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Synthesis of nitride compound using fluidized bed

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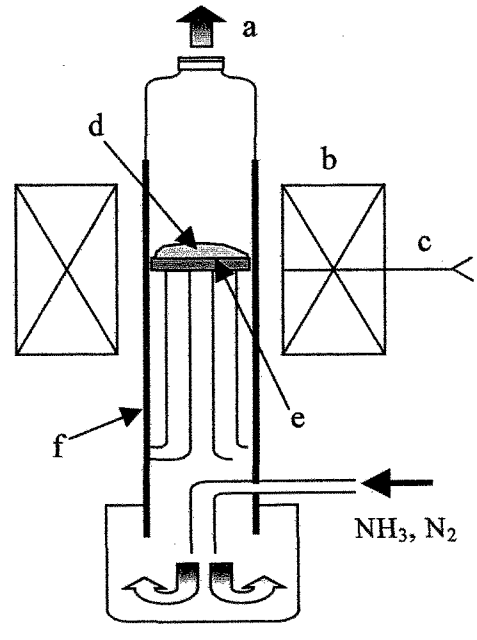
Compositionally uniformed nitride powders (GaN and GaN-ZnO solid solution) were synthesized from metal oxide powders using a fluidized bed in a NH_3 and/or a N_2 flow. GaN was synthesized by a two-step heating ; the first step was done at 700°C for 1h, and the second step was done at 900°C for 4h. A GaN-ZnO solid solution was synthesized at 900°C for 4h. The synthesized nitride powders were characterized by powder X-ray diffraction (XRD). Optical properties of the products were examined by UV-Vis diffuse reflectance spectra. The grain size of the products was smaller than that of the starting materials. On the other hand, the crystallite size of the GaN-ZnO solid solution was almost the same as that of the starting material of Ga_2O_3.
Key words: fluidized bed, nitride, oxynitride, photocatalyst

1. INTRODUCTION

Recently, GaN has been applied to optoelectronics materials such as LED [1]. Oxynitride solid solutions of a GaN-ZnO binary system have also been utilized as a photocatalyst for water decomposition driven under a visible light [2]. Generally, nitride compounds are synthesized by a conventional gas-solid reaction under a NH_3 flow. However, nitriding reaction in many cases is interfered by aggregation of powders. Therefore, compositionally uniformed nitride powders are hard to be synthesized in conventional gas-solid reactions. The development of a new synthetic process for compositionally uniformed nitride powders is important for nitride semiconductor fields. Synthesis of nitride solid solutions which contain two or more metal elements is also important to application fields of electronic devices.

Various types of fluidized bed have been utilized as a good reactor in many inorganic syntheses. Particularly, a fluidized bed reactor with a gas-solid system is utilized for ceramics fields, e.g., sintering of cement, calcination, synthesis of AlN, and so on [3]. Comparing with batch type reaction system, the fluidized bed reaction system has some advantages; (1) the whole part of solid reactants can be kept at a steady temperature, and (2) heat can be transferred very fast to substances because each reactant is constantly fluidized [4].



a : Gas outlet side b : Electric furnace
c : Thermocouple d : Starting materials
e : Filter (porous SiC)
f : Alumina tube
(diameter : 42 mm, length : 1000 mm)

Fig.1 Schematic diagram of fluidized bed reactor.

In this study, we synthesized compositionally uniformed powders of GaN and a GaN-ZnO solid solution using a fluidized bed reactor with a gas-solid reaction system.

2. EXPERIMENTAL

Nitride compounds were synthesized in a NH_3 and/or a N_2 flow using a fluidized bed reactor. Figure 1 shows the schematic diagram of the fluidized bed reactor. An alumina tube (42 mm in inner diameter and 1000 mm long) was placed vertically as a nitriding reactor. Starting materials were placed on a porous SiC filter at the center of the alumina tube. The starting materials for GaN and GaN-ZnO solid solution were Ga_2O_3 powders and mixtures of Ga_2O_3 and ZnO powders with a molar ratio of 1 : 1, respectively. Ga_2O_3 and ZnO powders were mixed in acetone, subsequently dried in air. The synthetic conditions of temperature, heating time, reaction gas ratio of N_2 and NH_3, and gas flow rate were optimized based on experimental results.

