

Growth and investigations of GaN-Ga₂O₃ nano-composites

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Gallium nitride (GaN) – gallium oxide (Ga₂O₃) nano-composites were synthesized through ammonolysis of Ga₂O₃ powder, with or without the addition of multi-wall carbon nanotubes (MWCNT). Both synthesized nano-composites having rod-shaped structure, while addition of MWCNT had resulted in hollow-like interior with some cavity walls. Vibrational measurement revealed that both samples contained mixture of GaN-Ga₂O₃, with GaN being the dominant. Optical measurements showed a high level of defects present in both samples. Violet-blue bands (VBL) were observed in both samples. Sample with added MWCNT exhibited blue shift relative to that of without MWCNT, which properties may governed by the contents of nitrogen.

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1. Introduction

Gallium nitride (GaN) and Gallium oxide (Ga₂O₃) are wide bandgap semiconductor (3.4 eV and 4.9 eV respectively) materials that have been widely studied owing to its potential applications in various fields, especially optoelectronics [1]. Various methods have been developed to synthesize these materials, namely thermal evaporation, chemical vapour deposition (CVD), molecular beam epitaxy (MBE), sputtering, and sol-gel. Such methods can be widely found in the literature [2-10].

The powder form of GaN and Ga₂O₃ served other purposes: i.e. as evaporation precursor in preparing GaN/Ga₂O₃ nanostructures (depending on gaseous ambient) and sintered ceramics. Powdered GaN can be prepared from nitridation of Ga₂O₃ powder at high temperature (~900 °C and above). While Ga₂O₃ powder can be obtained by calcinations of Gallium-oxide-hydroxide (GaOOH) powder, direct oxidation of GaN powder also produced similar results [8, 9].

Fundamental properties of GaN and Ga₂O₃ have been widely investigated in order to know the flaws within the material, thus motivate researchers and engineers to improve their synthesizing methods. Stand alone GaN or Ga₂O₃ has been widely studied; however, their composites were rarely reported. As GaN can be obtained through nitridation of Ga₂O₃ under ammonia flow, the reverse reaction could occur in the presence of oxygen and high reaction temperature (~900 °C and above) [8].

In this work GaN-Ga₂O₃ nano-composites were synthesized using direct ammonolysis of Ga₂O₃ powder, with or without the addition of multi-wall carbon nanotubes (MWCN) which served as a reduction agent. One of the modifications done in this work was the nano-composites were removed from the furnace at 950 °C, without cooling it down to room temperature. This

strategy is seldom reported in the literature. One common method adopted in most work was the synthesized products were removed from the furnace after cooling. The morphological, atomic compositional, vibrational, and optical aspects of the synthesized nano-composites were investigated.

2. Experimental details

The synthesizing of GaN-Ga₂O₃ nano-composite was done under two conditions, i.e. absence/presence of added MWCNT. The designations for the aforementioned conditions were Run(A) and Run(B) respectively. The starting reagents used throughout the work were Ga₂O₃ powder (99.99% purity), MWCNT (>95% purity), ammonia gas, and nitrogen gas.

The GaN-Ga₂O₃ composite was obtained under the ammonolysis of sample Run(A) and Run(B) separately in a hot-wall furnace. The furnace was ramped up to 950 °C prior to the onset of the experiment. When the furnace temperature reached 950 °C, powdered samples were introduced to the furnace via quartz boat. NH₃ gas was channelled into the furnace through a mass flow controller, in which the flow rate of NH₃ gas was set to 100 sccm throughout the experiment. The ammonolysis of sample Run(A) and Run(B) lasted for 1 hour. After that, the nano-composites were removed from the furnace. Pale-yellow powder was obtained in both samples despite being removed from a hot furnace.

The obtained nano-composites were characterized accordingly. Field-Emission Electron Microscopy (FE-SEM, Zeiss, Leo Supra 50VP) was employed to investigate the surface morphology of the samples. Energy Dispersive X-ray (EDX) was used to determine the composition of the composite. The vibrational properties

of the composite were investigated using Raman spectroscopy (Jobin Yvon HR 800UV), with $z(x, \text{unpolarized})\bar{z}$ scattering configuration. The operating wavelength of Raman spectroscopy was 514.5 nm, which obtained from Ar^+ laser. The optical properties of the composite were studied using photoluminescence (PL) method. The nano-composites were illuminated by a 20mW He-Cd laser with wavelength 325 nm for PL measurements.

