Journal of Alloys and Compounds 498 (2010) 52–56

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis and characterization of nanocrystalline gallium nitride by nitridation of Ga-EDTA complex

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ARTICLE INFO

Article history:
Received 20 February 2010
Accepted 8 March 2010
Available online 12 March 2010

Keywords:
Nitride material
Chemical synthesis
Crystal structure
X-ray diffraction (XRD)
Electron microscopy (TEM and SEM)
Photoluminescence

ABSTRACT

Gallium nitride (GaN) nanocrystals were synthesized by nitridation of Ga-EDTA (ethylene diamine tetra acetic acid) complexes at different temperatures starting from 600 to 900 °C. X-ray diffraction analysis, Fourier transform infrared spectroscopy and Raman studies revealed that the compound synthesized at 900 °C consists of single-phase GaN nanocrystals with wurtzite structure. The change in morphology of the GaN crystals at different temperatures was observed using scanning electron microscopy. The transmission electron microscopy showed the average size of the crystalline particles to be ∼20 nm. The room temperature photoluminescence exhibits band-edge emission of GaN at 3.46 eV for all the samples. The present study demonstrates that the nitridation of Ga-EDTA complex method has significant potential for the synthesis of GaN nanocrystals as a simple and inexpensive method.

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1. Introduction

Gallium nitride (GaN) is a wide band gap (3.4 eV) semiconductor. It has potential application in optoelectronic and electronic devices which are capable of operating at high temperature, high power and in harsh environment [1,2]. In addition, GaN powders themselves could be used as high quality phosphors. GaN has low electron affinity of 2.7–3.3 eV compared to carbon nanotubes (CNTs), zinc oxide (ZnO) which is 4.5 eV and Si, hence GaN is used for field emission devices [3–5]. Reports on the field emission characteristics of GaN nanowires have already revealed a high emission current density and a long emitter life time [6]. Many efforts have been made to grow high quality single crystals like silicon (Si), gallium arsenide (GaAs) and indium phosphide (InP), but large single crystals of GaN have not been obtained. Hence the non-availability of GaN bulk substrate, limits the homoepitaxial growth of GaN. The growth of GaN on foreign substrates such as sapphire, silicon, and silicon carbide (SiC) leads to high dislocations and strain due to large differences in lattice parameter and thermal expansion coefficient between substrate and epitaxial layers. It is essential to develop the GaN substrates for homoepitaxy by fabricating high quality GaN wafers. The effort has been made towards the synthesis of GaN powders. Ultra fine and highly pure GaN powders are important because they can be used as the source material for the sublimation growth of bulk GaN single crystal and wafer [7–10]. The conventional synthesis methods like nitridation of Ga metal and Ga_2S_3 by NH_3 results in low yield due to low reaction efficiency [11,12]. Simple and convenient synthetic routes are needed for preparing the GaN nanoparticles. Previously Liu et al. reported of GaN micro crystals being synthesized by spray-dry technique at higher temperature using metal – EDTA complex, which was prepared from the mixture of gallium nitrate $Ga(NO_3)_3$. H_2O and EDTA·NH_4 in aqua solutions, but the particles size was reported to be 400 nm due to high temperature synthesis of GaN at 1060 °C [13]. In order to decrease size of the particle, the present study was planned to synthesize GaN at low temperatures. Ga-EDTA complex was prepared by contacting $GaCl_3$ and EDTA at pH of 9 in aqueous solution. The complex was then nitridated between 600 and 900 °C to obtain GaN nanocrystals. This method yielded GaN crystals of average size around 20 nm. The GaN nanocrystals have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), transmission electron microscopy (TEM), photoluminescence (PL), Fourier transform infrared analysis (FTIR) and Raman spectroscopy.

