Electrical behavior of Mg doped cubic GaN on c-GaN structure

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Abstract
Magnesium doped cubic GaN films were epitaxially grown using a metalorganic chemical vapor deposition system. In an exploratory fashion, growth conditions were varied to obtain quasi mono-crystalline surfaces and by this mean remove the hexagonal fraction present in the samples. Hall effect measurements indicate a carrier concentration in Mg doped c-GaN films between $5 \times 10^{17}$ and $8 \times 10^{18} \text{cm}^{-3}$ with p-type carriers. Electrical studies were carried out in a homojunction formed by c-GaN films with different conductivity; our findings demonstrate the GaN homojunction has a rectifier effect, and presents a repeatable negative differential resistance attributed to the transferred electron effect in deep levels. We confirmed that the Mg doped c-GaN films are suitable for optoelectronic device manufacturing.

1. Introduction
Cubic gallium nitride (c-GaN)- and its alloys- is one of the most interesting III-nitride semiconductors due to its potential applications in optical (light emitting diodes, solar cells, photo-detectors), electronic (tunnel diodes, field effect transistors), power (high electron mobility transistors) and radio frequency (Gun diodes) devices; although cubic phase applications are similar to those developed for the hexagonal gallium nitride (h-GaN) it is expected that c-GaN devices have better performance and longer lifetimes, because the higher crystalline symmetry of the cubic nitrides with respect to the hexagonal phase, result in more isotropic properties and no spontaneous polarization induced-electric fields. In addition, several authors have reported advantages with respect to the hexagonal phase such as superior electronic properties, higher carrier mobility, higher drift velocities, and better doping efficiencies [1–3].

On the other hand, the main disadvantage in the synthesis of c-GaN is the lack of a native substrates and a low quality crystalline film. This low quality crystalline film can be attributed to the inclusion of a stable phase (h-GaN), which is due to the fact that the growth conditions for c-GaN must be precise and any slight variation generates intrinsic defects that induce the growth of the hexagonal phase, therefore experimental growth parameters must be set with precision. Therefore, the development of c-GaN devices is not very widespread and its applications are still under consideration to improve the device’s properties and achieve better operation. Despite this, there are reports about growth of c-GaN film with high crystalline quality, for example in 2008, Novikov et al. [4] reported the synthesis of c-GaN layers and substrates by molecular beam epitaxy technique (MBE), the c-GaN substrates obtained had thicknesses up to 100 μm with high crystalline quality. And in 2012, we reported the synthesis of free standing c-GaN monocrystalline template obtained by the nitridation process of the GaAs surface [5].

In comparison with h-GaN, the research about c-GaN devices with respect to the development of optical devices in ultra violet and blue regions has been very scarce. Only two relevant papers about c-GaN LED were reported over 10 years ago.
ago by H. Yang et al. in 1999 [6] and D. J. As et al. in 2000 [7], both groups manufactured a c-GaN LED on a gallium arsenide substrate, their results promoted more interest in the development of these devices. Later in 2010 Norzani Binti Zainal reported the fabrication of the first device on free-standing c-GaN substrate, which was an InGaN LED fabricated by Sharp Laboratories in Europe. Photoluminescence measurements at 15 K were required to observe clearly the emission of the InGaN layer. Electrical characteristics were similar to Multi-Quantum-Wells of LEDs at room temperature [8], which indicated similar confinement in single homostructure than that in multiple heterostructures. In recent years, there has been an academic interest that focuses on c-GaN/c-InGaN heterostructures for solar cells [9,10].

GaN devices exhibit a phenomenon called negative differential resistance (NDR), which has been reported by Golka et al. in 2006 [11] which studied a double barrier, dislocation free GaN–GaAIN (hexagonal phase) diode, it is considered that this effect is due to lower carrier density in some quantum wells. Yilmazoglu et al. reported in 2007 [12] experimental studies about the negative differential resistance in h-GaN Gun diode attributed to different doping regions [8]. However, there are no reports about NDR effects in c-GaN devices and even less in homojunction GaN until before this paper.