3. Results and discussions

Fig. 1 depicts the electron micrographs of the synthesized nano-composites. Both samples having grain-like morphology that joined together to form a rod-shaped structure. One notable feature that distinguishes these samples was the involving mechanism that formed the rod-shaped structure. It is discernible that sample Run(A) having a compact structure owing to the aggregation of multiple composite grains. Sample Run(B), however, having multiple cavity walls within one rod, in addition some of them having a hollow interior. The cavity wall could be due to the localized reduction on the compact structure caused by MWCNT. This is likely due to the size

of MWCNT is much smaller than the compact structure. On the other hand, the formation of hollow interior might be due to the forming of sheet-like layer composite, under high temperature, the layer rolled up, thus becoming a tubular structure. A schematic representation of such phenomena is elucidated in Fig. 1(d).

Fig. 1(c) shows the presence of nanowires in sample Run(B). It is widely known that the formation of GaN and Ga_2O_3 nanowires involved vapour-liquid-solid (VLS) mechanism. The prerequisite for such mechanism involves metal catalyst. Since sample Run(B) having the addition of MWCNT, carbothermal reduction of Ga_2O_3 had occurred. It is possible that MWCNT had reduced Ga_2O_3 to metallic gallium, thus serving as a metal catalyst that drives the growth of Ga-based nanowires. However, very less Ga-based nanowires have been observed, this might be due to the generation of gallium sub-oxide (Ga_2O), which exists in vapour form. The generation of metallic gallium would be less since the generation of $\text{Ga}_2\text{O}(v)$ is preferred. In addition it is possible that gallium vapour has been generated that would react with NH_3 to form GaN, thus re-precipitated into the nano-composites. A summary of chemical equations that occurred during the experiment were included [2-4, 7-10].