2. Experimental details

Ga-EDTA·NH_4 complex was prepared from the mixture of $GaCl_3$, and EDTA·NH_4 in aqueous solution at a pH of 9. The solution was stirred for 6 h and dried in an oven at 70 °C to obtain Ga-EDTA·NH_4 complex. The Ga-EDTA·NH_4 complex was taken in an alumina boat and placed inside the quartz reactor and NH_3 was allowed to react with the complex during the synthesis. The synthesis was carried out for a reaction period of 8 h at 600, 700, 800 and 900 °C. Then the temperature was brought down to 500 °C followed by nitrogen purging up to room temperature. The following reactions are suggested for the formation of GaN.

$$2\text{Ga-EDTA NH}_4 \rightarrow \text{Ga}_2\text{O}_3 + \text{EDTA fragments} \quad (1)$$

$$\text{Ga}_2\text{O}_3 + 2\text{NH}_3 \rightarrow 2\text{GaN} + 3\text{H}_2\text{O} \quad (2)$$

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0925-8388/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2010.03.068

Ga-EDTA·NH_4 complex decomposes to yield Ga_2O_3 intermediate which subsequently decomposes in the presence of ammonia to form GaN. The Ga_2O_3 intermediate, though it is in nano form, cannot be sintered to form bulk Ga_2O_3 as the melting point of the Ga_2O_3 (1900 °C) is rather high. The main function of EDTA is to provide nano size Ga_2O_3, so that it can rapidly react with ammonia and convert into nanocrystals of GaN.

Powder X-ray diffraction patterns (XRD) of GaN crystals were recorded using Cu-Kα radiation of wavelength 1.5418 Å at a scan speed of 1°/min. The morphologies of GaN were studied using LEO stereoscan-440 scanning electron microscopy (SEM). Tecnai-12, FEI, transmission electron microscopy (TEM) was used to determine the particle size. Energy dispersive X-ray diffraction analysis (EDAX) indicated the elements present in the synthesized compound. The room temperature photoluminescence (PL) spectrum of the GaN samples was recorded using He–Cd laser (325 nm) as the excitation source. Fourier transform infrared spectral analysis (FTIR) of the samples was carried out using Bruker IFS 66 V FT-IR spectrometer by KBr pellet technique. Raman spectra (300–1000 cm^{-1}) were recorded at room temperature using Renishaw Ramascope system – model 1000 with an excitation wavelength of 514.5 nm (Ar^+ laser).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of GaN powder synthesized at 600, 700, 800 and 900 °C. The XRD patterns show that the formation of GaN via intermediate states. The XRD spectrum of the powder synthesized at 600 °C shows only amorphous nature whereas the powders synthesized at 700 and 800 °C show GaN phase along with additional phases like beta gallium oxide (β-Ga_2O_3) and gallium nitrogen oxide nitrate ($2GaONO_3 \cdot N_2O_5$). Thermodynamic calculations also suggest that the synthesis of GaN proceeded through intermediate products like gallium sub oxide (Ga_2O) [14]. There are several reports on the synthesis of GaN through intermediate states [15–18]. The powder synthesized at 900 °C shows only a single phase of GaN. The lattice parameters were calculated from the XRD data are a = 3.19 Å and c = 5.19 Å which are in good agreement with reported values [17]. Fig. 1(b) shows the XRD spectrum of the compound synthesized at 600 °C after annealing in nitrogen atmosphere at 900 °C for a period of 3 h. It is evident that annealing results in the formation of crystalline GaN with mixed phases of gallium oxide and gallium oxinitrides. Therefore direct synthesis at 900 °C in NH_3 ambient has to be carried out to obtain pure phase of crystalline GaN.

Fig. 2 shows the SEM images of aggregated ultra fine GaN crystals synthesized at different temperatures. The samples synthesized at temperatures of 600, 700 and 800 °C show mixed (spherical and needle) kind of morphologies. This may be due to the presence of secondary phases where as the single-phase sample synthesized at 900 °C has only spherical agglomerated crystallites. TEM image of GaN nanocrystals synthesized at 900 °C is shown in Fig. 3. The image shows that GaN nanocrystals are mostly composed of uniform spherical particles with an average size of 20 nm. We also observe some hexagonal shaped nanocrystallites. The EDAX results (Fig. 4) show that the intensity of carbon and oxygen peaks decrease with the increase of the synthesis temperature. This behavior is attributed by complete decomposition of Ga-EDTA·NH_4 complex and desorption of EDTA at high temperature and formation of other phases like β-Ga_2O_3 and $2GaONO_3 \cdot N_2O_5$ varied with different GaN synthesis temperatures from 600 to 800 °C. Further decomposition of these phases and the formation of GaN at 900 °C were observed. This had been explained by Liu et al. [19].