This work complements the research reported previously [5,13]. Mg doped c-GaN films were grown on free standing c-GaN templates to study the optical and electrical properties of p-type doped films. In addition, we analyzed the electrical behavior of c-GaN p–n homojunctions in order to demonstrate the feasibility of a free-standing c-GaN device with our synthesis method; we observe repeatable NDR effects in the devices and propose a possible explanation.

2. Experimental procedure

Description of the low pressure metalorganic chemical vapor deposition reactor (LPMOCVD) used in the Mg doped c-GaN films as well as details on how to synthesize n-type conductivity c-GaN films on substrates obtained by nitridation of GaAs surface was described earlier [5]. We used bis-cyclopentadienyl magnesium (Cp2Mg) as magnesium source, trimethyl gallium (TMG) as gallium source, ammonia (NH3) as nitrogen source and purified hydrogen as carrier gas. The Cp2Mg optimal vapor pressure was 31.99 Pa, with a flow of 2 sccm we introduced 2 × 1017 Mg atoms per minute; TMG and NH3 flows were 1.5 sccm and 500 sccm, respectively. Films were synthesized in the range of 77.99 kPa (atmosphere pressure in Mexico city) to 73.32 kPa and the growth temperature was varied from 870 °C to 830 °C. According with X-ray diffraction and pole diagrams were measured in a PANalytical X’Pert PRO MRD system.

Scan Electron microscope (SEM) TESCAN model TS-S5136SB equipment was used to study c-GaN structures. Chemical composition analysis was possible by Scanning Ion Secondary Mass (SIMS) measurements realized using primary Cs+ ions with an incident angle of 45°; the parameters of the source were 5 KeV and 40 μA. Photoluminescence (PL) spectra of the epitaxial films were obtained at 10 K and 300 K using a He–Cd laser with a wavelength of 325 nm. Current–Voltage measurements of the homojunction were carried out in the semiconductor characterization system: model Keithley 4200-SCS.

3. Results and discussion

Fig. 1 shows the X-ray diffractogram of a typical Mg doped film growth on n-type c-GaN film, peaks at 2θ = 40° and 2θ = 86.2° correspond to the planes (200) and (400) of the cubic crystalline phase respectively. Intensity of the peak at 2θ = 34.5° has been related to the hexagonal (002) plane and the cubic (111) plane. Other weak peaks at 2θ = 32.3°, 2θ = 36.8°, 2θ = 59.1°, and 2θ = 72.6° correspond to hexagonal phase. By varying experimental parameters, we could confirm that the mixture of phases is caused by Mg inclusion in cubic structures, which generates some defects that favor formation of hexagonal planes. It was not possible to eliminate in its entirety the inclusion of the hexagonal phase, but this is less than 5% in optimized films.

Fig. 2 shows a pole diagram of an optimized Mg doped c-GaN film at 2θ = 34.5°; it is possible to see a mild signal at ψ = 0° perpendicular to the surface corresponding to the (0002) hexagonal plane, and four intense peaks around a tilt angle ψ = 54.7° corresponding to the (111) plane of the cubic structure, the pole diagram for a Mg doped film at 2θ = 40° [13] shows a punctual peak corresponding to c-GaN (200). These results indicate that Mg doped film maintain the cubic...
crystalline structure of the previous, non doped cubic film; so doped film has a quasi-monocrystalline cubic structure.

**Fig. 3.** shows an SEM image corresponding to a GaN structure, formed of a p-type film grown during 60 min and an n-type epitaxial film on GaN nitrided substrate. According with the SEM image, the thickness of the Mg doped film is around 1 μm and can be identified for its brightness (attributed to major backscattered electrons due to metal incorporation, EDS measurements indicates that brightness is related with Mg inclusion). A SIMS analysis was realized to verify the existence of the n–p homojunction, the Mg doped film in this sample was grown during 90 min in order to clearly observe the variation of the magnesium concentration, **Fig. 4** show SIMS concentration profile, we can see three regions: 1. GaN substrate, 2. n-type conductivity film and 3. p-type conductivity film. The n-type conductivity is attributed to nitrogen vacancies and unintentional oxygen incorporation [15,16]. In p-type film, magnesium introduces acceptor levels. The Ga/N atoms relation is stoichiometric in epitaxial structure, but in the substrate region the Ga/N atoms relation is not equal, which is attributed to the polycrystalline structure. High arsenic concentration present in films does not modify crystalline structure but it could contribute in the defect density of the GaN structure.

