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Preparation of gallium nitride from gallium–magnesium alloy powders

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ABSTRACT

Ga–Mg alloy powders were introduced to synthesise GaN powders with flowing ammonia. When the magnesium percentage in the alloy was 25 wt-% or below and the reaction temperature was about 750°C, all Ga atoms in the alloy were transformed into GaN, and the diameter of the GaN powders was about 40 nm. For the Ga–Mg alloy powders with a diameter ranging from 37 to 75 µm ammoniated at 750°C, only 3 h were spent to transform all the Ga atoms into GaN, indicating that the strategy suggested in this study was effective to produce GaN powders.

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GaN; Ga–Mg alloy;
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Introduction

GaN has a wurtzite structure with a wide direct band gap of 3.4 eV at 300 K [1–3]. This material has been applied in light-emitting devices, such as blue, near ultraviolet, violet light-emitting diodes and laser diodes [4–8]. GaN powders can be used as a precursor material for growth of 1-D GaN nanodevices [9], GaN films and bulk GaN single crystals [10] (an optimal substrate for the GaN film to be grown on by molecular-beam epitaxy or metal–organic chemical vapour deposition). GaN nanopowders can also be used directly in nanosized devices for the applications requiring quantum dot (QD) or other size-dependent compound properties [11].

Two methods to prepare GaN powders have been established. In the first technique, the powders are obtained via the reaction between ammonia and liquid metal gallium [12–15]. In the process, there is a dense film covering on the whole surface of liquid gallium, which renders the conversion of the residual liquid gallium into GaN difficult and inefficient. In the second method, the GaN powders are manufactured via a reaction between gallium compounds (such as GaO₂H [16], Ga₂O₃ [17] and GaCl₃ [18]) and ammonia or nitrogen. Using fine gallium compound powders as reactants facilitates the large-scale production of high-purity GaN powders but involves large costs because the gallium compound comes from gallium metal. Thus, if the big block of liquid gallium is substituted with fine gallium powders, GaN produced by directly ammoniating elemental Ga may be convenient and effective.

Alloying is a common approach to convert liquid gallium block into gallium powders. The elements Mg,

Li, Y, and Ca are the commonly used alloying elements for IIIA metals to synthesise their nitrides [19,20]. However, because M_xGaN_y (M = Mg, Li, Y, and Ca) is accompanied by GaN in the process of ammoniating Ga–M alloy [21,22], studies focused on the preparation of GaN powders by this process are rarely reported. If M_xGaN_y can be avoided, GaN may be successfully and effectively produced by the process.

In this study, the Ga–Mg alloy powders were introduced to prepare GaN powders. The effects of reaction temperature and magnesium content on the alloy powders were evaluated, and the conditions were found to prevent M_xGaN_y. When the magnesium content in the alloy was less than 25 wt-% and the reaction temperature was about 750°C, the Mg₃GaN₃ in the products would vanish.

Experimental section

Preparation of Ga–Mg alloy bar

A corundum crucible with a capacity of 30 mL was placed in a resistance-heated furnace and then heated to 680°C. The weighted liquid metal gallium with a purity of 99.9 wt-% and a protective agent (a mixture of MgCl₂, KF, and CaF₂) were poured into the crucible sequentially. After 5 min, the weighted magnesium blocks with a purity of 99 wt-% were pressed into the liquid gallium and the protective agent was sprinkled on the melt surface. When the magnesium blocks were molten, the melt was stirred, and the protective agent was sprinkled again on its surface. The melt was kept for 30 min to allow the composition to melt uniformly, then the alloy melt was cast in the cylinder mould with an inner diameter of 10 mm.

