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Free standing c-GaN films grown by low-pressure metalorganic chemical vapor deposition on GaP (100) substrates

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ABSTRACT

Gallium nitride (GaN) films were synthesized by low pressure metalorganic chemical vapor deposition on GaP (100) substrates. Samples were grown using three-step growth method, which includes a) a nitridation process of the GaP surface, b) the growth of a GaN buffer layer and c) the growth of the high-temperature epilayer. X-ray diffraction, Raman spectroscopy and FESEM and HRTEM were used to study the changes in the surface, which suggests that the cubic phase nucleation takes place during nitridation process and remained at the top surface, which results in preferential growth of c-GaN.

1. Introduction

Nowadays, III-nitride based semiconductors have great potential that can be used to manufacture new optoelectronic devices, because of the high quality electro-optical characteristics such as larger bandgap and higher carrier velocity and mobility for multiple applications in different fields, for example, fabrication of high-efficiency solar cells [1], biological detection system [2], and spintronics [3]. The synthesis of GaN bulk material is apparently a very complicated process, although recently some remarkable progress has been made in making of these materials [4]. These materials are generally grown heteroepitaxial on foreign substrates like Al_2O_3, Si and SiC mainly. The main reasons than hinder GaN epitaxial growth on this type of substrates are their coefficient of thermal expansion and their large difference in lattice constant. GaN can be formed in hexagonal or cubic phases, these remains in function of the orientation of the substrate and growth conditions. These materials can be synthesized with hexagonal structure (stable phase) at thermodynamic equilibrium conditions [5,6], but also it is possible obtain cubic structure (metastable phase) with slight thermodynamic variations in experimental conditions by hydride vapor phase epitaxy and molecular beam epitaxy (MBE) techniques and metal-organic chemical vapor deposition (MOCVD) [7–11]. Several efforts have been carried out to obtain GaN thin films with cubic structure (c-GaN) [12–14]. Due to higher crystalline symmetry of the cubic nitrides respect to hexagonal phase result in no spontaneous polarization induced-electric fields, which are undesirable due to decrease the operation lifetimes of optical and electronic devices [15,16]. Nonetheless, there are several researches in which c-GaN film growths of good crystalline quality are reported on different substrates as silicon, silicon carbide, magnesium oxide and gallium arsenide [11,13,17,18]. Where, the nucleating layer is a key process to reduce the hexagonal inclusions.

Also, preliminary growth stages, such as, the nitridation process and the growth of a buffer layer have been used with the same objective [12]. To improve GaN films, is necessary a search for more suitable substrates, we have succeeded in synthesizing a monocrystalline c-GaN thin layer on the GaN template by conversion from GaAs by nitridation process [7].

On the other hand, GaP has been scarcely used as substrate in the grown of c-GaN thin films, even it has cubic structure. The lattice mismatch between GaP and GaN is lower than GaAs, Si or SiC substrates. Besides, GaP has superior thermal stability than GaAs at higher temperatures [19], the thermal expansion lineal coefficient of GaP is 18% lower than GaAs. Only a few investigations reported the growth of c-GaN thin films on GaP (001) by metal-organic vapor phase epitaxy and MBE respectively [19,20]. Wuu et al. avoided the hexagonal inclusion varying the growth temperature of GaN interlayer between GaN buffer and the high temperature GaN epilayer [19]. Kim et al. modified

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the V/III atomic ratio to obtained cubic structure in Ga-rich conditions [20]. There is no work in the literature about freestanding c-GaN films on GaP substrates. In this work, we report the study of the GaN nucleation, the analysis of the precursor stages in the synthesis of c-GaN films on GaP substrates and the optical characteristic of freestanding c-GaN films.

2. Experimental details

The process, is a low-pressure MOCVD used in the synthesis of c-GaN thin films by thermal nitridation of gallium phosphide, details of the growth apparatus have been described elsewhere [7]. Wafers of GaP (100) 10° off to (110) have been used as a substrate, samples cut to a size of 10 × 10 mm^2 were degreased and then etched by dipping into an HCl + HNO_3 (3:1) solution at around 50 °C. Immediately after the samples were introduced into a MOCVD reactor and before the thermal nitridation process the samples were thermally cleaned at 400 °C for 15 min in the flow H_2 to remove the native oxide layer. Nitridation process of the samples has been made in the flow NH_3 of 500 sccm at a temperature in the range of 800–1000 °C. In the case of structures with GaN epitaxial layer, the deposition occurs immediately after the nitridation process. Trimethylgallium (TMG) and ammonia (NH_3) were used as precursors for Ga and N, respectively. H_2 was used as the carrier gas.

Table 1 shows the different experimental conditions for: A. Nitridation process, B. Nitridation process and epitaxial growth without buffer layer, C. Nitridation process and epitaxial growth with previous buffer layer, D. Nitridation process, buffer layer, epitaxial growth and thermal crystallization. A schematic of the growth process for obtain c-GaN film is illustrated in Fig. 1.

