Characterization of GaN films grown on GaAs by AP-MOVPE

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Abstract. In this paper we present the results of the synthesis of GaN in an AP-MOVPE system heated by infrared lamps starting from gallium nitride films obtained by nitridation of gallium arsenide. Although dependence of the characteristics of the different parameters of the deposition process on the properties of the layers has been widely studied, the influence of the nature and design of the heating source has been only scarcely reported. We show that the ratio between the two phases depends on the characteristics of the heating source, as well as on other growth parameters. Our results show a compromise between the characteristics of the photoluminescence spectra, the surface morphology and the cubic phase to hexagonal phase ratio. The growth conditions can be adjusted for optimal performance.

1. Introduction
Since the first epitaxial deposit of gallium nitride was realized by H. P. Maruska in 1969 by chemical vapour epitaxy technique [1], the interest on this material has been increasing steadily due to its chemical, electrical and optical properties. Its wide band gap makes this material as one of the most promising semiconductors for applications in optoelectronic devices in the blue and ultraviolet regions, in high temperature and in high power electronic devices. Gallium nitride has two crystalline structures; its hexagonal phase (h-GaN) is stable and its metastable cubic phase (c-GaN). The only difference between both structures is the bond angle to the second neighbor in the cubic structure, which is rotated 60° yielding a different stack of atoms [2]. Both phases show different chemical and physical properties. c-GaN has several advantages to h-GaN like lower phonon scattering lower carrier density, easiness of cleavage and better compatibility with conventional zincblende substrates [3, 4].

Since c-GaN is a metastable phase, an equilibrium process will result in h-GaN. The growth of the cubic phase must be forced using thermodynamic parameters that are far from equilibrium. Techniques such as Molecular Beam Epitaxy (MBE) or Vapour Phase Epitaxy (VPE) are normally carried out on a super saturation regime forcing the species to precipitate and to form the desired compounds [5, 6]; if the substrate presents a cubic phase, the atoms will tend to be arranged in the same structure [7]. Gallium arsenide (GaAs) is the substrate most used because it has a zincblende cubic phase helping the nucleation of c-GaN.

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Due to the large lattice mismatch between c-GaN and GaAs, around 20%, and the incorporation of h-GaN, that cannot be avoided [8]. The films have a high density of defects, like dislocations, stacking faults boundary layers degrading their optical and electrical characteristics. Several variants have been reported to improve the quality of the films and to reduce the incorporation of h-GaN, like use RF-radical nitrogen source, ultra-low pressure growth or low temperature deposition or nitridation process before the growth has also been reported [5, 9]. In this paper we present the results of GaN films grown on GaAs considering the distance of the infrared heat source to the susceptor and the V/III molar ratio in order to reduce the incorporation of h-GaN and improving c-GaN.

2. Experimental procedure

Gallium nitride films were obtained at a Metal-Organic Vapour Phase Epitaxy (MOVPE) system shown in figure 1. The process was realized at atmospheric pressure in Mexico City (586 Torr).

The experiments were carried out in a horizontal silica reactor; Trimethylgallium (TMG) and ammonia were the gallium and nitrogen sources. Pd purified hydrogen was used as carrier gas. A SiC coated graphite susceptor could accommodate one 2” wafer but in our experiments we used 1 cm² substrates. Six 1.6 kW lamps were used to heat the sample and they were placed directly under the sample holder as show figure 1. The temperature control was measured by a thermocouple inserted in the centre of the susceptor; the actual substrate temperature was previously determined to be 20°C below the control value, this difference was measured inserting a thermocouple inside the reaction chamber directly over the susceptor. The current needed to maintain a temperature of 850°C ranged from 41 to 45 A as the distance form the susceptor to the lamps was varied from 8.0 to 12 mm.