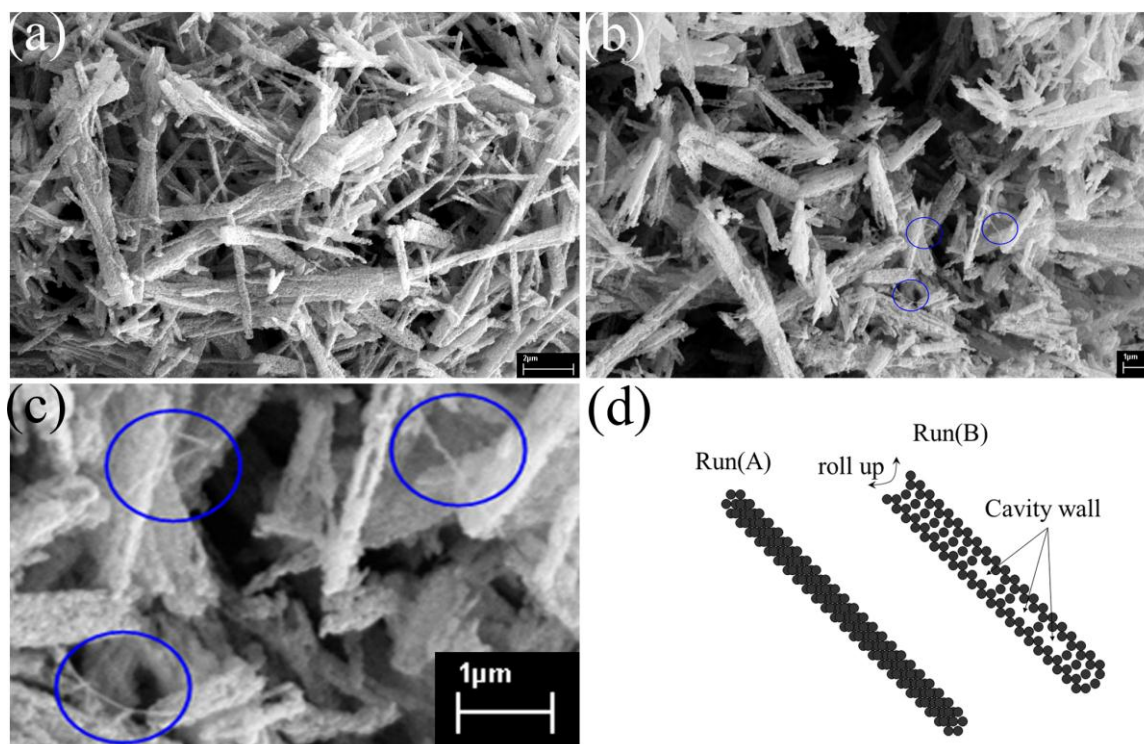


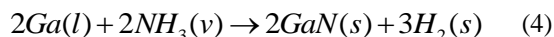
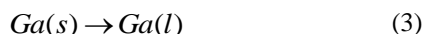
Fig. 1. Electron micrographs for sample Run(A) (a), Run(B) (b). Magnified view of sample Run(B) (c). Drawing shows an illustration of the synthesized nano-composites. Scale bar in Fig. 1(a) and (b) is $2\mu\text{m}$ and $1\mu\text{m}$ respectively.

For sample Run(A), the overall chemical equation will be:



For sample Run(B), possible chemical reactions occurred:

(i). If metallic gallium is generated:



(ii). If Ga₂O vapour is generated:



As the nano-composites were removed from the furnace without the onset of cooling it, oxidation of GaN occurred (GaN does not undergo complete oxidation process):



Table 1. Ratio of elements obtained from atomic percentage (at %) of each respective elements using EDX.

Ratio of elements	Run(A)	Run(B)
N/O	0.98	1.22
N/Ga	0.47	0.28
O/Ga	0.48	0.23

Table 1 displays the ratio of elements (obtained from EDX) of sample Run(A) and Run(B). It is discernable that the nitrogen content from sample Run(B) is higher than that of Run(A). From Eq. (1), Ga₂O₃ reacted directly with NH₃ to obtain GaN. However, a complete transformation of Ga₂O₃ to GaN requires longer time since the vapour pressure of Ga₂O₃ is much lower than that of metallic gallium and Ga₂O. The addition of MWCNT, in addition to its higher surface-to-volume ratio in sample Run(B) provides an alternative route by reducing the vapour pressure of Ga₂O₃.

The amount of gallium present in sample Run(B) is much lower than that of Run(A). This can be elucidated by the generation of Ga₂O in sample Run(B). As Ga₂O exists in vapour phase, it is plausible that the vapour is carried away by the flow of NH₃, thus forming GaN in other parts of the furnace. Such phenomenon is commonly reported in the literature [4].

Fig. 2 depicts the Raman spectra of sample Run(A) and Run(B). Both of the samples consist of a combination of GaN and Ga₂O₃ Raman bands, with GaN being dominant. The dominant Raman band for Ga₂O₃ typically reported lies in 200cm⁻¹. Here, this band existed as a shoulder, which indicates GaN being the dominant material. Additional Ga₂O₃ Raman band was noted in sample Run(A). This indicated that the amount of Ga₂O₃ present in sample Run(A) was greater than Run(B), which in agreement with the EDX data as reported (Table 1).

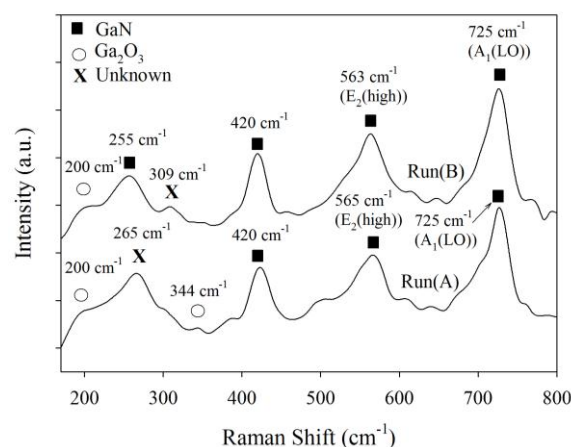


Fig. 2. Raman spectra of samples Run(A) and Run(B).