Fig. 5 shows the room temperature Photoluminescence (PL) spectra of the GaN samples. The GaN samples synthesized at different temperatures show a band-edge emission at 3.46 eV. The PL spectrum shows a mild blue shift indicating an increase in band gap of GaN when compared to bulk emission at 3.4 eV at room temperature. This clearly illustrates that the increase in band gap is due to finite size effect. A broad band emission at 3.35 eV is ascribed to the presence of oxygen (in the form of Ga_2O_3) in synthesized samples. The intensity of this broad band emission decreases with increase of synthesis temperature of GaN, suggesting a decrease in oxygen content for the samples synthesized at higher temperatures. These results in good agreement with EDAX results illustrated in Fig. 4. The sample synthesized at 600 °C shows amorphous nature which also exhibits band-edge emission. Quantum confinement effect in amorphous GaN had already been reported in the literature [20]. From this result it is clear that the formation of amorphous GaN is possible at low synthesis temperature through this route with additional phases and impurities like carbon and oxygen.

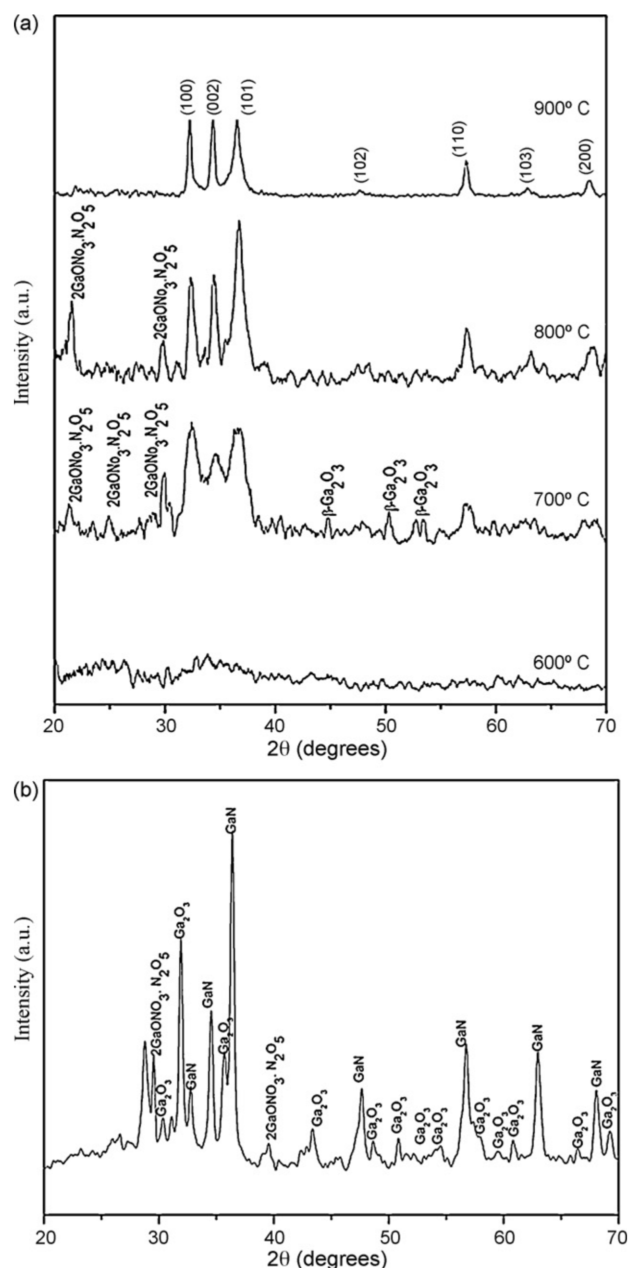

Fig. 1. (a) XRD pattern of GaN compound synthesized at different temperatures. (b) XRD spectrum of the sample synthesized at 600 °C after annealing at 900 °C in nitrogen ambient.