After synthesis, the samples were characterized using various techniques. The X-ray diffraction patterns were obtained with $CuK_{\alpha1}$ in a PANalytical X´Pert PRO MRD system. High Resolution Secondary Electron Microscopy (HRSEM, ZEISS AURIGA) equipment was employed to characterize the morphological characteristics of the samples employed. High Resolution Transmission Electron Microscopy (HRTEM JEOL ARM 200F) was employed to confirm the formation of gallium nitride after the nitriding process. Micro Raman measurements were performed using Horiba Jobin HR 800 system with an excitation source of He-Ne operating at a wavelength of 632.8 nm with a power of 50 mW.

3. Results and discussion

An in-situ nitridation process before GaN growth allows the formation of a thin cubic layer at the GaP-GaN interface, which reduces the mismatch between the substrate and the epitaxial film, unlike GaAs nitriding work where a cubic phase at the beginning of nitriding process is obtained and then have a mixture of phases (cubic and hexagonal).

To investigate the characteristics of GaN films produced by in-situ nitridation of GaP substrates and subsequent deposition of GaN epitaxial by the MOCVD process, several sets of nitridation processed films and their equivalent were prepared.

The resulting diffraction patterns were obtained after careful alignment with respect to the substrate surface and presents

Table 1
Experimental parameters of the GaN samples.

Sample	Nitridation T (°C)/t (min)	Buffer layer T (°C)/t (min)	Thermal Cryst. T (°C)/t (min)	Epitaxial GaN T (°C)/t (min)	Thickness (nm)	FWHM (arcmin)
A	900/90				205	
B	900/60	520/10	900/15	900/30	370	44.44
C	950/30	520/10	900/15	900/60	800	38.88

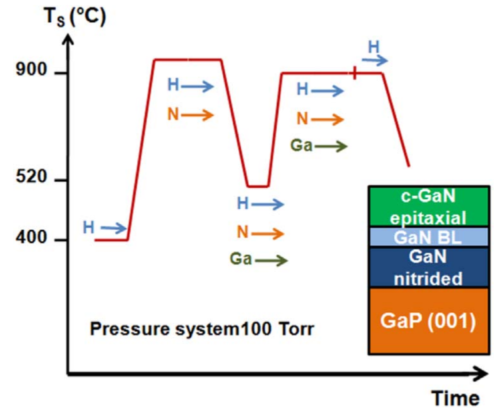

Fig. 1. Schematic representation of the process of growth of GaN films on GaP.

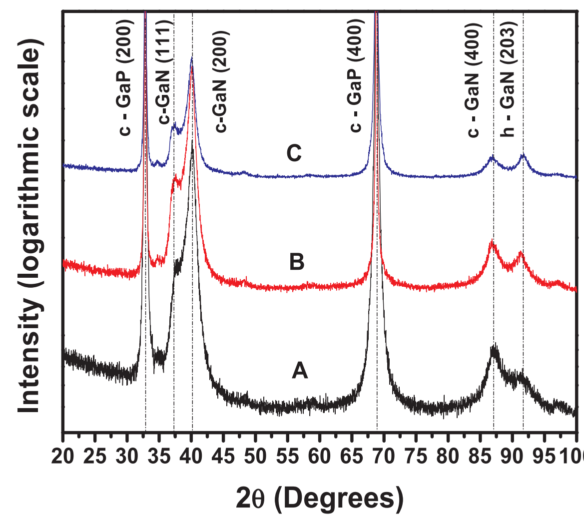

Fig. 2. X-ray diffractogram of GaN on GaP.

contributions from both the deposited film and gallium phosphide substrate, as the penetration depth of the $CuK_{\alpha1}$ X-ray beam was greater than the thickness of the film. Fig. 2 shows the X-ray diffractogram from three different samples. We can see six peaks, two of them corresponding to the substrate employee, GaP (200) at 32.8° and (400) at 68.8°. The other peaks correspond to GaN, showing the cubic and hexagonal phases with different orientations. For c-GaN we have detected the following orientations, (111) at 37.2°, (200) at 40.4° and (400) at 87.3°. For h-GaN we can see one peak at 91.3° (203). So, we confirm that have a mixture formed by orientations of both phase, cubic accompanied by a small contribution from hexagonal phase. The data is in well agreement with the Joint Committee for Powder Diffraction Standards (JCPDS) data for bulk GaP and GaN. The lattice parameters calculated from high angle diffraction peaks are a_{GaN} = 0.446 nm and a_{GaP} = 0.545 nm, resulting in a large lattice mismatch of − 18.1%, resulting in a compressive strain in the GaN layer near the interface. Looking at the overall diffractograms, there is no significant structural changes. Accordingly, we obtained a high quality cubic GaN film.

Fig. 3a shows the HR-SEM image of the cross-section of a cleaved sample of a structure consisting successively of a substrate of GaP, a nitride layer of GaN and an epitaxial layer of ~ 0.3 µm of 2D GaN. The GaN epitaxial films has thicknesses ranging from 0.3 to 0.8 µm in cross section measurements as seen in the SEM micrograph. Thus, growth rates over 50 nm/min can be obtained for nitridation process and 25 nm/min for epitaxial film. Fig. 3b shows two images of HRTEM at different scales of one of the samples in the nitridation phase where it is possible to confirm the formation of cubic gallium nitride.

Mainly, the dissociation of the molecular nitrogen is given by the