Hexagonal wurtzite GaN falls under the space group of C_{6v}^4 , having two formula units per primitive cells. GaN has Raman modes of $A_1+E_1+2E_2$, $2B_1$ (silent), and infrared active A_1+E_1 . Hence, the Raman-modes for GaN situated at 563~565cm⁻¹ (E_2 (high)) and 725cm⁻¹ (A_1 (LO)) [11, 12]. The additional modes at 255cm⁻¹ and 420 cm⁻¹ was not allowed under the space group of C_{6v}^4 , but there have been proofs showed that these modes belonged to GaN [13, 14]. The symmetry assignments for these modes have been assigned as zone-boundary phonon and acoustic overtone respectively. The 420cm⁻¹ vibrational mode have been much debated about its origins. In one report, 418 cm⁻¹ vibrational mode was observed and its presence was due to nitrogen atoms replacing oxygen atoms in the Ga-N₆ bond configuration [14]. This observation occurred when Ga₂O₃ was used as a precursor in synthesizing GaN. In addition, a vibrational mode located at 416cm⁻¹ was observed in Ga₂O₃ [15]. The 420 cm⁻¹ vibrational mode as-reported was likely due to the transformation of Ga₂O₃ to GaN.

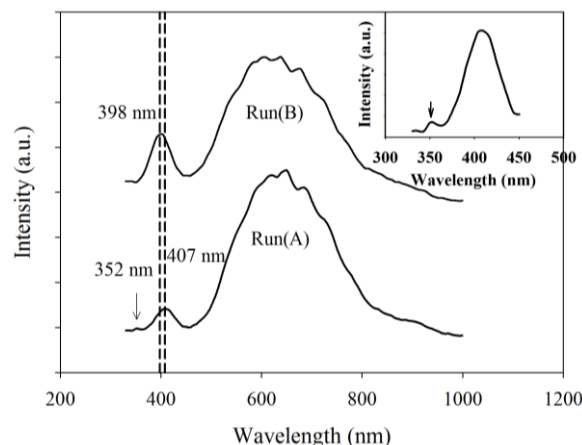


Fig. 3. PL spectra of samples Run(A) and Run(B). The inset spectrum is a magnification from sample Run(A) that displays the presence of 352nm peak.

Photoluminescence measurement is a powerful analysis tool that can determine both band emission and defects that present in a material. Fig. 3 shows the PL spectra of both samples. Violet-blue luminescence (VBL) and ultra-violet luminescence (UVL) were observed in sample Run(A) and Run(B) respectively. GaN grown with high crystal quality and purity would have an intense peak at ~ 367 nm. BL and UVL were observed in lieu of the aforementioned peak. Such peaks are often attributed to the defects present in the grown sample [5, 16, 17]. On the other hand, red luminescence (RL) band was observed for both samples. This band could be attributed to the transition from conduction band to a deep-acceptor level [16]. Since there were various versions of this band reported in terms of peak positions and plausible causes, it is difficult to determine its true nature. The detailing of this band would be done in the future.

From Raman spectra, the vibrational modes of GaN were detected. Since the absence of 367 nm peak in our PL spectra, in addition towards the growth method used in this experiment, the presence of oxygen which acted as a shallow donor for GaN was not excluded. Undoped GaN is predominantly n-type, due to gallium vacancy (V_{Ga}). The presence of oxygen would form a complex with it, i.e. $V_{\text{Ga}}\text{O}_\text{N}$, which resulted in the onset of BL [16, 17]. Sample Run(A) has a BL band which probably due to the aforementioned complex. Interestingly, the band blue shifted in sample Run(B) which resulted UVL band being detected. This could be due to the concentration of nitrogen in sample Run(B) being greater than Run(A), which resulted in a decrease of the $V_{\text{Ga}}\text{O}_\text{N}$ complex.

The inset shows a magnified spectrum of sample Run(A) at the UV region. A small peak (352 nm) was detected. Such peak may be attributed towards the V_{Ga} of Ga_2O_3 , as both synthesized nano-composites consist of a mixture of GaN and Ga_2O_3 [18, 19]. The possibility of band emission of Ga_2O_3 was excluded since the excitation source was much lower than the bandgap of Ga_2O_3 .

4. Conclusions

In summary, the observations in our PL spectra were consistent to that of Raman spectra and EDX. The addition of MWCNT eased the formation of GaN from Ga_2O_3 by generating Ga_2O , which is much more readily reacted with NH_3 . It is discernable that the amount of Ga_2O_3 was greater in sample Run(A), as the oxygen content was greater (EDX), moreover additional Ga_2O_3 Raman bands were observed. The morphological aspects of the nano-composites were greatly affected by the addition of MWCNT, i.e. hollow interior and cavity walls were observed, also nanowires. These changes may well be attributed towards the nitrogen content present in the nano-composites.

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