Preparation of GaN via Ga–Mg alloy ammoniation

The Ga–Mg alloy bar was polished to eliminate the oxides on its surface, and then broken into powders with a diameter 35–75 μm by grinding it in a mortar. Subsequently, the powders were poured into a corundum crucible and placed into a vacuum furnace. When the vacuum in the furnace was pumped to 100 Pa, the furnace would be filled with ammonia. After the pressure in the furnace reached 1 atm, the flow of ammonia was adjusted to 1 L min^{-1} . The furnace was heated to a certain temperature and then maintained at that temperature for a designated time. When the temperature was reduced to room temperature, the products were filtered with 0.1 M hydrochloric acid and deionised water sequentially. The remainder was ultimately dried at 110°C for 1 h in a vacuum drying chamber, and collected for characterisation.

Characterisation of samples

The final samples were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption isotherms, energy dispersive X-ray analysis (EDS), and transient steady-state fluorescence spectrometer. XRD analysis was obtained on Damx-rA (Rigaku) diffractometer with $\text{CuK}\alpha_1$ radiation with a scanning speed of 8° min^{-1} . The SEM images (second electron images) and EDS spectrum were recorded on a JSM-7000F field emission microscope. The N_2 adsorption isotherms were taken on a JW-BK100A surface area and pore size analyser at -195.7°C . The photoluminescence (PL) spectrum was obtained using a spectrometer (Edinburgh FLS9) with a 325 nm xenon lamp as light source.

Results and discussion

Figure 1 presents the XRD patterns of Ga–Mg alloy powders with 15 wt-% magnesium. The diffraction peaks were consistent with those of Ga_2Mg and Ga_5Mg_2 . No other peaks were observed in the pattern, except for those corresponding to Ga_2Mg and Ga_5Mg_2 , indicating that only Ga_2Mg and Ga_5Mg_2 in Ga–Mg alloy powders.

Figure 2 presents the XRD patterns of the samples made from 75Ga–25Mg (wt-%) alloy powders ammoniated at different temperatures (950, 850, and 750°C for 3 h). By indexing the peaks in the patterns, the phases in different samples were marked in the figure. As the ammoniated temperature changed, the phases in the samples varied. For the samples obtained at 750°C, only GaN and MgO existed (MgO was produced by the reaction of magnesium in the alloy with the oxygen adsorbed on the surface of the alloy powders and/or the residual O_2 in the vacuum furnace). At 850°C, Mg_3GaN_3 appeared in addition to MgO and GaN.

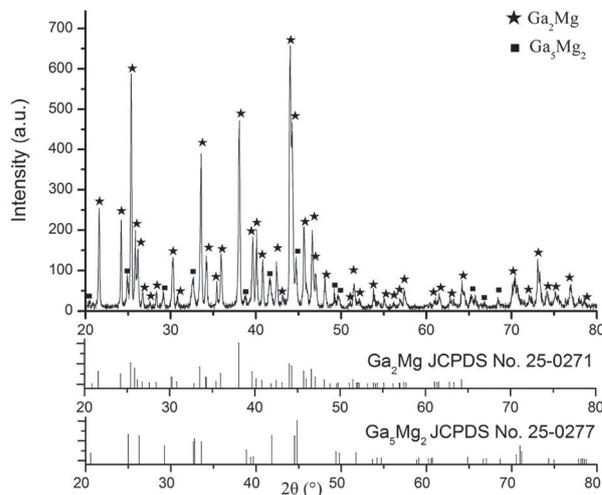


Figure 1. The XRD patterns of the Ga–Mg alloy powders (15 wt-% Mg).

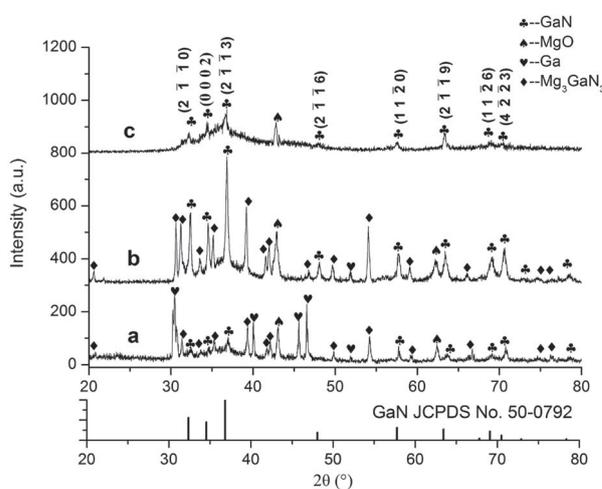


Figure 2. XRD patterns of samples produced from 75Ga–25Mg (wt-%) alloy powders nitrided at different temperatures ((a) 950; (b) 850; (c) 750°C).