In the FTIR spectrum of the samples synthesized at 600 °C, there is a broad envelop between 2700 and 3700 cm^{-1} due to the OH stretching of water shown in Fig. 6(a). It is also confirmed by its bending vibration that gives intense sharp peak at 1630 cm^{-1}. The broad peak between 500 and 700 cm^{-1} is attributed to GaN and Ga-O vibrations.

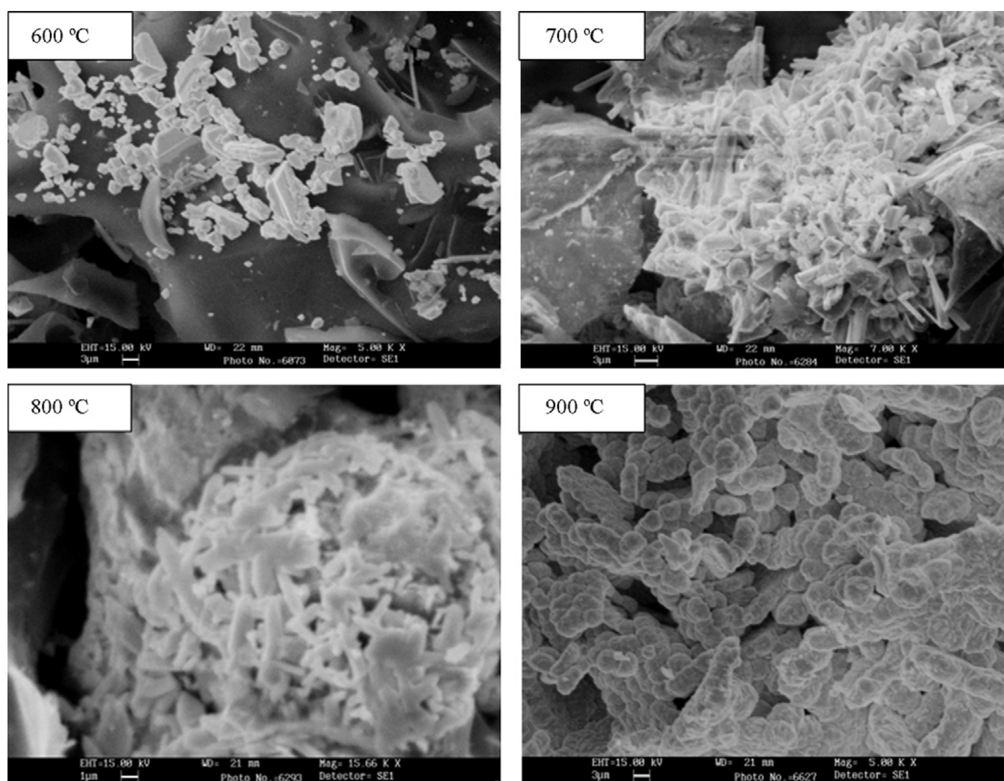

Fig. 2. SEM images of GaN synthesized at different temperatures.

The FTIR spectrum of the samples synthesized at 700 °C is shown in Fig. 6b. The OH stretch of water gives a very broad envelop without giving much resolution for its bending vibration. The peak at 1000 cm^{-1} is assigned to hydrogen bend modes [21].

The FTIR spectrum of the samples synthesized at 800 °C displays nearly similar characteristics as that of Fig. 6(b). The water content appears to be less. The peak due to Ga-O vibration also shows a decrease in intensity. The sample synthesized at 900 °C also shows similar features of Fig. 6(c), but the water content appears to be still less. The intensity of Ga-O peak is also less than that of Fig. 6(c) but the peak due to GaN appears at 577 cm^{-1}, where as in Fig. 6(c) it appears at 617 cm^{-1} which may be due to the presence of small quantity of Ga-O content in the sample synthesized at 800 °C. The results obtained from the FTIR analysis for GaN nanocrystal are closely matched with the previous reports [21–25]. The formation

