Structural and optical changes of undoped GaN layers grown via radio-frequency magnetron sputtering obtained from GaN powders

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Abstract—Undoped GaN layers were grown via radio-frequency magnetron sputtering, using a target manufactured with undoped GaN powders. Where the GaN powders were sintetized by nitridation of metallic gallium at 1000 °C in ammonia flow for two hours. X-ray diffraction patterns demonstrated that there are not a significant difference between the diffraction angles of the GaN powders and the GaN layers. The x-ray diffraction patterns for the GaN powders showed narrow peaks with a crystal size of 41 nm, while the GaN layers showed broad peaks with a crystal size of 7.7 nm. Scanning electron microscopy micrographs demonstrated the formation of crystals of irregular size with an average length of 1.56 µm for the GaN powders, while a homogeneous surface morphology with a thickness of 6.6 µm for the GaN layers was observed. Photoluminescence spectra showed a high emission at 3.49 eV (355.13 nm) for the GaN powders and an emission band energy located at 3.42 eV (361.54 nm) for the GaN layers, both emission bands were related to the band-to-band transition for the GaN. Raman spectra for the GaN powders showed the $A_1(\text{TO})$, $E_1(\text{TO})$, and $E_2(\text{High})$ classical vibration modes. The GaN layers only showed the $A_1(\text{TO})$ mode.

Index Terms— GaN; Layers; Powders; Sputtering.

I. INTRODUCTION

The III-V semiconductor compounds have attracted the interest of the researchers due to its direct band gap, inside of the III-V semiconductor compounds, the group III - Nitride (GaN, AlN and InN) stands out because of their optical and electrical properties. Gallium nitride (GaN) was at first synthesized in 1932 by Johnson - Parson - Crew [1] and its importance was demonstrated by Radio Corporation of America laboratories (RCA) in 1968 [2]. Nowadays the GaN is a fundamental material for the LED lighting technology, with applications in the conservation of electrical energy and the reduction of emissions to the

atmosphere produced by hydrocarbons, through the replacement of incandescent bulbs with LED bulbs. Other applications of the GaN are in laser diodes, UV detectors, microwave devices and ultra high power devices [3 – 6].

The GaN can crystallize in the hexagonal structure (wurtzite, $E_g = 3.4$ eV) or stable phase, and in cubic structure (zinc blende, $E_g = 3.2$ eV) or metastable phase. The structural, optical and electrical properties of the GaN depend on the growth conditions, as well as on its nucleation process [7 – 9]. GaN layers are generally obtained via metalorganic chemical vapor deposition (MOCVD), metalorganic vapor phase epitaxy (MOVPE), and molecular beam epitaxy (MBE) [10, 11]. However, these methods use substrates with a lattice constant approximate to the GaN, which could produce lattice defects between the substrate and the layer [12]. A form of decrease the difference between substrate and the layer in heteroepitaxy is the buffer layer. The buffer layer generally reduces the difference in the thermal expansion coefficients of the substrate and GaN. A rarely used technique to obtain GaN buffer layers is radio-frequency magnetron sputtering, which might require the availability of undoped GaN powders with high purity and single phase to be used as raw material in the targets production [13 - 16]. This work presents the obtaining of undoped GaN layers via radio-frequency magnetron sputtering, which were grown using a target manufactured with undoped GaN powders.

II. EXPERIMENTAL

Undoped GaN layers were obtained via radio-frequency magnetron sputtering, which were grown using a target manufactured with undoped GaN powders. The undoped GaN powders were sintetized by nitridation of metallic gallium at 1000 °C in ammonia flow for two hours. The following describes the processes for obtaining undoped GaN powders, as well as the undoped GaN layers:

A. Undoped GaN powders

Undoped GaN powders were obtained at atmospheric pressure (744 mmHg), using ultra-high purity metallic gallium (99.999%) as reagents, as well as anhydrous ammonia of ultra-high purity (NH_3) as reactant gas. To synthesize the undoped GaN powders, only 3.02 g (43 mmol) of metallic gallium was used. Equation (1) shows the proposed chemical reaction to synthesize undoped GaN [17]:

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Metallic gallium was placed in a high-alumina boat and preheated on a hot plate at 200 °C with manual agitation for two hours. After this time, the metallic gallium was introduced into a three-zone furnace, which was purged three times using N₂ flow for 30 minutes at room temperature. The temperature was then increased to 800 °C and the N₂ flow was kept constant at 150 sccm for one hour to remove the oxide from the metallic gallium. Later, the process temperature was raised to 1000 °C for two hours. When the temperature reached 850 °C, the NH₃ flow was opened (150 sccm) and the N₂ flow was closed. After the nitridation process was finished, the temperature was lowered to 600 °C, whereupon the NH₃ flow was closed and the N₂ flow was opened (150 sccm). The temperature was lowered to room temperature. Undoped GaN synthesized was extracted from the reactor and ground to obtain the GaN powder. The total weight obtained of undoped GaN powders using this process was 3.42 g (71.6 mmol). A diagram of the process is shown in Fig. 1.

