Use of polymeric carbon nitride in the nitridation of gallium oxide to gallium nitride

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Gallium nitride (GaN) powder was prepared from $\beta$-gallium oxide ($\beta$-Ga$_2$O$_3$) powder using polymeric carbon nitride (PCN) as a nitridation reagent and characterized by powder X-ray diffraction, $^{71}$Ga magic-angle spinning nuclear magnetic resonance spectroscopy, Raman spectroscopy, and scanning electron microscopy. $\beta$-Ga$_2$O$_3$ was completely nitridated to GaN at the temperature above 800°C. The change in the morphology after the nitridation can be explained by two successive reactions, i.e., the reduction of Ga$_2$O$_3$ to gaseous Ga$_2$O and its subsequent nitridation to GaN, with the rate of the former reaction being slower than that of the latter.

Key-words: Gallium nitride, Gallium oxide, Polymeric carbon nitride, $^{71}$Ga MAS NMR

Gallium nitride (GaN) is a promising semiconductor material for use in ultraviolet light-emitting and laser diodes, because of its wide-band gap (3.88 eV at room temperature) and thermal and chemical stability. GaN powder sintered into mechanically robust and machinable ceramics represents an economical alternative to GaN single-crystal supports for optoelectronics. The gallium and nitrogen sources most widely used for synthesizing Ga$_2$O$_3$ powder are gallium oxide (Ga$_2$O$_3$) and ammonia (NH$_3$), respectively. Ga$_2$O$_3$ can alternatively be converted to GaN by routes which do not employ NH$_3$ as a nitridation reagent, but alternative nitridation reagents are limited. For example, Zhao et al. synthesized GaN by heating a mixture of Ga$_2$O$_3$ and amorphous carbon nitride (C$_x$N$_y$H$_z$) or melamine, which was pressurized into a pellet and placed into a silica ampoule. Buha et al. prepared GaN from $\gamma$-Ga$_2$O$_3$ nanopowders using cyanamide and urea as nitridation reagents. Acetonitrile (CH$_3$CN) is also a useful nitridation reagent for the preparation of GaN powder from Ga$_2$O$_3$. This work reports the preparation of GaN powder from $\beta$-Ga$_2$O$_3$ powder using a graphitic C$_x$N$_y$H$_z$ ternary polymer like melon, poly(amoimino)heptazine, [C$_n$N$_y$(NH)$_z$]$_m$ (hereafter, referred to as polymeric carbon nitride, PCN) as a nitridation reagent. The PCN thermally decomposes to highly reactive C and N fragments such as CNH, NH$_2$, and C$_2$N$_2$ species. Therefore, the PCN can be applied as a powerful reactant for conversion of metals or metal oxides to the corresponding nitrides. We showed that PCN is a useful nitridation reagent for the preparation of AlN from $\delta$-Al$_2$O$_3$ without the need for any additional carbon source. The synthesis method and characterization of PCN powder are described in a previous paper. A crucible containing PCN powder was deposited upstream in an alumina tube with a 34 mm inner diameter and separated from $\beta$-Ga$_2$O$_3$ powder (99.99%, Wako Chemical Co.) in an alumina crucible. The former crucible was located at ca. 650°C when the hot zone was heated to the reaction temperature (750 to 900°C) under a flow of argon (Ar). The duration at each reaction temperature is 1 h, unless stated otherwise. The PCN to Ga$_2$O$_3$ weight ratio was 3:1. The Ar flow rate and temperature ramping rate were 100 ml/min and 5°C/min, respectively. The sample was taken from the furnace after it had cooled to room temperature under a flow of Ar. No further purification was carried out. The gas evolved during the reaction was bubbled through a solution of Fe$^{3+}$ and Fe$^{2+}$ ions to trap HCN gas.

The sample powders were characterized by powder X-ray diffraction (XRD) using a PANalytical X’Pert PRO MPD X-ray diffractometer with Cu-K$_\alpha$ radiation operating at 40 kV and 30 mA and by high-resolution $^{71}$Ga magic-angle spinning (MAS) NMR spectroscopy. The NMR spectra were recorded using a radio frequency of 183.0 MHz (Unity INOVA 600 spectrometer). The samples in a rotor were spun at 23 kHz. Chemical shifts (δ) were referenced to 1 M aqueous gallium(III) nitrate solution. Raman spectra were collected on a Raman microscope (XploRa Plus, Horiba Jobin Yvon) with an excitation wavelength of 532 nm using an objective lens with 100 x magnification. The oxygen content in the GaN powder was determined using an EMGA-920 oxygen analyzer (Horiba). The morphology of the sample powders was investigated by scanning electron microscopy (SEM, Hitachi S-4200)

