Preparation of GaN Powder by Mechanochemical Treatment of Gallium under Ammonia Gas Environment

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A new route for synthesizing GaN from gallium metal by grinding in NH_3 gas atmosphere is proposed in this paper. The proposed route is to grind Ga metal under ammonia gas atmosphere by using a planetary mill with unisized ZrO_2 balls. The grinding, which induces mechanochemical reaction between the two, has been conducted. The formation of GaN was confirmed in XRD patterns, and the peak intensity of GaN increases with grinding time.

Gallium nitride (GaN) is a semiconductor material with wide band gap (3.4 eV), used in optoelectronic, high-power, and high-frequency devices. It is a binary group III/group V direct band gap semiconductor. Its sensitivity to ionizing radiation is low (like other group III nitrides), making it a suitable material for solar cell arrays for satellites. Until 1993, the only blue light-emitting devices commercially available were based on silicon carbide, which has an indirect band gap, and is not capable of sufficient brightness to be of wide interest. The development of the first high-brightness GaN light-emitting diode (LED) by Nakamura et al.[1] completed the range of primary colors and made possible applications such as daylight visible full-color LED displays, white LEDs, and blue laser devices.

GaN bulk crystal would be useful for application in many engineering devices, and this can be prepared by an ammonothermal method using ammonia gas as a solvent at high temperature and pressure.[2] In this method, a high reactivity precursor would be required, and it should be a powder of GaN. The powder can be obtained by the following methods: One is heating Ga_2O_3 under ammonia gas at about 1000 °C for over 3 h.[3,4] The second is to prepare GaN through solution processes and then heated at 800 °C for 1–8 h under nitrogen/ammonia gas.[5–7] However, these methods need high temperature and several operational steps.

A simple and novel method for preparing GaN powder by mechanochemical treatment of gallium metal under NH_3 gas environment is proposed in this paper. This method has a possibility to prepare GaN powder in a single step without heating.

Gallium (Ga) metal (Wako pure chemical industries, Ltd., Japan) was used as a starting material. A planetary ball mill (P-7, Fritcsh, Germany), having a pair of ZrO_2 mill pots, was used for the grinding of Ga metal in NH_3 gas atmosphere to induce mechanochemical reaction between the two. The inner diameter and length of the mill pots are the same values as 40 mm. 2 g (2.9×10^{-2} mol) of Ga metal was charged into the mill pot made of ZrO_2 with 24 ZrO_2 balls (diameter: 10 mm), and then the mill pot was set in a container made of stainless steel (overpot) as shown in Figure 1, in which NH_3 gas is charged. The inner air in the mill pot was degassed with a vacuum pump, and then NH_3 gas was charged and pressurized at

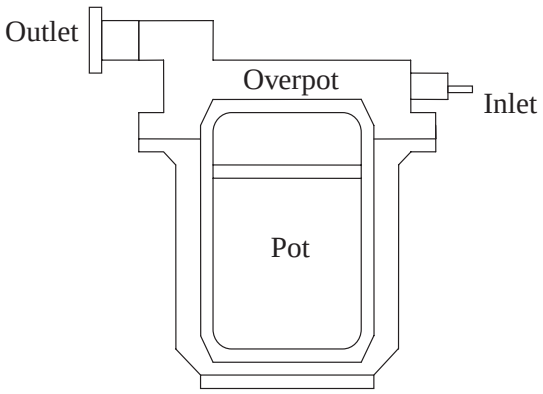

Figure 1. Illustration of ZrO_2 pot with Ga sample within overpot and NH_3 flow arrangement.

0.8 MPa. These operations were conducted twice. Then, the mill pot was set at the mill device to run at 700 rpm. After the prescribed time for grinding, the product was removed out from the pot and characterized by an X-ray diffraction analyzer (RINT 2000, Rigaku, Co., Ltd., Japan).

Figure 2 shows XRD patters of the starting sample (Ga) (a) and the samples ground for 1, 3, and 4 h ((b)–(d)). The peaks of Ga disappear in the patterns of the ground products as shown in patterns (c) and (d), while the peaks corresponding to GaN are seen to appear in these patterns; (b), (c), and (d). The peak intensity of GaN increases with grinding time.