The Mg_3GaN_3 was formed when the Ga–Mg alloy was ammoniated above 780°C [17,18]. While at 950°C, in addition to Mg_3GaN_3 , MgO and GaN, a large amount of gallium was present. The existence of the gallium was attributed to the decomposition of GaN above 900°C [23]. To synthesise GaN, liquid gallium had to be heated to a sufficiently high temperature in ammonia or nitrogen. Moreover, the rate of gallium transformation into GaN would increase with an increase in heating temperature [9–11]. However, the aforementioned results lead to the conclusion that an increase in temperature was not always beneficial to the ammoniation of Ga–Mg alloy powders in ammonia.

For the samples produced at 750°C, no peaks corresponding to gallium or magnesium appeared in its XRD patterns, suggested that all Ga and Mg atoms in alloy powders had been transformed into their compounds. Moreover, no apparent peaks corresponding to Mg_3N_2 and Mg_3GaN_3 were observed in the pattern, which indicated that both the percentages of Mg_3N_2

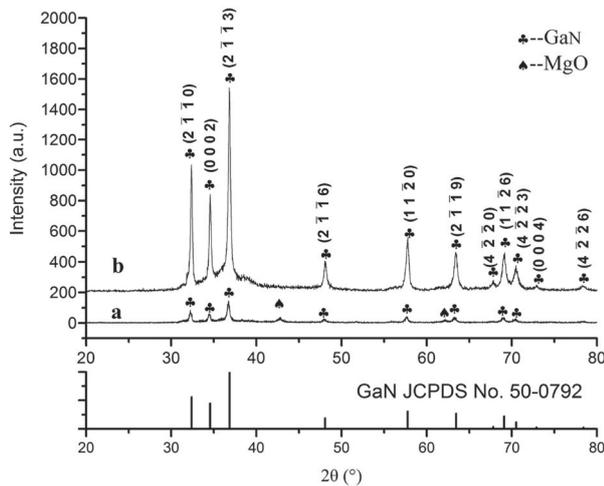


Figure 3. XRD patterns of samples produced from 75Ga–25Mg (wt-%) alloy powders ammoniated at 750°C for 3 h and 850°C for 0.5 h ((a) the unwashed samples; (b) the washed samples).

and Mg_3GaN_3 in the samples were less than the detection limit (1 wt-%) of the X-ray spectrometer, or their diffraction peaks were overwhelmed by the peaks corresponding to GaN and MgO because of their highly imperfect crystallisation. The XRD patterns of the GaN also suggested that the crystallisation of GaN was imperfect.

To verify whether Mg_3N_2 and/or Mg_3GaN_3 existed in the samples produced at 750°C, another ammoniating process was designed. The alloy powders were ammoniated at 750°C for 3 h, and then the temperature was increased to 850°C within 20 min and held at the same temperature for 0.5 h. The XRD patterns of the samples and its washed samples are shown in Figure 3. The diffraction peaks were evident and sharp, thus, phase crystallisation in the samples was perfect. According to the full width at half maximum (FWHM) of the diffraction peaks, the grain size was calculated to be 40 nm from the Debye–Scherrer formulation. Indexing the peaks in the patterns, only one phase – GaN was found in the washed samples, and two phases – GaN and MgO were found in the unwashed samples. Combining the result with the suggestions in Figure 2(c), it can be deduced that when the alloy powders were ammoniated at 750°C for 3 h, few of Ga atoms were converted into Mg_3GaN_3 and most of them were transformed into GaN. In addition, comparing with the GaN powders produced at 750°C, the crystallisation of the GaN powders was markedly improved by ammoniation. The temperature (750°C) and duration (3 h), which were needed to convert all Ga atoms in the alloys into GaN, were less than those needed to convert Ga or Ga_2O_3 into GaN. Thus, the process suggested in the study can be used to prepare GaN successfully and effectively.

