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Structural and Optical Properties of GaN Thin Films Grown on Si (111) by Pulsed Laser Deposition

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In this work we present results and analysis concerning the processing and characterization of Gallium Nitride (GaN) thin films (TF) grown on Si (111) substrates by pulsed laser deposition technique (PLD), which were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and Raman spectroscopy (RS). The GaN films showed the hexagonal phase with a preferential orientation in the (100) direction, SEM pictures showed a cauliflower-like morphology. Room temperature PL studies showed the so called GaN-yellow band, at 2.29 eV, as well as the donor-acceptor (DA) pair luminescent transition around 3.0 eV. At 10 K, phonon replicas, separated by 69 meV, were observed. By RS, the optical mode on 710 cm^{-1} was observed, corresponding to the longitudinal optical phonon, A_1(LO), as reported for this material.

Keywords: *Gallium nitride, Pulsed Laser Deposition, Photoluminescence.*

1. Introduction

The nitride semiconductors, particularly GaN, have useful applications as light-emitting devices and as robust semiconductors for possible uses in transparent microelectronics[1]. Most of the best quality thin films are produced by molecular beam epitaxy (MBE) or metal-organic chemical vapour deposition (MOCVD), thus the exploration of fast and not so expensive techniques, like sublimation[2] or PLD[3-6], that makes possible to obtain good quality materials, results of interest for the materials science community. With PLD technique is possible to grow thin films into high vacuum level, at low substrate temperatures and at fast growth rate of the order of Å/pulse, to obtain stoichiometric films. The plasma formation ejected with the PLD-plume dissociates the N_2-molecules from a nitrogen atmosphere and in this way having highly reactive atomic N radicals. Some results concerning the growth of GaN films by PLD were reported by Vinegoni et al[4]. They got films with small homogeneously distributed granular structures over the entire sample surface. Moreover high crystalline quality epitaxial have been processed by Vispute et al[5]. on Al_2O_3(0001) substrate.

GaN crystallizes in the hexagonal or wurtzite (α) phase is the more stable one, whereas the zincblende structure is the metastable (β) phase[7]. In order to avoid delamination of thin films grown by PLD, it is usually required to have a good crystalline lattice match between the substrate and the GaN film, and simultaneously proper growth conditions, mainly high temperature (700- 850 ºC) of the substrate. The most employed substrate is sapphire with the (0001) direction[8,9], however silicon also represents an alternative as substrate, because it has advantages over sapphire, like cost, high thermal conductivity, large area substrates, among others[10,11].

2. Experimental

Monocrystalline Si wafers (1 cm^2), with (111) orientation, were used as substrates, they were cleaned with hydrofluoric acid (HF) at 100% concentration for few seconds and dry with N_2 gas. The chemical treated substrates were immediately

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introduced into the PLD-growth chamber. For the PLD process a circular target (one-inch diameter and 3 mm thick) of GaN was used, which was obtained by compressing high purity powder (Aldrich) 99.99 % at 1 Kbar. A Nd-YAG laser with 1064 nm wavelength, 12 ns pulse duration, a power of 2.8 W and a repetition rate of 50 Hz, was used for the ablation process. The substrate temperature was kept at 850 °C during the PLD process and the growth chamber was feeded with N_2 gas flow of 40 sccm, reaching a pressure of 10^{-1} Torr during the growth process of the films. The deposition time was fixed at 20 minutes, in order to obtain films 150 nm in thickness.

The optical characterization was carried out in a conventional PL-set up from 10 K to room temperature (RT). For PL measurements a He-Cd laser was used as exciting light, at 325 nm, with a power of 40 mW. Raman spectra were obtained by using a He-Ne laser (633 nm, 30 mW) in a LabRam HR Evolution equipment. The XRD diffraction patterns were measured in the grazing angle configuration with a Bruker Advance diffractometer, whereas micrographs were obtained with a JSM6300 scanning electronic microscope.

3. Results and Discussion

GaN film was polycrystalline in nature, as determined by XRD. Figure 1 shows the corresponding diffraction pattern, which covers from 28 to 40 degrees (in the 2θ axis), because in this region it is possible to clear up the diffraction signal from the background noise. Above 2θ=40° we did not found any diffraction signal.

As it can be seen there are well defined diffraction peaks due to GaN film[12], the peak at 31.7 is related to the (100) plane, whereas the peak at 34.4 corresponds to the (002) plane, while the peak at 36.2 is associated to the (101) plane; all of them are related to the wurtzite crystalline structure according to PDF 01-073-7289 card. The intensity of each one of the GaN diffraction peaks were compared to the respective intensities of the peaks, as reported in the PDF card. According to this comparison, it is possible to assert that the preferential orientation corresponds to the (100) plane. On the other hand, the peak at 39.4 is related to the (420) orientation of the β-Ga_2O_3 phase, PDF 00-006-0529.

