Growth of Gallium Nitride Thin Film with the Aid of Polymethyl Methacrylate
(Pertumbuhan Filem Nipis Galium Nitrida dengan Bantuan Polimetil Metakrilat)

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ABSTRACT

Wurtzite structure gallium nitride (GaN) thin film was grown on a c-plane sapphire (0001) substrate through spin coating method followed by nitridation process. Readily available and cheap gallium (III) nitrate hydrate ($Ga(NO_3)_3 \cdot xH_2O$) powder was used as the gallium source. Besides that, ethanol-based precursor solution which has better wetting properties and fast evaporation rate was prepared. In addition, a thin layer of polymethyl methacrylate was introduced as a bonding adhesive layer for the growth of the GaN thin film. X-ray diffraction results indicated that the deposited film consists of nanocrystallite GaN with hexagonal wurtzite structure. Field-emission scanning electron microscopy showed the morphologies of the small and well-defined spherical grains that coated on the substrate. The synthesized GaN thin film demonstrated a pronounced and broad exciton peak at 380 nm in Photoluminescence spectrum. Raman scattering measurements showed two features that correspond to the E_2 (high) and A_1 (LO) phonon modes of the hexagonal GaN.

Keywords: Nitridation; Sapphire; spin coating

ABSTRAK

Struktur Wurtzite filem nipis galium nitrida (GaN) telah ditumbuhkan di atas substrat c-satah nilam (0001) melalui kaedah salutan putaran diikuti oleh proses penitridaan. Serbuk Galium (III) nitrat hidrat ($Ga(NO_3)_3 \cdot xH_2O$) yang mudah didapati dan murah telah digunakan sebagai sumber galium. Selain itu, etanol berasaskan pelopor penyelesaian yang mempunyai sifat pembasahan yang lebih baik dan kadar penyejatan yang cepat telah disediakan. Di samping itu, lapisan nipis polimetil metakrilat telah diperkenalkan sebagai lapisan pelekat ikatan untuk pertumbuhan filem nipis GaN. Keputusan pembelauan sinar-X menunjukkan bahawa filem terdiri daripada nanokristalit GaN dengan struktur wurtzite heksagon. Pemancaran medan mikroskop elektron imbasan menunjukkan morfologi bijirin kecil dan berbentuk sfera telah ditumbuhkan pada substrat. Filem GaN nipis menunjukkan satu exciton puncak yang ketara dan luas pada 380 nm dalam keputusan fotoluminesen. Ukuran serakan Raman menunjukkan dua ciri-ciri yang sesuai dengan E_2 (High) dan A_1 (LO) fonon mod GaN heksagon.

Kata kunci: Nilam; penitridaan; salutan berputar

INTRODUCTION

Wide and direct band gap gallium nitride (GaN) semiconductor has attracted extensive attention owing to its numerous potential applications in the opoelectronic and electronic devices. For instance, it has been successfully applied in light-emitting devices and detectors operate in ultraviolet (UV), blue or green spectral region, as well as high- temperature, high-frequency and high-powered electronic devices.

Today, many techniques for the growth of GaN films have been reported. The most common methods are molecular beam epitaxy (MBE), metal-organic chemical vapour deposition (MOCVD), metal-organic chemical vapour phase epitaxy (MOVPE) and radio frequency magnetron sputtering. Nevertheless, these techniques involve sophisticated technologies which are relatively expensive and complicated. As a result, spin-coating technique has been suggested as an alternative way to produce GaN thin films. As compared with the conventional methods mentioned before the spin coating technique is rather simpler, cheaper, safer and scalable for the growth of thin films.

Although there are some very good works using the spin coating technique to grow the GaN thin films, there are still significant challenges. The main issues are associated with the difficulty in the preparation of the precursor solution and challenges associated with the poor wetting of the water-based precursor solution on hydrophobic substrates (such as glass, silicon and sapphire). Therefore, it is highly desirable to have a precursor solution that can overcome these obstacles.