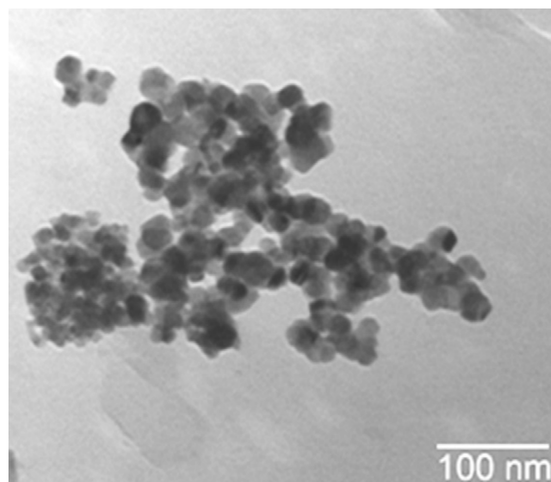

Fig. 3. TEM image of GaN nanocrystals synthesized at 900 °C.

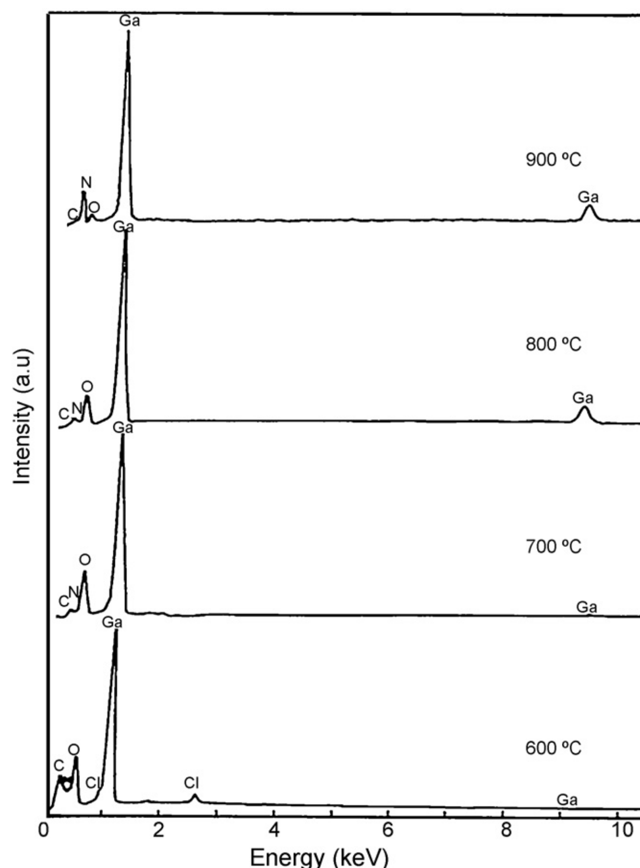

Fig. 4. EDAX pattern of GaN powders synthesized at various temperatures.

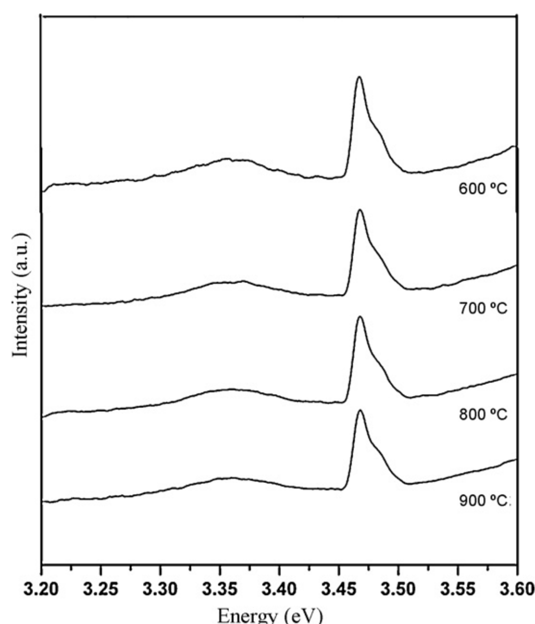

Fig. 5. Room temperature PL spectrum of synthesized GaN powders at different temperatures

of GaN under ammonia proceeds stepwise via intermediate states like β-Ga_2O_3 and gallium oxynitrides, which is also conformed by XRD and FTIR analysis.