The reason Mg_3GaN_3 did not appear in the samples resulting from ammoniating 75Al–25Mg (wt-%) at 750°C for 3 h, but appeared in the samples obtained

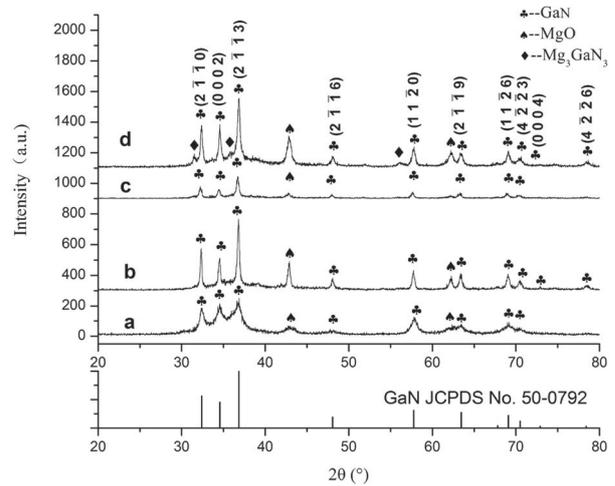


Figure 4. XRD patterns of the unwashed samples fabricated from Ga–Mg alloy powders with different magnesium percentages ((a) 10 wt-% Mg, (b) 20 wt-% Mg, (c) 25 wt-% Mg, (d) 30 wt-% Mg).

at temperatures exceeding 850°C for 3 h has yet to be determined. The reason may be that the rate of Mg converted into Mg_3N_2 was far smaller than that of it converted into MgO at 750°C. When Mg was heated to about 750°C in oxygen and nitrogen, most of Mg was oxidised into MgO, and scarcely any Mg was left for Mg_3N_2 . Since no Mg_3N_2 appeared in the process, no Mg_3GaN_3 would be generated. But at the temperature of 850°C, the rate of Mg converted into Mg_3N_2 increased sharply (from Handbook of Chemical Reactions of Elements [24], when the temperature reached 750°C, the reaction between melted magnesium and ammonia or nitrogen intensified), many metal Mg was transformed into Mg_3N_2 , and then into Mg_3GaN_3 .

The quantity of oxygen which remained in the vacuum furnace and/or was adsorbed on the surfaces of alloy powders was definite, and the quantity of Mg for MgO was definite. If the Mg content in the alloy exceeded a certain amount, Mg_3GaN_3 might be obtained by ammoniating Ga–Mg alloy powders at 750°C for 3 h. Figure 4 presents the XRD patterns of the samples fabricated from Ga–Mg alloys with different magnesium percentages (10, 20, 25, and 30 wt-%). The alloys were all ammoniated at 750°C for 3 h and then at 850°C for 0.5 h. The phases in the samples varied, as could be deduced from indexing the peaks in the figure. When the magnesium percentage in the alloy was 25 wt-% or below, the phases in the samples were GaN and MgO; however, when the magnesium percentage reached 30 wt-%, Mg_3GaN_3 , in addition to GaN and MgO, was found in the products. The emergence of Mg_3GaN_3 indicated that not all Ga atoms in the alloy were transformed into GaN. Thus, the magnesium percentage in the alloy must be limited within 25 wt-% to convert all Ga atoms in the alloy into GaN.