Phase purity of the products was characterized by powder XRD using a Mac Science MX-Labo diffractometer. The crystallite size of powders was evaluated from FWHM (Full Width at Half-Maximum) of XRD patterns. Optical properties of the products were examined by UV-Vis diffuse reflectance spectra using a JASCO UV-Vis spectrophotometer. Grain size of the powders and aggregation of the particles were observed by scanning electron microscopy (SEM).

3. RESULT AND DISCUSSION

3.1 Synthesis of GaN

Figure 2 shows XRD patterns of the GaN samples synthesized. A single phase of GaN was obtained only using a two-step heating. The two-step heating consisted of the heating in the first step at 700°C for 1h, followed by the second heating step at 900°C for 4h. In both of the steps, a N_2-NH_3 (1 : 1) gas flow with 1200 ml / min was used. In the case of the one-step reaction at 900°C for 4h, the starting material of Ga_2O_3 still remained in the product (Figure 2a). Figure 3 shows a photograph of the GaN sample synthesized at the one-step reaction. The powder of the GaN sample seems to agglomerate. This indicates the interference of the nitriding reaction by the aggregation of oxide powders, implying that both of the nitriding reaction and the aggregation are taken place competitively. On the other hand, no impurity phase was detected in the sample prepared by the two-step reaction. This means that the nitriding reaction can proceed well in the first step heating at 700°C, where the aggregation of oxide does not occur.

Figure 4 shows UV-Vis diffuse reflectance spectra of the GaN samples synthesized. Color of the powder synthesized at one-step reaction was dark yellow (Figure 4a). On the other hand, the color of the powder synthesized at two-step reaction was dark brown (Figure 4b). Hotta *et al*

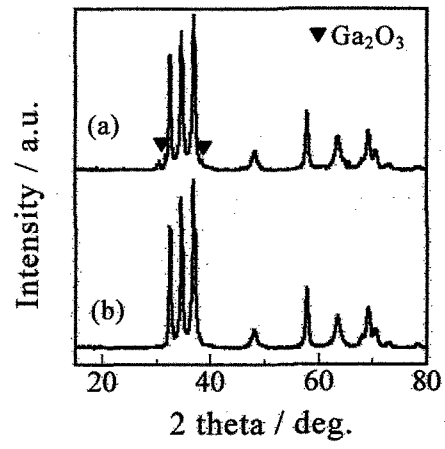


Fig. 2 XRD patterns of GaN synthesized at (a) 900°C for 4h and (b) 700°C for 1h followed by heating at 900°C for 4h.

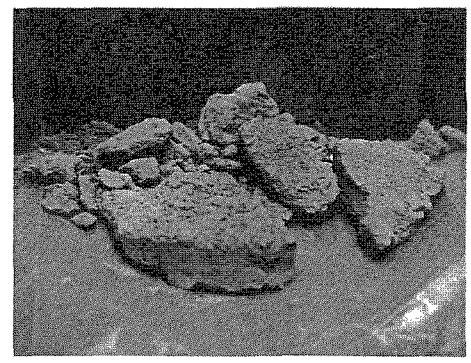


Fig. 3 The photograph of GaN sample synthesized at 900°C for 4h (one-step reaction).