Photoluminescence measurement at 300 K for undoped c-GaN films only show a peak at 387 nm corresponding to band–band emission, also it is not possible observed band–band emission due to hexagonal phase (366 nm) or yellow band emission attributed to intrinsic defect [13,17].

Photoluminescence spectra tests for Mg doped films were performed at 10 K and 300 K, but here we present the spectrum at 10 K to examine the transitions attributed to Mg inclusion in c-GaN, see **Fig. 5.** It is possible to observe the band–band emission of the cubic phase at 381 nm (3.25 eV), analyzing the broad emission related to Mg doped we have determined by theoretical adjustment by Gauss method (red dashed line), a main acceptor level at 413 nm (E_v+200 meV) and a deep acceptor level at 439 nm (E_v+375 meV), which has low intensity. It is not possible adjustment a curve considering only Mg contribution peak at 413 nm, in this case the Mg contribution peak should be around 420 nm with a higher intensity and a width less. Analyzing several samples...
we conclude the deep acceptor level it is a fundamental emission in our samples. Yellow band emission was observed in the Mg doped films.

Table 1 summarizes the electrical parameters of the n-type and p-type cubic films characterized by Hall measurements using the Van der Pauw method. Mg doped films have low resistivity and high carrier density; these values are consistent with those reported by other authors [14,18]. Electrical current–voltage (I–V) measurements were carried out at room temperature with direct voltage supply and pulsed supply in individual devices.

As we mentioned above, the electrical characterization about c-GaN devices is scarce; so we carried out a study to confirm that the contacts are ohmic and be assure that the I–V curves obtained corresponding to p–n homojunction. Fig. 6a, shows the I–V curve of the c-GaN homojunction, which presents rectifier effect as expected from an n–p junction; however, the series resistance is large and the turn-on voltage was around 5.5 V, and in order to reduce the series resistance it is necessary to remove or decrease the thickness of GaN substrate. Some devices emitted orange light for a few seconds, this emission corresponds to a yellow band effect that occurs in GaN due to intrinsic defects or undesired impurities as C or O [15,16]. According with X-ray diffraction, SIMS analysis and PL measurements we confirm that Mg doped generates defects in p-type region and the n–p boundary allowed deep levels. Orange emission around 2 eV indicates a deep donor–deep acceptor recombination which is higher than the donor–acceptor recombination is; it is possible that blue emission occurred but it is negligible. Furthermore, we observed repeatable negative differential resistance effect (NDR) in the majority of n–p homojunctions, see Fig. 6b. Although this behavior is related to quantum structures and has been studied in III–N quantum devices, there are no reports on GaN homojunctions [11,18]. We attribute the NDR effect in the c-GaN homojunction to the existence of a region with different carrier density at higher energy and with low mobility in the interphase generator for deep acceptor levels and deep levels due to defects; the rectifier effect is recuperated because the trapped carriers fill the sites available [19].

4. Conclusions

In conclusion, we grew epitaxial Mg doped c-GaN films with quasi-monocrystalline structures and the hexagonal inclusion was controlled adjusting growth parameters. PL emissions attributed to Mg doping indicates a donor level at 3.0 eV and a deep donor level at 2.82 eV. Cubic GaN homojunction shows repeatable NDR effect due to changes in the carrier mobility in defect regions and deep acceptor levels. As a result, we have demonstrated the feasibility of use of c-GaN structures in device manufacturing; however, more research on the subject is necessary in order to fabricate c-GaN devices with better features.

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