In this paper, we report the growth of wurtzite structure GaN thin film on a sapphire (Al_2O_3) substrate via spin coating followed by nitridation process. To overcome the above mentioned problems, readily available and relatively cheap gallium (III) nitrate hydrate ($Ga(NO_3)_3 \cdot xH_2O$) powder which is easily dissolved into the water or ethanol was used as the gallium source. Besides that, the ethanol-based precursor solution has better wetting properties and fast evaporation rate as

compared with the water-based precursor solution that was used. Apart from that, water-soluble polymer, i.e. polymethyl methacrylate (PMMA) which is inexpensive, easily available, transparent, easy procedures for deposition without contaminating the substrates and easily degradable at high temperatures was introduced for the first time as a bonding adhesive layer prior to the spin coated of the precursor solution. All the results showed that the wurtzite GaN thin film can be synthesized through this simple, easy to handle, and cost-effective method.

EXPERIMENTAL DETAILS

In this work, wurtzite GaN thin film was deposited on the c-plane Al_2O_3 (0001) substrate by using spin coating method followed by nitridation process. The flow chart of this process and the schematic diagram of film's structure are presented in Figure 1.

Prior to the deposition of the Ga_2O_3 thin film, the 1 × 1 cm c-plane Al_2O_3 (0001) substrate was sonically cleaned in acetone then in deionized water for 10 min each. A thin layer of 950 PMMA A2 was then spin coated onto this substrate. This layer served as a bonding adhesive layer. The prepared GaN precursor was then spin-coated on the c-plane Al_2O_3 (0001) substrate. The said GaN precursor in this study was prepared by mixing 3 g of gallium (III) nitrate hydrate ($Ga(NO_3)_3 \cdot xH_2O$) powder (99.9%, Sigma Aldrich) with 130 mL ethanol (99.7%). The solution was stirred until it became clear and transparent. The spin-coating process was repeated several times to obtain films of varying thickness.

Each coated thin film was nitridated in a conventional tube furnace. The coated thin film was placed in a quartz boat at the center of the tube furnace. The furnace was fired to 950°C from room temperature and the coated thin film was heated under a constant flow of highly pure ammonia (NH_3) gas, with a flow rate of 100 sccm for 2 h. The GaN crystal nucleus was formed as more O^{2-} atoms in the precursor were replaced by N^{3-}. The reaction could be described by:

$$Ga_2O_3 + 2NH_3 \rightarrow 2GaN + 3H_2O. \tag{1}$$
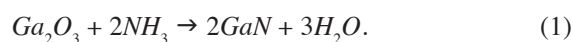
After nitridation, the NH_3 supply was switched off and the flowing nitrogen (N_2) was introduced to flush out the NH_3 excess. The thin film was then retrieved from the oven for characterization. A yellowish layer was deposited on the surface of the thin film.

High resolution X-ray diffraction (XRD; PANalytical X'Pert Pro MRD) with a Cu- Kα_1 radiation source ($\lambda =$ 1.5406 Å) was used to evaluate the crystalline structures and properties of the deposited thin film. A field-emission scanning electron microscopy (FE- SEM; Nova NanoSEM 450) was used to examine the morphology, microstructures and thickness of the as-synthesized thin film. The optical properties of the GaN thin film were studied using photoluminescence (PL) and Raman spectroscopy (Horiba Jobin Yvon HR800UV). For the PL measurement, a helium–cadmium laser operating at 325 nm was used as the excitation source. For the Raman measurement, an argon ion laser operating at 514.5 nm was used as the excitation source.
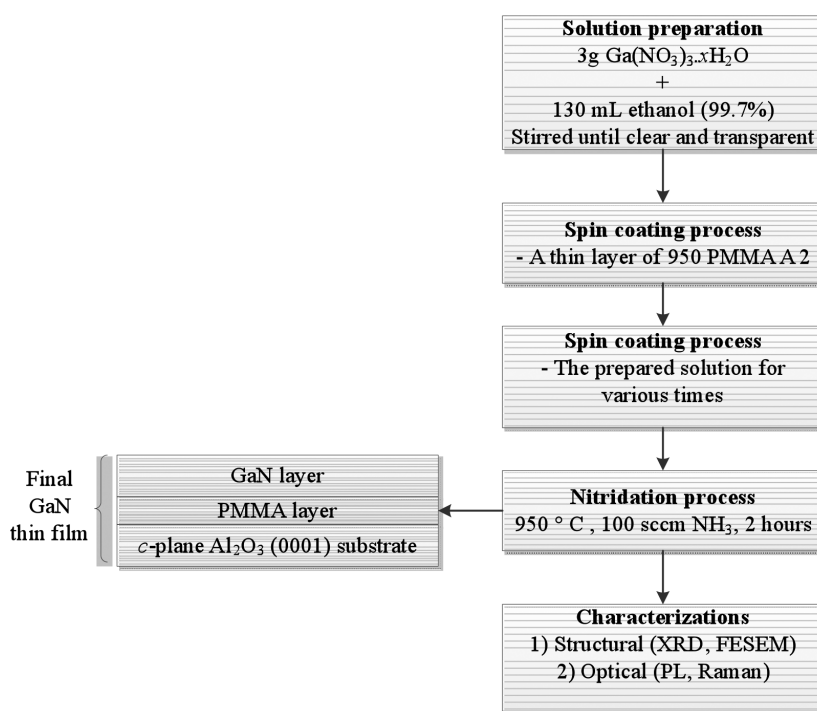