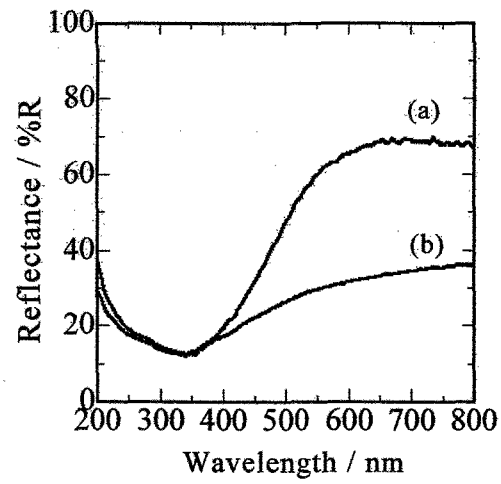


Fig. 4 UV-Vis diffuse reflectance spectra of GaN synthesized at (a) 900°C for 4h and (b) 700°C for 1h followed by heating at 900°C for 4h.

reported that the color of nitride compounds prepared from the corresponding oxides depend on the conversion ratio of nitrogen and oxygen in nitriding reactions [5]. However, both of the samples synthesized at one-step heating and two-step heating have a band gap of GaN : 3.39 eV (UV absorption : about 360 nm) [6]. This indicates the formation of GaN phase. Although the color of the powders depend on the synthetic conditions, XRD patterns and UV-Vis diffuse reflectance spectra indicate the formation of single phase GaN in the powder synthesized by the two-step heating.

3.2 Synthesis of GaN-ZnO solid solution

Figure 5 shows XRD patterns of the GaN-ZnO solid solution samples synthesized in various conditions. A single phase of the solid solution was obtained by the one-step reaction at 900°C for 4h in a NH_3 flow with 1200 ml / min (Figure 5c). This fact is in contrast to the case of GaN where the single phase was only obtained by the two-step heating. In the GaN-ZnO solid solution binary system, the nitriding reaction of Ga_2O_3 may be first taken place to give GaN. At this stage, the GaN powders produced are dispersed in the ZnO powders. This situation can not promote the aggregation of GaN due to less contact among GaN powders, otherwise promoting the solid solution formation reaction between GaN and ZnO. In the case of synthesis at 900°C for 4h in the N_2-NH_3 (1 : 1) flow with 1200 ml / min, only a small amount of Ga_2O_3 remained in the product (Figure 5b). This indicates that the nitriding reaction by the NH_3 flow is more progressive than by the N_2-NH_3 flow. In the case of synthesis at 1000°C for 1h in the N_2-NH_3 (1 : 1) flow with 1200 ml / min, much amount of Ga_2O_3 remained (Figure 5a). Accordingly, even if the starting materials were heated at high temperatures, the GaN-ZnO solid solution can not be obtained in a short time. In addition, the solid solution powders synthesized at high temperatures also showed a tendency to be black in color (Figure 6a).

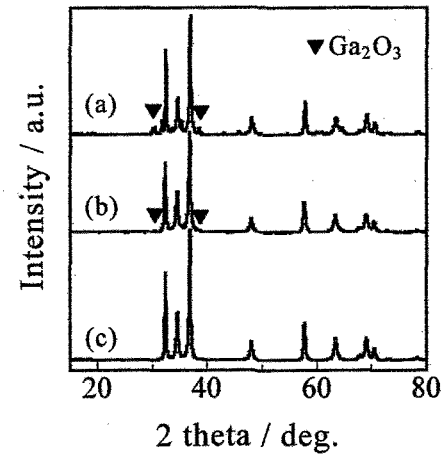


Fig. 5 XRD patterns of GaN-ZnO solid solution synthesized at (a) 1000°C for 1h in N_2-NH_3, (b) 900°C for 4h in N_2-NH_3, and (c) 900°C for 4h in NH_3.