B. Undoped GaN layers

Once the undoped GaN powders were synthesized, the compression process was performed to obtain the targets for the radio-frequency magnetron sputtering deposit. First, the finest grinding of undoped GaN powders was done, using a mortar in order to homogenize the powders size before its compaction. Then, the undoped GaN powders were lubricated using 0.5 ml of methanol. Later, they were placed in a crusher and in a blackhawk SP25B press (25 ton). Once the powders were compacted, the target of undoped GaN powders was extracted. After, the undoped GaN target was individually sintered at 900 °C for one hour in an N₂ flow, into a three-zone furnace. When the target was manufactured, it was introduced in the equipment Kurt J. Larker of Intercovamex, for the growth of undoped GaN layers on silicon substrates (100), via radio-frequency magnetron sputtering. The equipment has a target size of 25.4 mm diameter and 5 mm thickness. The growth conditions of the GaN layers are the following; power of 50 W, empty pressure of 25 mTorr, growth time of 8 hours, distance between substrate and target of 40 mm. All the process was done at room temperature and in nitrogen gas [16]. Fig. 2, shows the undoped GaN target performed with the undoped GaN powders for the obtaining of the undoped GaN layers.

Fig. 1. Process diagram to obtain the undoped GaN powders.

C. Characterizations

The undoped GaN layers and undoped GaN powders were characterized by x-ray diffraction (XRD) using a Philips XPERT MPD equipment with a wavelength (Cu K α) of 1.5406 Å. The surface morphology was obtained via scanning electron microscopy (SEM) using a JEOL JSM-5300 equipment. Photoluminescence spectra (PL) was measured at room temperature with an excitation wavelength of 243 nm and a 310 nm filter using a fluorescence spectrophotometer Hitachi F- 7000 FL with a 150 W xenon lamp. The Raman scattering characterizations of the undoped GaN layers and undoped GaN powders were obtained using a Horiba Jobin Yvon HR-800 Micro Raman spectrophotometer.

Fig. 2. Undoped GaN target performed with undoped GaN powders obtained by nitridation of metallic gallium.

III. RESULTS AND DISCUSSION

A. Structure

Fig. 3a) shows the x-ray diffraction pattern of the undoped GaN powders and the Fig. 3b) presents the x-ray diffraction pattern of the undoped GaN layers.

The peaks observed in Fig. 3 were indexed in the ICDD card 00-050-0792 for the undoped GaN powders and in the ICDD card 04-003-5899 for the undoped GaN layers. In both cases, the *a* peak is located in the plane orientation (100), *b* at (002), *c*, which has the highest intensity, at (101), *d* at (102), and *e* at (110). The calculated lattice constants for the wurtzite structure were $a = 3.18 \text{ \AA}$ and $c = 5.18 \text{ \AA}$, with ratio c/a of 1.62. It is possible to observe from Fig. 3 that there is not a significant difference between the angles of the diffraction patterns of Fig. 3a) and Fig. 3b). However, the x-ray diffraction pattern in Fig. 3a) showed narrow peaks, which could indicate the presence of large crystals. For undoped GaN powders, the FWHM obtained for (100) plane orientation was 0.15° , 0.17° for (002), 0.17° for (101), 0.22° for (102) and 0.24° for (110). On the other hand, the x-ray diffraction pattern of Fig. 3b), showed broad peaks, which could indicate the presence of nanocrystals [17]. For undoped GaN layers, the FWHM obtained for (100) plane orientation was 0.86° , 1.43° for (002), 1.15° for (101), 0.01° for (102) and 1.05° for (110). Using the ICDD PDF-4+ 2018 software and the Debye-Scherrer equation [18], the crystal size was computed finding an average of 41 nm for the undoped GaN powders and an average of 7.7 nm for the undoped GaN layers.

B. Electron microscopy

Fig. 4a) shows the surface morphology of the undoped GaN powders obtained via nitridation of metallic gallium at 1000°C for two hours in ammonia flow. In this figure, it is possible to observe crystals of irregular size with an average length of $1.56 \mu\text{m}$. Crystals of different size can be identified at 2200x magnification. Fig. 4b) shows the surface morphology of undoped GaN layers obtained by radio-frequency magnetron sputtering using an undoped GaN powders target. Undoped GaN layers had a thickness of $6.6 \mu\text{m}$, which was measurement using a profilometer. In Fig. 4b) was observed a homogeneous surface morphology. Fig. 4b) also showed some agglomerates of the deposited material. These results agree with the x-ray diffraction patterns showed in Fig. 3.