Figure 5 represents the secondary electrons SEM images of GaN samples (produced from 75Ga–25Mg

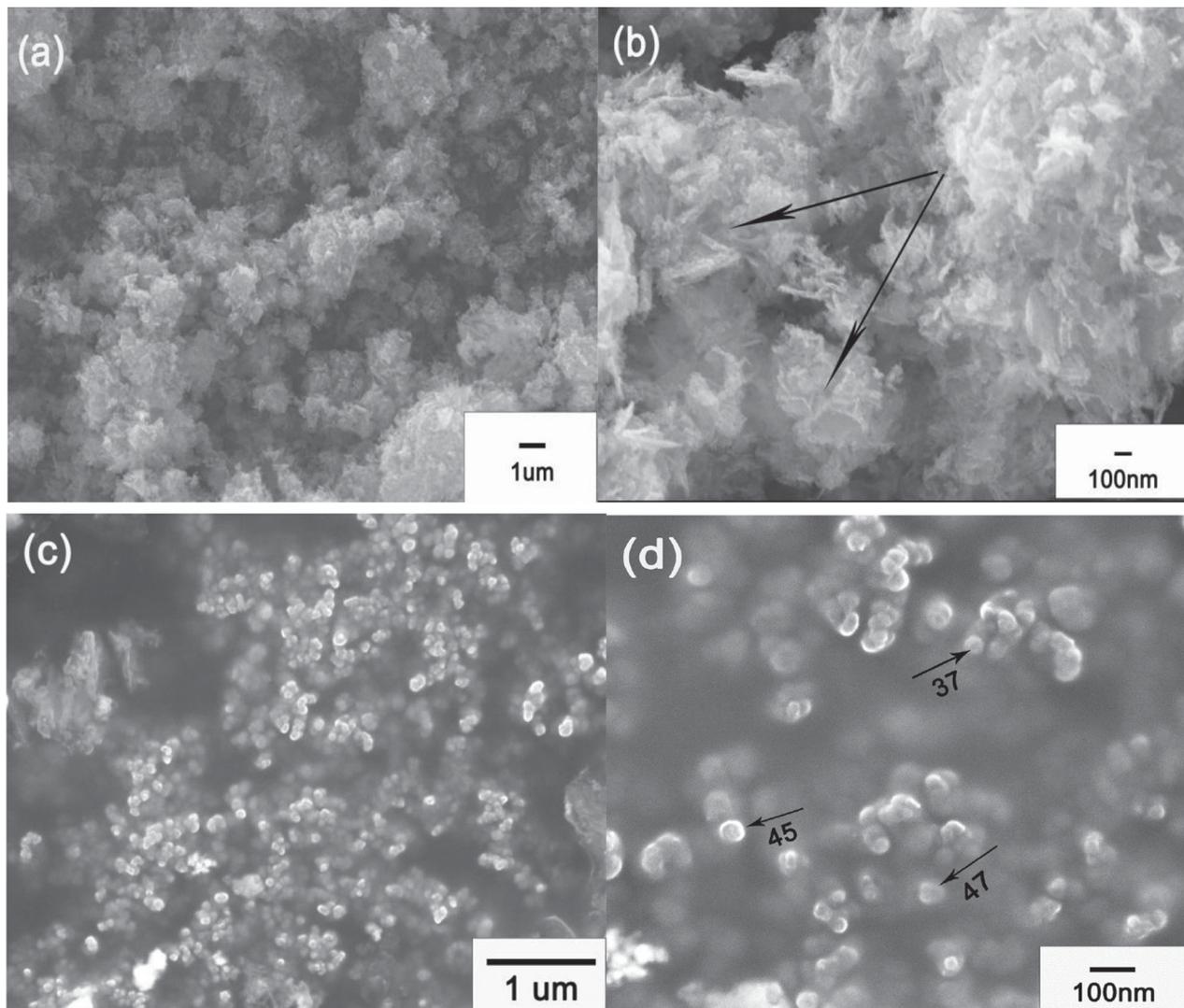


Figure 5. SEM images of washed samples with different magnification.