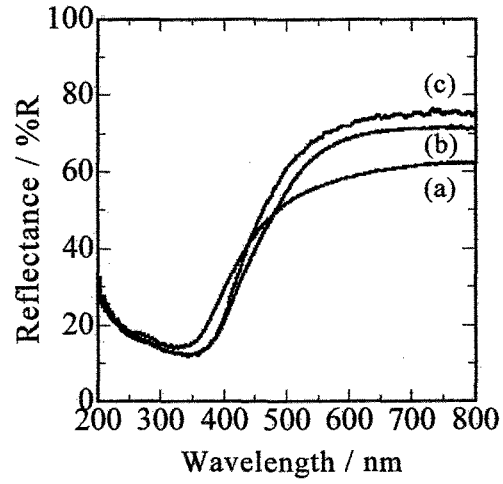


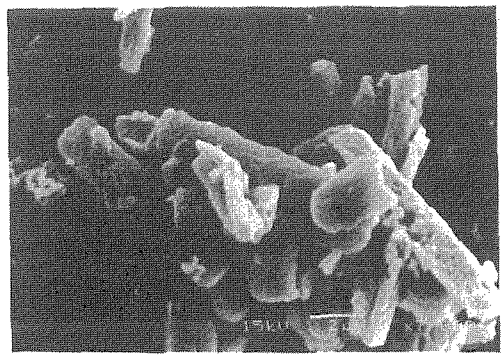
Fig. 6 UV-Vis diffuse reflectance spectra of GaN-ZnO solid solution synthesized at (a) 1000°C for 1h in N_2-NH_3, (b) 900°C for 4h in N_2-NH_3, and (c) 900°C for 4h in NH_3.

3.3 Grain size and crystallite size of powders

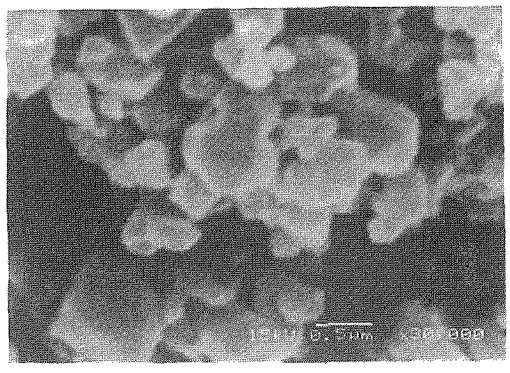
Figure 7 shows SEM images of the starting material of Ga_2O_3 and the products of the GaN-ZnO solid solution. The grain size of the products (about 1-2 μm) is much smaller than that of the starting material (about 3-5 μm).

Table I shows the grain size and the crystallite size of Ga_2O_3 and the GaN-ZnO solid solution. The crystallite size of the GaN-ZnO solid solution was virtually held in the same degree as that of Ga_2O_3. On the other hand, the grain size obviously became much smaller after the nitriding reaction.

In general, each grain particle in a polycrystalline powder consists of multiple crystallites that join together in different orientations. Such a grain is so-called primary grain. Furthermore, the aggregation of the primary grains leads to secondary grains, which are usually objects for particles observed in SEM images. This may be true for our samples. Upon the nitriding reaction, the secondary grains of the starting materials of Ga_2O_3 may be broken into small peaces of primary grains because the secondary grain particles are loosely joined together. In contrary to this, the shape of primary grains which consist of tightly packed crystallites seems to be unchanged against the nitriding reaction. The primary grains of the solid solution resulted in nitriding reaction can not aggregate each other in a short reaction time (4h in our study). Comparing with conventional solid-state nitriding reactions which in practice require a long reaction time (10-20h), an almost complete nitriding reaction is achieved only for 4h using our fluidized bed reactor.



(a) Starting material of Ga_2O_3 2 μm



(b) GaN-ZnO solid solition 0.5 μm

Fig. 7 SEM images of (a) starting material of Ga_2O_3 and (b) product of GaN-ZnO solid solution.

Table I Grain size and crystallite size of Ga_2O_3 starting material and GaN-ZnO products.

	Grain size (μm)	Crystallite size (Å)
Ga_2O_3	3-5	331
GaN-ZnO	1-2	315

4. CONCLUSION

A GaN-ZnO solid solution could be synthesized from the mixture of metal oxide powders using the fluidized bed reactor. Compositionally uniformed solid solution powders were obtained in a quite short reaction time of 4h. The grain size of the product was much smaller than that of the starting material. The gas-solid reaction using the fluidized bed is a new useful synthetic method for nitride powders.

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