Taking into account the two more intense diffraction peaks, (101) and (100), crystallite sizes of 16 and 26 nm respectively, were calculate by using the Scherrer-equation.

The diffraction peaks undergo a small shift, lower than 2θ= 0.7, as compared to the theoretical values. This small shift could be due to tensile strain produced by the mismatch lattice between the film and substrate[13]. Just for matter of comparison, the strongest peak at 29.4 corresponding to the (111) crystalline orientation of the Si substrate, does not suffer any shift.

Figure 2 depicts a SEM-micrograph of the film surface, the image was taken at 100 000X, it was not possible to obtain an image at higher magnification because the sample got charged avoiding a further magnification. From the SEM image it can be noticed a cauliflower-like morphology, also porous surface showing an uncompleted surface coverage can be observed.

The room temperature PL spectra were taken at two different points, separated 0.5 cm from each other, on the surface of the same sample in order to verify the homogeneity of the PL emission. It is possible to observe three bands, the yellow luminescence (YL) band, centered at 2.25 eV, the blue emission luminescence (BL) at 2.82 eV and the near band edge (NBE) emission, at 3.0 eV. In general, it is possible to see that the relative emission intensity of these bands is different at each point, so the PL spectra depends on laser spot position as it can be seen in Figure 3. It has been reported that the YL could be due to different radiative defects, different hypothesis about the so called GaN-yellow band have been proposed in order to explain its origin, one of the most accepted is due to transitions from shallow donors to deep acceptors[14,15], on the other hand, some researchers have associated it to native defects, like Ga vacancies because of unintentionally impurities incorporated during the material growth process[16,17]. On the other side, the NBE emission,

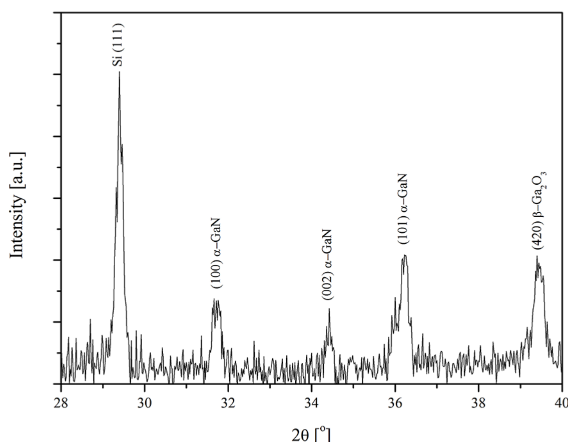

Figure 1. XRD pattern of the GaN film grown on (111) Si substrate.

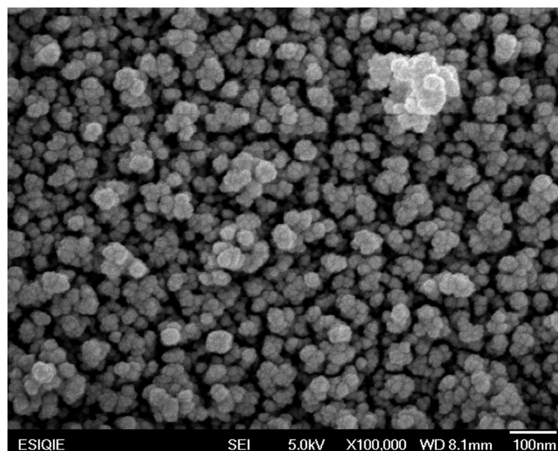

Figure 2. SEM image of GaN film grown on Si (111) substrate.

it is usually associated to DA-pair luminescent transition according to Reshchikov et al.[16,18,19]. According to literature BL is related to β-Ga_2O_3 nanostructures[20]. This emission is originated from the recombination of an electron on a donor formed by oxygen vacancies and a hole on an acceptor formed by gallium vacancies[21]. The oxygen incorporation is due to target handling and high pressure during the growth process.

Taking into account this fact, we measure the PL emission, at both points on the sample surface, as a function of temperature. Both sets of spectra show the PL evolution in the range from 10 to 300 K. As it can be seen, there is a dependence of the intensity and the position of the PL bands, as well as a quenching of the PL signal as expected[22]. Figure 4 shows the set of PL spectra obtained at the 1st point. Variation of the shape and position of YL with temperature has been the topic of several publications[14,16,23]. When the temperature increases from 10-300 K, the position of the YL band undergoes a small shift, around 40 meV, towards 2.29 eV, at 10 K. The spectra depicted also the ultraviolet luminescence band (UVL), approximately at 3.37 eV, which quenches and completely vanishes at temperatures above 150 K.