(wt-%) alloy particles) with different magnifications. As shown in Figure 5(a,b), GaN particles aggregate together, forming a larger-sized aggregation. Some small pores (indicated by arrows in Figure 5(b)) are found among GaN particles. These pores may come from the MgO which was removed by hydrochloric acid and deionised water. The morphology of GaN particles is clearly exhibited in Figure 5(c,d). GaN particles are approximately spherical, and the size of their diameter is about 40 nm (indicated by the arrows in Figure 5(d)). The specific surface area of the samples produced from 75Ga–25Mg (wt-%) alloy powders was also measured using the N_2 adsorption isotherms conducted on a JW-BK100A surface area and pore size analyser at the temperature of -195.7°C . Figure 6 presents the N_2 adsorption/desorption isotherms of samples. By using the isotherms, the specific surface area of the samples was calculated to be $12.85\text{ m}^2\text{ g}^{-1}$. On the basis of this value, the size of GaN particles can be evaluated using Formula (1):

$$S \cdot r \cdot \rho / 3 = 1 \quad (1)$$

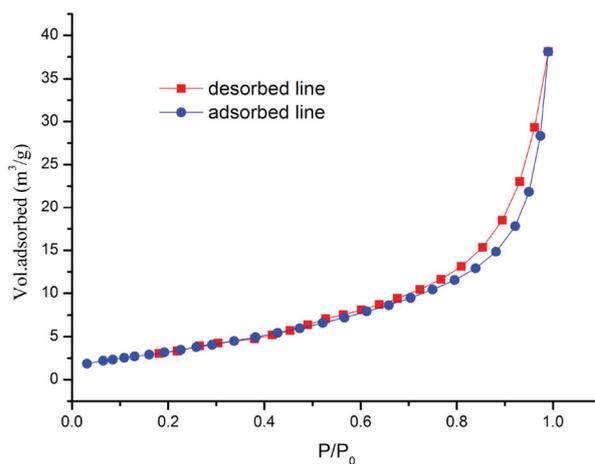


Figure 6. N_2 adsorption/desorption isotherms of samples at -195.7°C .

where S is the specific surface area equal to $12.85\text{ m}^2\text{ g}^{-1}$, r is the radius of GaN particles, and ρ is the density of GaN (6.1 g cm^{-3}), the radius r can be evaluated and is about 40 nm. The BET result was consistent with the