FIGURE 1. Flowchart of GaN growth on the c-plane Al_2O_3 (0001) substrate

RESULTS AND DISCUSSION

The XRD spectra of the GaN thin film on the Al_2O_3 (0001) substrate (Figure 2) was measured under the theta–2theta (θ–2θ) scan mode. All the observed diffraction peaks were in agreement with the Joint Committee for Powder Diffraction Standards data for bulk GaN (JCPDS file No. 05-0792). These diffraction peaks correspond to the (10-10), (0002), (10-11), (10-12) and (11-20) planes of the hexagonal wurtzite GaN phase. The cubic phase of GaN and the Ga_2O_3 diffraction peaks were not observed. These results indicated that the production of GaN from the precursors was highly successful because all the Ga_2O_3 layers were fully transformed into GaN. The average crystallite size of the deposited GaN thin film was estimated using the Scherrer formula:

$$\tau = \frac{K\lambda}{\beta \cos\theta}, \tag{2}$$

where τ is the crystallite size of GaN, K is a shape factor with value of 0.9, λ is the wavelength of the incident beam (1.5406 Å for the Cu-Kα_1 radiation) β is the full-width at half-maximum (FWHM) of the most intense diffracted peak (in radians) and θ is the Bragg's angle of the diffracted peak. In this work, the (0002) diffraction peak is chosen for the calculation of the crystallite size because it has the highest intensity. The average crystallite size of the deposited GaN thin film is approximately 33.3 nm.

The FE-SEM micrographs of the GaN thin films deposited on the c-plane Al_2O_3 (0001) substrate are illustrated in Figure 3(a) and 3(b). A relatively smooth surface morphology without any crack or pit can be observed from the low-magnification micrograph (Figure 3(a)). Small and well-defined spherical grains of different sizes can be clearly seen at higher magnification (Figure 3(b)). The mean diameter of the particles is approximately 35 nm. These particles are closely packed and can completely cover the c-plane Al_2O_3 (0001) substrate. The cross-sectional FE-SEM image of the deposited GaN thin film (Figure 4) shows a uniform and flat GaN thin film on the c-plane Al_2O_3 (0001) substrate with a thickness of approximately 300 nm.

The PL measurement was performed at room temperature to determine the optical properties of the GaN thin film. The PL spectrum of GaN growth on the c-plane Al_2O_3 (0001) substrate is shown in Figure 5. The PL measurement was performed within the wavelength range of 340 to 450 nm, that is, the near-band-edge (NBE) region of GaN. A pronounced and broad exciton peak at 380 nm (3.26 eV) was clearly observed. A multiple-Gaussian fitting procedure was applied to the PL spectrum to study the spatial distribution of specific recombination channels. As presented in Figure 5, the Gaussian fitting analysis showed that the pronounced and broad exciton peak at 380 nm (3.26 eV) can be divided into two Gaussian functions, which were designated as the Gaussian fitting peaks 1 and 2. The Gaussian fitting peak 1 (at ~364 nm) is associated with the NBE region of the GaN (Qun et al. 2008), whereas Gaussian fitting peak 2 (at ~390 nm) corresponds to the donor–acceptor pair recombination, which can be attributed to oxygen-related complexes and vacancy defects (Popovici et al. 2007). The oxygen complex and vacancies may have been induced by the nitridation process at high temperatures or by the precursor of the sol-gel method.