Figure 1 shows XRD patterns of samples obtained by calcining $\beta$-Ga$_2$O$_3$ powders at various temperatures. The sample obtained at 750°C exhibited only peaks assigned to $\beta$-Ga$_2$O$_3$ (ICDD-PDF #00-43-1012). In the sample calcined at 780°C, intense peaks corresponding to GaN (ICDD-PDF #00-50-0792) were detected together with the peaks attributable to unreacted $\beta$-Ga$_2$O$_3$. The samples calcined at 800 and 900°C exhibited only diffraction peaks assigned to GaN; the peaks for the former sample were wider than those for the latter due to its lower crystallinity. The conversion of $\beta$-Ga$_2$O$_3$ to GaN was also monitored by $^{71}$Ga MAS NMR spectroscopy, as shown in Fig. 2. The $^{71}$Ga MAS NMR spectra of the sample obtained at 750°C exhibited two powder patterns resulting from the second-order broadening of the central transition. The high quadrupole coupling constants of GaO$_6$ and GaO$_4$ sites in $\beta$-Ga$_2$O$_3$ (11.0 and 8.3 MHz, respect-
 vantely) hindered the recording of spectra of polycrystalline samples without severe intensity distortions of the broad powder pattern. Calcination at 780°C resulted in an intense peak (at 327 ppm) assigned to GaN and weaker peaks assigned to \(\beta\)-Ga\(_2\)O\(_3\). The sample at 800°C showed only a broad GaN peak. As shown in Fig. 2(d), the longer duration (3 h) at 800°C made the peak narrower due to the enhancement of the crystallinity. The NMR spectrum of the sample obtained at 900°C exhibited a narrow GaN peak with a shoulder on the lower field side. The shoulder can be explained by either a nitrogen deficiency in GaN or a Knight shift due to the presence of conduction electrons.

Raman scattering of hexagonal GaN has been extensively studied in numerous works. Figure 3 shows Raman spectra of samples obtained at 800 and 900°C. The hexagonal GaN possesses eight sets of optical phonon modes, which are classified into Raman-active \(A_1 + E_1 + 2E_2\), infrared-active \(A_1 + E_1\), and silent \(2B_1\). GaN is noncentrosymmetric, so that the \(A_1\) and \(E_1\) modes are further split into longitudinal optical (LO) and transverse optical (TO) components. As shown in Fig. 3(a), five phonon modes corresponding to hexagonal GaN were observed at 246, 306, 408, 551, and 707 cm\(^{-1}\) for the sample obtained at 900°C. The bands at 551 and 707 cm\(^{-1}\) corresponded to \(E_2\) (high) and \(A_1\) (LO) modes, respectively. The positions of these two modes were shifted to lower frequency (by ca. 20 and 30 cm\(^{-1}\), respectively), as compared with those of bulk GaN. The reason for this large frequency discrepancy is not clear at present. The \(A_1\) (TO) and \(E_1\) (TO) modes appeared as unresolved shoulders on the lower frequency side of the \(E_2\) (high) mode. The two additional bands at 306 and 408 cm\(^{-1}\) were assigned to acoustic overtones, and the band at 246 cm\(^{-1}\) was ascribed to the zone boundary phonon activated by surface disorders and finite size effects. As shown in Fig. 3(b), each phonon mode for the sample obtained at 800°C was broadened and the intensity ratio of \(I(E_2)/I(A_1)\) was lowered relative to the spectrum of the sample obtained at 900°C because of its lower crystallinity.

The reactivity of the PCN powder was similar to that of melamine. However, in contrast to the use of melamine, the process for removing residual carbon after the nitridation was not...
needed when PCN was used. The difference in the amount of residual carbon between PCN and melamine indicated that there is a difference in thermal decomposition products at reaction temperatures between PCN and melamine.

The oxygen contents of samples obtained at 800 and 900°C were determined to be 3.5 and 1.9 wt%, respectively. Assuming that O$_2$ and H$_2$O molecules are adsorbed on the powder surface$^{9,17}$ and their contributions to the oxygen content are the same for both samples, the lower oxygen content for the latter sample suggests that the nitridation reaction is more complete.

The morphologies of GaN particles obtained at 800 and 900°C were observed by SEM (Fig. 4). As shown in Figs. 4(a) and 4(b), $\beta$-Ga$_2$O$_3$ particles were in form of rectangular rod. After their nitridation, the rectangular contour was almost completely retained, but faces of the rods were coarsened. Such a change in the morphology, which was also observed for the ammonolysis of $\alpha$-Ga$_2$O$_3$ powders$^{21}$ and $\alpha$-Ga$_2$O$_3$ single crystals,$^{22,23}$ can be explained by two successive reactions, i.e., the reduction of Ga$_2$O$_3$ to gaseous Ga$_2$O and its subsequent nitridation to GaN, with the rate of the former reaction being slower than that of the latter.

In summary, PCN was demonstrated to be a useful nitridation reagent for the preparation of GaN powder from Ga$_2$O$_3$ powder. The reactivity of the PCN powder was similar to that of melamine in the point that $\beta$-Ga$_2$O$_3$ was completely nitridated to GaN at temperatures above 800°C. However, in contrast to the use of melamine, the process for removing residual carbon after the nitridation was not needed when PCN was used. Two successive reactions in the conversion from Ga$_2$O$_3$ to GaN were suggested from the change in the morphology of $\beta$-Ga$_2$O$_3$ particles after the nitridation.

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