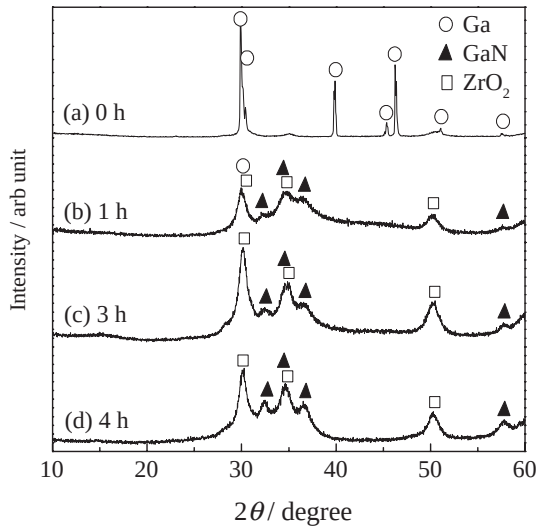

Figure 2. XRD patterns of starting sample (a) and sample treated for 2 h (b).

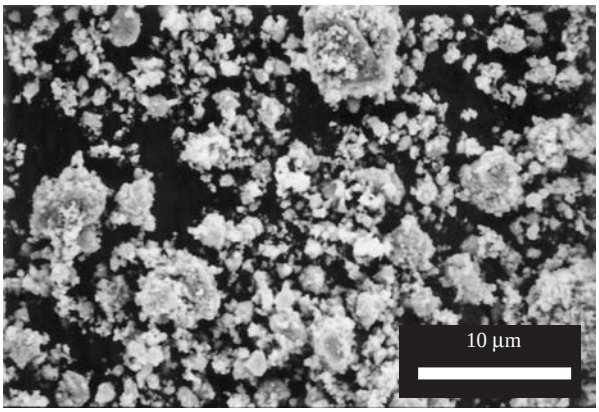

Figure 3. SEM image of the sample ground for 4 h.

This indicates that GaN has been synthesized by the grinding operation and that this phase is formed through the mechanochemical reaction between Ga and NH_3 during the grinding operation.

Thus, the reaction equation is given by eq 1.

$$2Ga + 2NH_3 \rightarrow 2GaN + 3H_2 \quad (1)$$

From eq 1, 2.9×10^{-2} mol Ga would react with 2.9×10^{-2} mol NH_3 to obtain the required GaN powder, however, at 0.8 MPa NH_3 pressure, mol of NH_3 is only 1.6×10^{-2} and can react with Ga metal up to 56%. Most of the unreacted Ga metal could remain as amorphous phase and the shoulder/peak at around 28° in 2θ may correspond to the unreacted Ga-metal in the milled product.

Furthermore, the peaks of ZrO_2 are seen in the patterns (b)–(d), and this is due to wear of the balls and mill pot. It is necessary to remove the abrasive powder from the GaN powder in order to be the precursor for the ammonothermal process to grow GaN bulk. To avoid the abrasive powder from the mill device, it would be effective that the mill liner and media are covered with high-strength polymer such as nylon 66. The abrasive powder of this nylon 66 can be removed out by heating operation. Further investigation on the grinding (mechanochemical treatment) for preparing pure GaN powder would be needed.

Figure 3 shows the SEM image of sample ground for 4 h. Though it is difficult to distinguish GaN powder in the sample, a few micron-sized particles and its agglomerations are observed.

We have developed a new route for synthesizing GaN from Ga by grinding in NH_3 gas with a planetary mill. The grinding of Ga metal in NH_3 gas induces mechanochemical reaction between the two, resulting in formation of GaN powder. The amount of GaN powder increases with grinding time. An abrasive powder of ZrO_2 from the mill device mixed in the product because of its wear during the grinding. It would be necessary to separate this abrasive powder from the product to purify the GaN powder, when this powder would be used, for example, as a precursor for growing single crystal by an ammonothermal method.

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