Fig. 3. a) X-Ray diffraction pattern of the undoped GaN powders, b) X-Ray diffraction pattern of the undoped GaN layers.

Fig. 4. a) SEM micrograph of the undoped GaN powders, b) SEM micrograph of the undoped GaN layers.

C. Photoluminescence

Fig.5 shows the photoluminescence (PL) spectra for the undoped GaN powders (black line) and undoped GaN layers (red line), measured at room temperature. The PL spectrum of the undoped GaN layers was decomposed in four components. The *a* peak showed a high emission due to the band-to-band transition in 3.49 eV (355.13 nm), which corresponds to the ultra violet emission for the hexagonal GaN. The emission band energy located at 3.42 eV (361.54 nm) (*b* peak-first component) corresponds to band-to-band transition also for the hexagonal GaN, where the difference of 0.07 eV between band-to-band emissions could be related

to the greater amount of structural defects (stacking faults) in the GaN powders [19]. The blue emission band located at 2.96 eV (418.67 nm) (*c* peak-second component) exhibited a metastable blue luminescence, and a yellow luminescence band. The yellow emission band was located at 2.72 eV (454.83 nm) (*d* peak-third component) for the undoped GaN layers, this is related to transitions from three distinct deep donors to the shallow gallium vacancies acceptor [19]. The *e* peak (fourth component), showed an emission band energy located at 2.31 eV (492.73 nm), which is attributed to the complex nature of the yellow luminescence band. Finally, the *f* peak located in 2.21 eV (560.37 nm) (red-yellow band), is related to the presence of carbon impurities and interstitial gallium atoms [17].

D. Raman scattering

Fig. 6 shows the Raman spectra for the undoped GaN powders (black line) and undoped GaN layers (red line) respectively.

The Raman spectrum for the undoped GaN powders shows the vibration modes $A_1(\text{TO})$, $E_1(\text{TO})$ and $E_2(\text{High})$ for the wurtzite structure of GaN. From this same figure it was possible to observe the separation between the $E_1(\text{TO})$ and $E_2(\text{High})$ modes, which could confirm the obtaining of Ga-rich GaN powders [17]. In other hand, the $A_1(\text{TO})$, $E_1(\text{TO})$ and $E_2(\text{High})$ vibration modes were drastically diminished by the Si substrate signal, where it was only possible to observe the $A_1(\text{TO})$ mode, this vibration mode was magnified and showed in the inner inset of Fig. 6 [20, 21]. The frequency values were 525.61 cm^{-1} for the $A_1(\text{TO})$ mode, 546.54 cm^{-1} for the $E_1(\text{TO})$ mode and 555.58 cm^{-1} for the $E_2(\text{High})$ vibration mode.

IV. CONCLUSIONS

Undoped GaN layers were obtained via radio-frequency magnetron sputtering, which were grown using a target manufactured with undoped GaN powders. The undoped GaN powders were sintetized by nitridation of metallic gallium at 1000°C in ammonia flow for two hours. XRD characterizations showed that there are no a significant difference between the angles of the diffraction patterns. Besides, the x-ray diffraction pattern for the undoped GaN powders showed narrow peaks, which could indicate the presence of large crystals with a crystal size of 41 nm, while for the undoped GaN layers, the diffraction pattern showed broad peaks, which could indicate the presence of nanocrystals with a crystal size of 7.7 nm. From SEM micrographs it was possible to observe crystals of irregular size with an average length of $1.56 \mu\text{m}$ for the undoped GaN powders, as well as a homogeneous surface morphology for the undoped GaN layers with a thickness of $6.6 \mu\text{m}$. PL spectra showed a high emission at 3.49 eV (355.13 nm) for the undoped GaN powders, while for the undoped GaN layers an emission band energy located at 3.42 eV (361.54 nm) was observed. These emission bands were related to the band-to-band transition for the hexagonal GaN. The difference of 0.07 eV between band-to-band emissions could be related to the greater amount of stacking faults in the GaN powders. Raman spectra for the undoped GaN powders showed the classical vibration modes with values

of 525.61 cm^{-1} for the $A_1(\text{TO})$ mode, 546.54 cm^{-1} for the $E_1(\text{TO})$ mode and 555.58 cm^{-1} for the $E_2(\text{High})$ vibration mode. On the other hand, it was only possible to observe the $A_1(\text{TO})$ mode for the undoped GaN layers.

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Fig. 5. Photoluminescence spectra for the undoped GaN powders, and undoped GaN layers.

Fig. 6. Raman scattering for the undoped GaN powders, and Raman scattering for the undoped GaN layers.

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