From Figure 5, two additional sharp peaks can be clearly observed at 341 and 350 nm. These two peaks
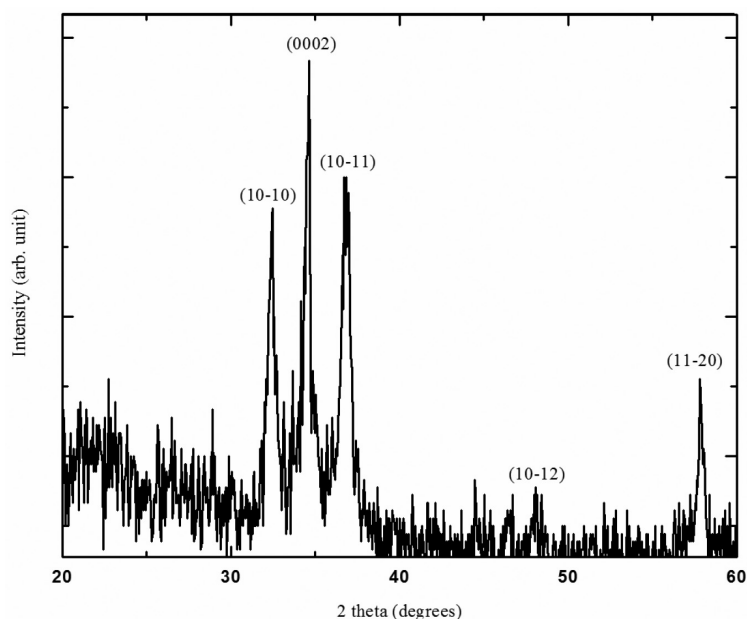

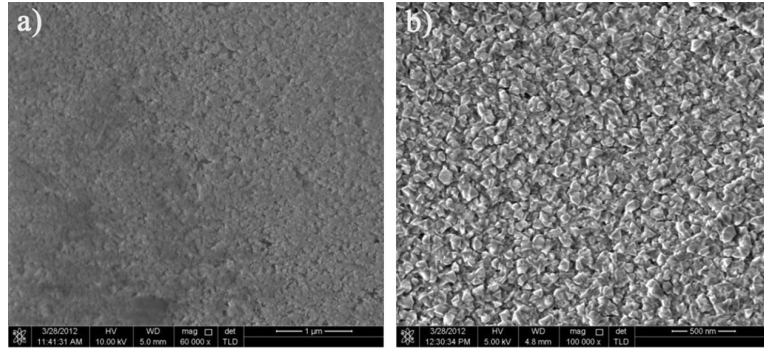FIGURE 2. XRD spectrum of the GaN thin film deposited on the c-plane Al_2O_3 (0001) substrate

FIGURE 3. Top-view FE-SEM micrographs of the GaN thin film deposited on *c*-plane Al$_2$O$_3$ (0001) substrate at (a) lower and (b) higher magnification
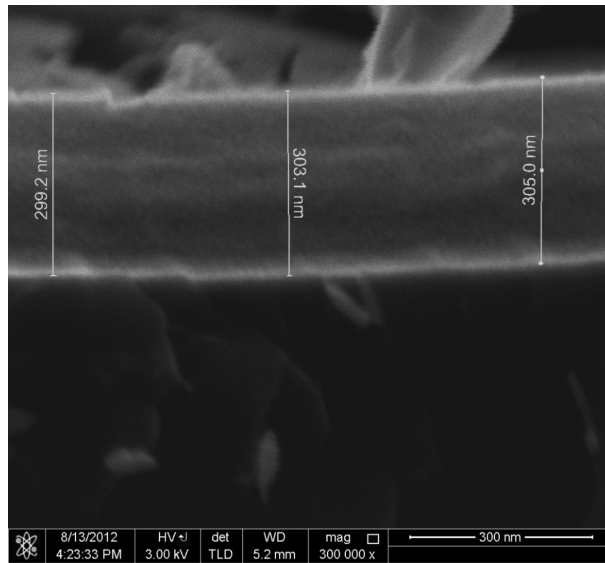