The growth process consisted of four steps as follows:

- Cleaning of the substrate. The 1 cm² GaAs (001) substrate was chemically etched in a solution of H₂SO₄:H₂O₂:H₂O=5:1:1 at 60°C, immersed in HCl:H₂O=1:1 and rinsed with DI water. Finally the substrate was introduced in the reactor and annealed in H₂ at 520 °C for 30 minutes to remove the surface oxide.
- Nitridation process. GaAs surface was exposed to NH₃ (300 sccm) for 90 minutes at 900 °C, GaN film was formed over substrate as result of this process. The hydrogen flow was 7 slm.
- Annealing. The GaN buffer layer was annealed at 580 °C for 30 minutes, to improve the crystalline quality of the film.
- Epitaxial growth. GaN film was grown at 850 °C using 500 sccm NH₃ and TMGa for 120 minutes. For the first group of experiments the TMGa flow was kept constant at 0.75 sccm and the distance from the heat source (quartz infrared lamps) to the susceptor was varied between of 8 and 12 mm. For a second set of experiments the distance from the heat source to...
the susceptor was kept constant at 10 mm and TMGa flow was varied to obtain different V/III molar ratios according to table 1.

**Table 1.** Flow rates for Ga source and corresponding molar ratio.

| TMGa Flow (sccm) | V/III Molar ratio |
|------------------|-------------------|
| 0.75             | 3200              |
| 1.0              | 2400              |
| 1.5              | 1600              |
| 2.0              | 1200              |
| 3.0              | 800               |

3. Results and discussion

GaN epitaxial films were characterized by different techniques. X-Ray diffraction (XRD) was employed to determine the crystalline structure, atomic force microscopy (AFM) was used to observe the surface morphology, phonon dispersion was characterized by Raman spectroscopy and photoluminescence (PL) was used to determine the emission spectra of the layers. The crystalline structure of the films is influenced by changes of the thermal distribution near substrate due to modifications of the distance from heat source to the susceptor, as shown in figure 2.

![Figure 2. Change of the phase in GaN films due to the influence of the infrared heat source.](image-url)
Seven peaks are identified in the samples; two of them correspond to GaAs (002) at 32.1º and (004) at 70.05º. The other peaks correspond to GaN, showing the cubic and hexagonal phases with different orientations. For c-GaN they are: (111) at 34.05º and (002) at 39.5º. For h-GaN we can see three peaks, at 36.30º for (10-11) GaN, 58.2º for (11-20) GaN and 64.5º for (10-13) GaN. When the distance is short the hexagonal phase is predominant, however when the distance increases the cubic phase is favoured. Fig. 3 shows the XRD spectrum of sample Nr 59 where the cubic phase is dominant. Increasing the distance of the heating source from the susceptor, results in a less efficient heat concentration, resulting in a less abrupt profile and increase of the temperature of the gas stream inside the reactor. This favors reactions previous to the deposition, affecting the composition of the films leading to an increase of the cubic phase.

The topography of the surface was determined by AFM. Fig. 4 shows a typical microgram of the layers. The roughness of the films was between 321 nm for films with a predominately hexagonal phase and 1046 nm observed when the cubic phase was dominant. It is possible notice the size of the grain and their boundaries.

Raman characterization showed transitions of both phases, but the signal from h-GaN was more intense even in predominantly cubic layers. Fig 5 shows the Raman Spectrum of sample Nr 59. The peaks at 563 and 576 cm⁻¹ correspond to the E1(TO) and E2 transitions of h-GaN, while the shifts at 548 and 737 are related to TO and LO transitions of the cubic phase [3, 10]. According to the spectrum in figure 3 this film is predominantly cubic but the Raman peaks of the hexagonal phase are more intense and better outlined, this indicates a better crystalline quality of h-GaN.
Photoluminescence measurements were made using a 325 nm He-Cd laser. A typical spectrum is shown in fig. 6. The hexagonal and cubic phases can be identified by the emission at 361 and 386 nm respectively. Between 450 and 600 nm a broad emission caused by several defects can be seen. This is very common in GaN and it is known as the yellow band [9]. The larger intensity of the band to band peak and the reduction of the yellow band emission are related to a shift of the former towards longer wavelengths as shown in fig. 7. Further studies are needed to determine if this effect is caused by a reduction of the band gap or an increase of doping impurities in the material.

4. Conclusions
The GaN films grown on GaAs at AP-MOVPE system are a mixture of cubic and hexagonal phase. Varying the distance of the infrared heat source was possible to increase the portion of the cubic phase in the epitaxial film. An abrupt temperature profile favours the hexagonal phase while a gradual temperature profile favours the cubic phase.

The optical characteristics mainly of c-GaN layers could be improved adjusting of V/III molar ratio. The band-band emission of c-GaN was better than the band-band emission for h-GaN. Raman spectra indicate a larger density of crystalline effects in the cubic phase.

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