Fig. 7 shows the Raman spectra of the GaN nanocrystals synthesized at 800 and 900 °C. Five phonon modes corresponding to pure GaN are observed at 419, 535, 556, 568 and 728 cm^{-1} for samples synthesized at 900 °C. The 419 cm^{-1} phonon mode corresponds to the acoustic overtone, and the other four phonon modes correspond to A_1(TO), E_1(TO), E_2 (high) and A_1(LO) modes, respectively [26,27]. The sample synthesized at 800 °C shows E_2 (high) and A_1 (LO) mode only. As the synthesis temperature decreases, the E_2 (high) mode broadens and blue shifts indicating that the crystalline quality of the nanocrystals increases with temperature. This result is in good agreement with the XRD.

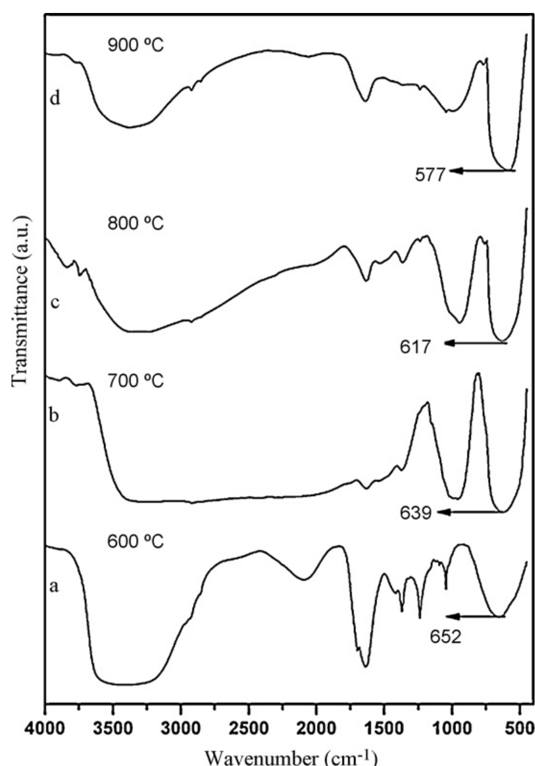

Fig. 6. FTIR spectra of GaN powders synthesized at 600, 700, 800, and 900 °C

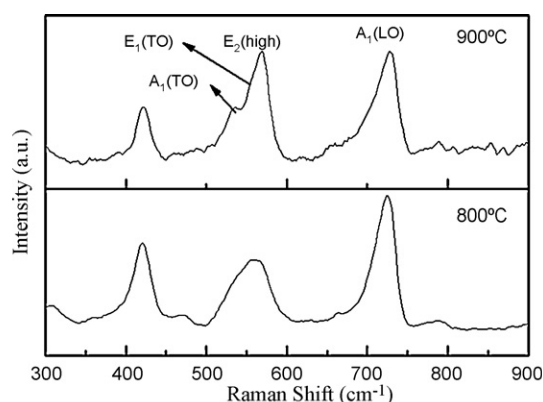

Fig. 7. Raman spectra of GaN powder synthesized at 800, and 900 °C.

4. Summary

GaN nanocrystals with wurtzite type structure are synthesized at lower temperature by a simple and inexpensive method than the previously reported method. The changes in morphology of the synthesized GaN nanocrystaline powders at different synthesis temperatures are noted. The TEM image shows that the average size of GaN nanocrystals is ~20 nm. Room temperature PL spectrum of GaN synthesized at 600 to 900 °C shows a mild blue shift which has been explained by the size effect of GaN crystallites.

Acknowledgement

One of the authors (VG) acknowledge the Department of Science and Technology, and CSIR, Government of India, New Delhi for financial support, for the award of Senior Research fellowship and also Professor M. Palanisamy, Department of Chemistry, Anna University Chennai, India for his valuable suggestions.

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