FIGURE 4. Cross-sectional FE-SEM image of the GaN thin film deposited on the *c*-plane Al$_2$O$_3$ (0001) substrate
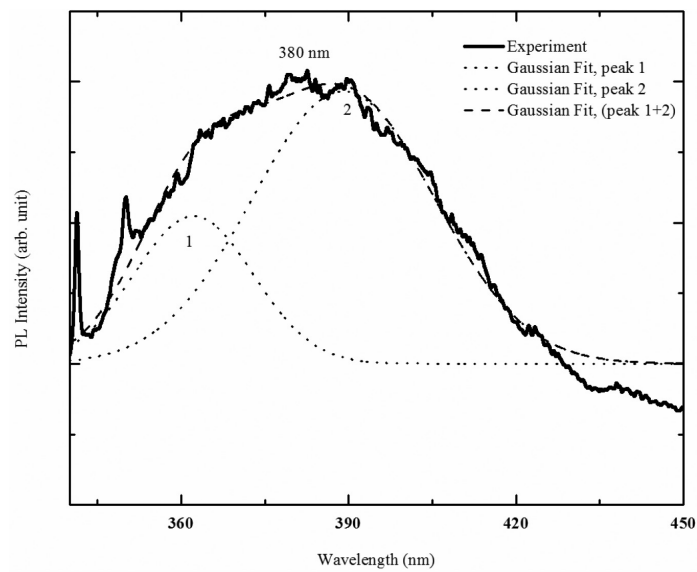

FIGURE 5. Room temperature PL spectrum of the GaN thin film deposited on the *c*-plane Al$_2$O$_3$ (0001) substrate

can be attributed to the Raman characteristics of the nanocrystallite GaN. The respective Raman shifts of these peaks are 1462 and 2193 cm^{-1} whose origins correspond to the second and third orders of the longitudinal-optical (LO) phonon modes of GaN, respectively (Criado et al. 2006). The presence of these multiphonon Raman scattering modes is due to the coupling between the LO phonon mode and the available electron carriers during excitation above the band gap value (Dhara et al. 2007).

Generally, GaN crystallizes into a hexagonal wurtzite structure with four atoms in the unit cell and belongs to the space group ($C6_3mc$). All its atoms occupy sites of symmetry C_{3v}. The Raman spectrum measured with the Ar ion laser on the GaN thin film was presented in Figure 6. The Raman scattering experiment was carried out in the $z(x,$unpolarized$)\bar{z}$ scattering configuration, where the z and $\bar{z}$ are the directions of the incident and scattered light, respectively (Fong et al. 2013). Under this configuration, the allowed zone-center phonon modes of wurtzite GaN

are E$_2$ (low), E$_2$ (high) and A$_1$ (LO) (Chuah et al. 2007). The E$_2$ (high) mode represents the atomic oscillation in the c-plane, whereas the A$_1$ (LO) mode is the atomic oscillation along the c-axis of the wurtzite unit cell (Jain et al. 2009). The E$_2$ (low) mode is given the atomic displacements perpendicular to the c-axis (Chuah et al. 2007).