The high energy side of the PL spectrum, above 3.0 eV, of GaN film, at 10K, is shown in Figure 5. It can be seen additional PL structures located at 3.362, 3.293, 3.223, 3.154 eV, which are separated 69 meV from each other, these three regular spaced structures account for the coupling of phonons to the PL emission at 3.362 eV, moreover the respective vibrational frequency corresponds to the transversal optical phonon (TO) designated as E_1 with a frequency of 559 cm^{-1} [24]. This coupling of TO phonon, E_1, in GaN, has been also reported by Z. Chen et al.[25], in GaN grown by MOCVD on Al_2O_3 substrates.

Figure 6 shows the temperature dependence of these PL structures, as it can be seen all the phonon replicas follow this trend in 10 to 150 K temperature range, with the largest energy shift being about 52 meV.

The set of PL spectra obtained at the second emission point of the GaN film are shown in the Figure 7. It is also possible to observe a dependence of the intensity, as well as the position, of the PL bands. At room temperature there are two signals, the first one correspond to YL around at 2.30 eV, whereas the second one, due to DA-pair luminescent transition, is located at 3.05 eV[26]. It is observed, that the

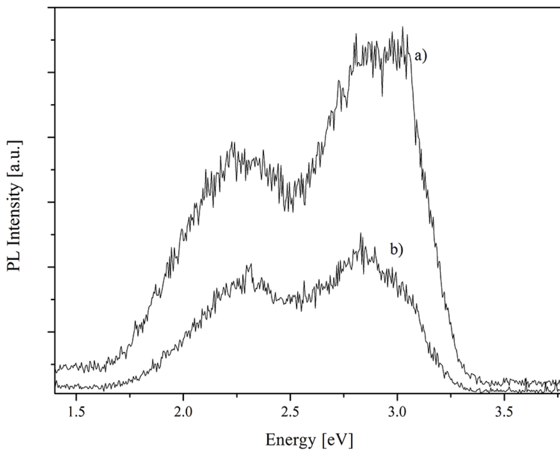

Figure 3. Room temperature PL spectra of a GaN film taken at two different points on the surface: a) 1st point, b) 2nd point.

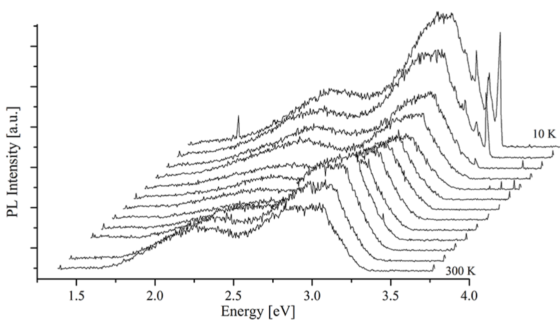

Figure 4. PL spectra as a function of temperature, 10 to 300 K, for a GaN film taken at the 1st point on the surface.

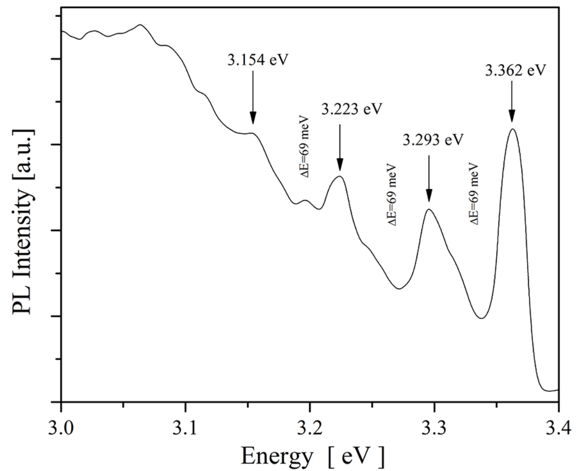

Figure 5. 10 K PL spectrum of a GaN film, showing the phonon replica.