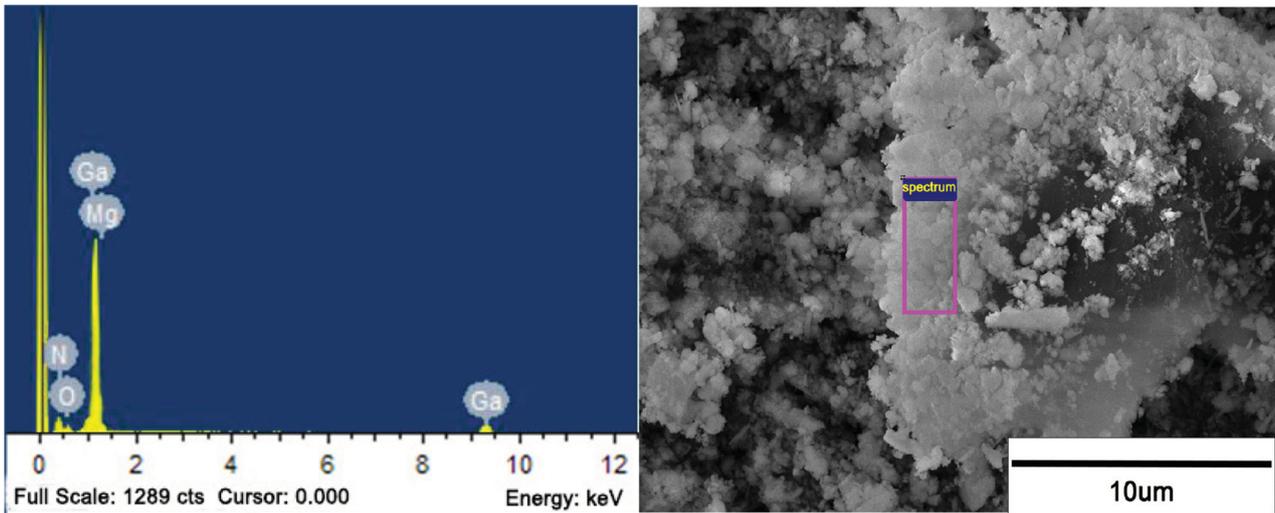


Figure 7. EDS spectrum of the washed samples produced from 75Ga–25Mg (wt-%) alloy powders.

Table 1. EDS analysis of the washed samples.

Element	N	O	Mg	Ga	Total
Wt (%)	14.26	4.71	3.58	77.45	100
Atom (%)	41.21	11.46	4.06	43.21	100

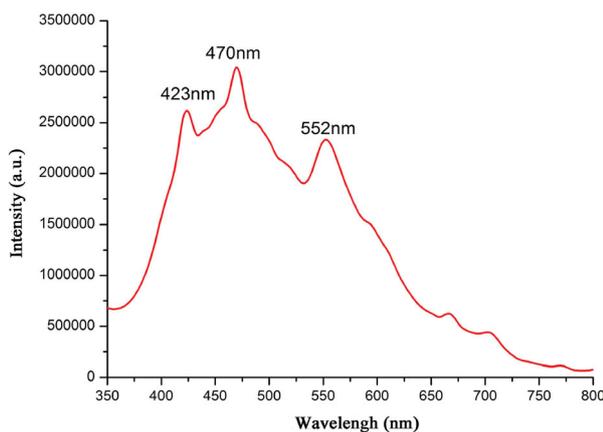


Figure 8. PL spectrum of the washed samples at room temperature.

findings deduced from the SEM image (Figure 5(d)) and the XRD pattern (Figure 3(b)).

Figure 7 presents the EDS spectrum the washed samples produced from 75Ga–25Mg (wt-%) alloy powders. The results showed that Ga, O, Mg and N elements were found in the samples. The mass and atomic percentages of above elements are shown in Table 1. GaN was evidently the main component in the washed samples, the O elements resulted from the oxygen adsorbed on the surface of the samples [25]. The Mg elements were likely attributable to the magnesium dissolved in the GaN samples or the Mg^{2+} adsorbed on the surface of samples during washing in hydrochloric acid.

Figure 8 exhibits the PL spectrum of the washed samples at room temperature. It can be seen that there were three obvious luminous peaks at 423, 470 and 552 nm, respectively. The peak at 423 nm was the result

of the radiation recombination from a shallow donor level for N vacancies and other lattice defects to valence band [26]. The peak at 470 nm was caused by the deep donor level [27]. Meanwhile, the yellow band luminescence peak (552 nm) was attributed to the edge dislocation density and Ga vacancies [28].

Conclusion

Ammoniating Ga–Mg alloy in the flowing ammonia was suggested to produce GaN powders, and the effects of reaction temperature and magnesium content on the products were evaluated. The main conclusions can be listed as follows:

- (1) When the alloy powders were ammoniated at 750°C, and the magnesium percentage in the alloy was less than 25 wt-%, all Ga atoms in the alloy was transformed into GaN, avoiding the presence of Mg_3GaN_3 in the products.
- (2) The size of GaN powders was about 40 nm when the alloy powders were ammoniated at 750°C for 3 h and 850°C for 0.5 h.
- (3) The temperature and time spent on converting all Ga atoms in the alloys into GaN were less than those needed to convert the liquid metal Ga or Ga_2O_3 into GaN, thus the process to prepare GaN powders was successful and effective.

Disclosure statement

No potential conflict of interest was reported by the authors.

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