Three dominant peaks located at 420, 567 and 731 cm^{-1} were observed, as shown in Figure 6. According to Cheng et al. (1999), the peak near 420 cm^{-1} satisfactorily agreed with the phonon vibration frequency of the Al (g) mode of Al$_2$O$_3$. The peak at 567 cm^{-1} corresponds to the E$_2$ (high) mode of the hexagonal wurtzite GaN. The stronger peak at 731 cm^{-1} corresponds to the A$_1$ (LO) phonon mode of the hexagonal GaN (Fong et al. 2013). The allowed Raman phonon mode of E$_2$ (low), which is located near 140 cm^{-1}, was not observed because it is very weak in nature and is located outside the Raman system detection range. Furthermore, the background of the Raman spectra was high at 800 to 2000 cm^{-1}. Similar results were also
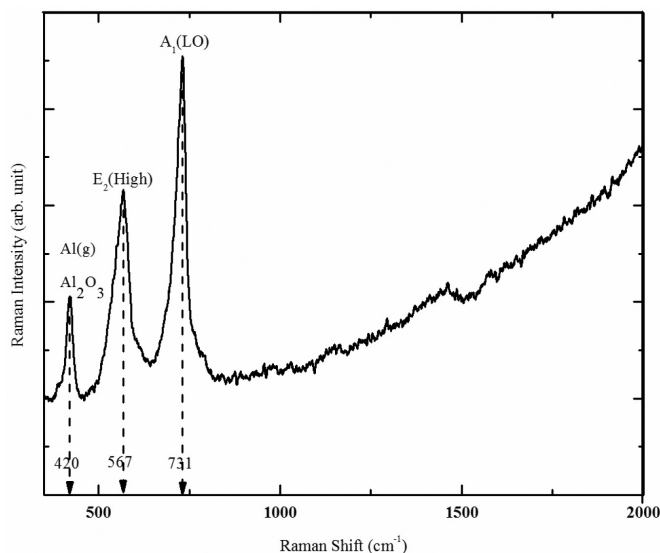

FIGURE 6. Raman spectrum of the GaN thin film deposited on the
c-plane Al$_2$O$_3$ (0001) substrate

TABLE 1. Comparison of reported Raman-active optical phonon modes of E$_2$ (low),
E$_2$ (high), and A$_1$ (LO) in wurtzite GaN

Reference	Optical phonon modes (cm^{-1})			Remarks[a]
	E$_2$(L)	E$_2$(H)	A$_1$(LO)	
Present work	-	567	731	
Davydov et al. 1998	144	567	734	Unstrained GaN
Haboeck et al. 2003	145	567	735	200 – 400 μm thick n-GaN on sapphire substrate with N about 10^{17} - 10^{20} cm^{-3}
Perlin et al. 1992	144	568	732	Bulk GaN
Skromme et al. 2002	144	567	733	Bulk GaN with $N \leq 5 \times 10^{16}$ cm^{-3}
			739	Bulk GaN with $N = 2 \times 10^{17}$ - 3×10^{17} cm^{-3}

[a] The symbol N represents the carrier concentration

obtained from Bao et al. (2010) and Chalker et al. (1999), where the background of the Raman spectrum was high after 800 cm^{-1}. However, the reasons for these phenomena are unclear at present.

The obtained optical phonon modes are compared to the reported results for unstrained (Davydov et al. 1998) and thick (Haboeck et al. 2003) GaN films, as well as for bulk GaN (Skromme et al. 2002). The comparative results are summarized in Table 1. An excellent agreement is obtained for the derived E$_2$ (high) value. The E$_2$ (high) is usually highly sensitive to stress and is used to analyze the stress and strain state in films. Thus, the results suggest that the deposited GaN thin film does not experience compressive strain. Conventionally, GaN films grown on Al$_2$O$_3$ substrate are subjected to compressive strain because Al$_2$O$_3$ has a higher thermal expansion coefficient (perpendicular to the *c*-axis) and a large lattice difference as compared with the GaN layer. The results for A$_1$ (LO) confirm some results in the literature but contradict others. Similar discrepancies have been reported in other studies. These inconsistencies have been attributed to the frequency (wavenumber) shifts caused by the coupling effects between the LO. These shifts are commonly known as the LO phonon–plasmon (LPP) coupling effects. As the carrier concentration increases in *n*-type GaN layers, the A$_1$ (LO) peak shifts to a higher wave number and the line width broadens (Perlin et al. 1992).

CONCLUSION

Wurtzite nanocrystallite GaN thin film was successfully grown on a *c*-plane Al$_2$O$_3$ (0001) substrate via spin coating method followed by nitridation process. The results demonstrated that this simple and inexpensive method can feasibly grow wurtzite structure GaN thin films. The results suggested that the PMMA polymer is a potential adhesive layer for the growth of GaN. Nevertheless, further studies are still necessary to improve the crystalline quality of the GaN thin films that were obtained through the proposed method. Furthermore, some practical purposes and application still need to be done in the future studies.

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