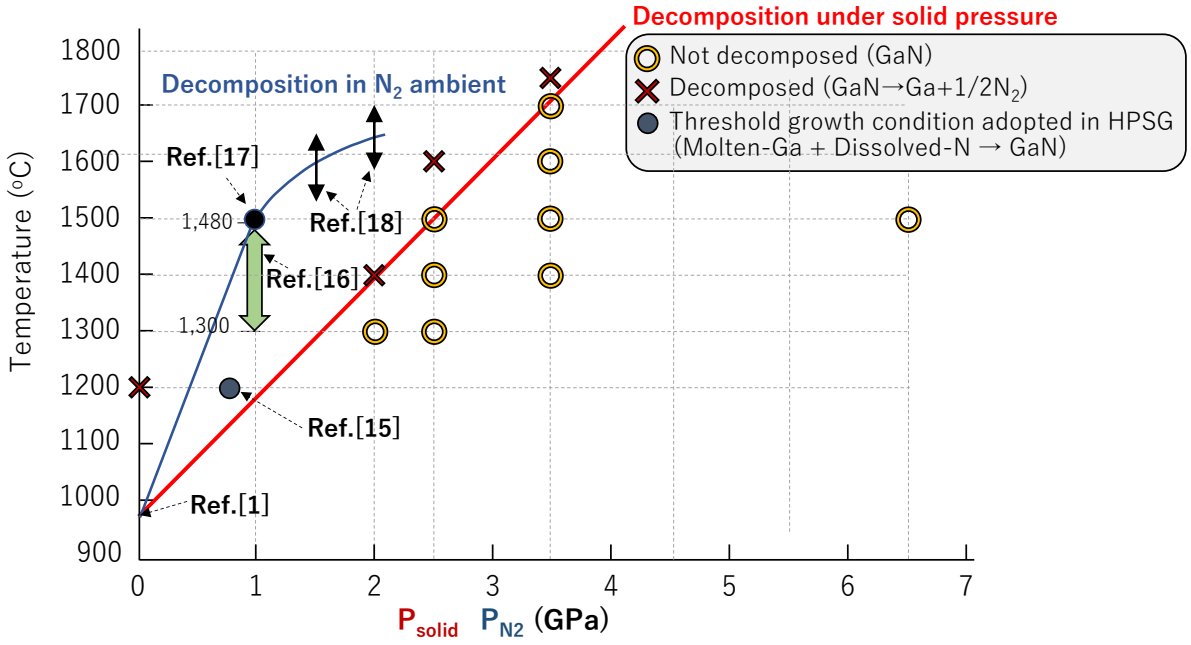
Decomposition under solid pressure
Not decomposed (GaN)
Decomposed (GaN→Ga+1/2N2)
Threshold growth condition adopted in HPSG
(Molten-Ga + Dissolved-N → GaN)
Decomposition in N2 ambient
Ref.[17]
Ref.[18]
Ref.[16]
Ref.[15]
Ref.[1]
1,480
1,300
Temperature (°C)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
0
1
2
3
4
5
6
7
Psolid PN2 (GPa)

Figure 3.

Figure caption

Figure 1. Experimental setup for the investigation of the decomposition temperature under a solid pressure using a belt-type high-pressure apparatus that can be operated up to a pressure of 8 GPa and at a temperature of less than 2400 °C.

Figure 2. XRD patterns after high-temperature and -pressure annealing of GaN film using the belt-type high-pressure apparatus.

Figure 3. Decomposition curves of GaN observed under solid pressure (red) and under a high ambient nitrogen pressure (blue). The double-ended green arrow indicates the temperature range, in which implanted Mg in GaN is activated. The solid circle indicates the reported decomposition temperatures at a fixed pressure. The black solid arrows marked with Ref. [18] denote the decomposition range extracted from the literature.