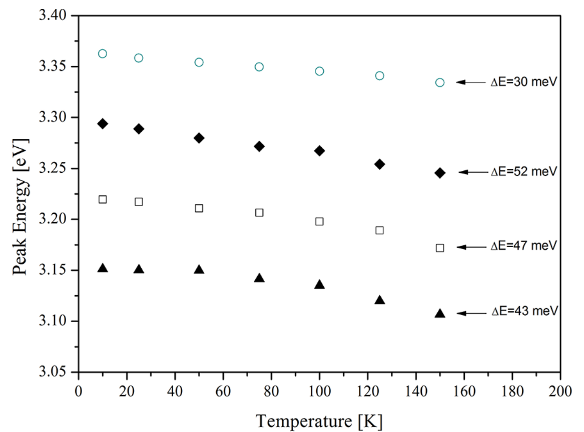

Figure 6. Position of the PL zero phonon line, ZPL, and phonon replica as a function of temperature for the GaN film, at the first focusing point.

YL emission intensity is higher than the NBE emission at lowest temperature (10 K).

The PL spectrum at 10 K, also presents the ultraviolet luminescence band (UVL) as shown in Figure 8. The phonon replica structures, at 3.349, 3.281, 3.21, 3.141 eV, are also separated by 69 meV, whereby we assume, as before, that they are due to coupling with TO phonon[25].

The temperature dependence of the PL structures of the ultraviolet luminescence band (UVL) taken at the second point, is shown in Figure 9. It can be seen that the phonon replica structures follow a similar trend, as that of Figure 6. In this case all these structures vanish above 125 K.

Phonon modes of GaN have received considerable attention due to that the information that these could provide is important in considering the electron transport, the non-radiative electron relaxation process, among others. However, the phonon frequencies of GaN wurtzite phase depend slightly of the growth process of the films. A Raman spectrum of the GaN sample grown on Si (111) is shown in Figure 10, it was recorded at room temperature. The peak centered at 710 cm^{-1} was multiplied by a factor 50 in order to get better

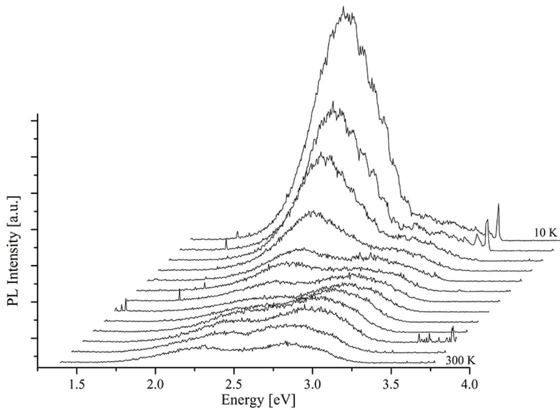

Figure 7. Temperature dependence of the PL spectra from 10 to 300 K for GaN film at the 2nd point.

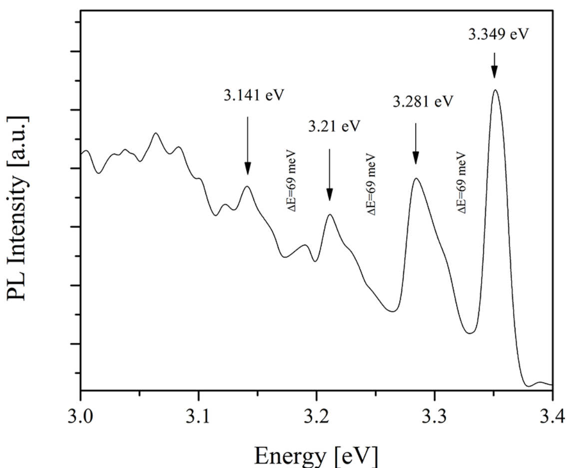

Figure 8. Low temperature (10 K) PL spectrum of GaN film in the UVL band at the 2nd point.

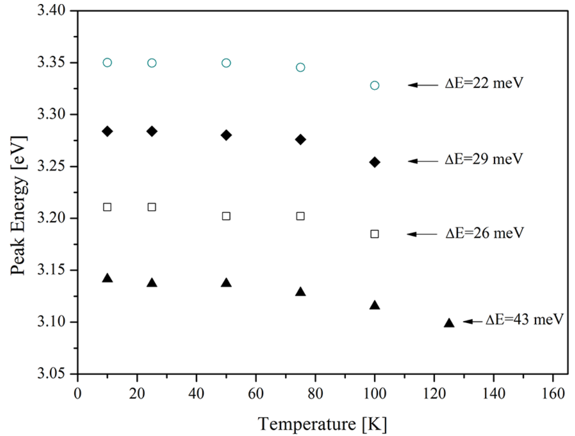

Figure 9. Position of the PL zero phonon line, ZPL, and phonon replica as a function of temperature for the GaN film, at the second focusing point.

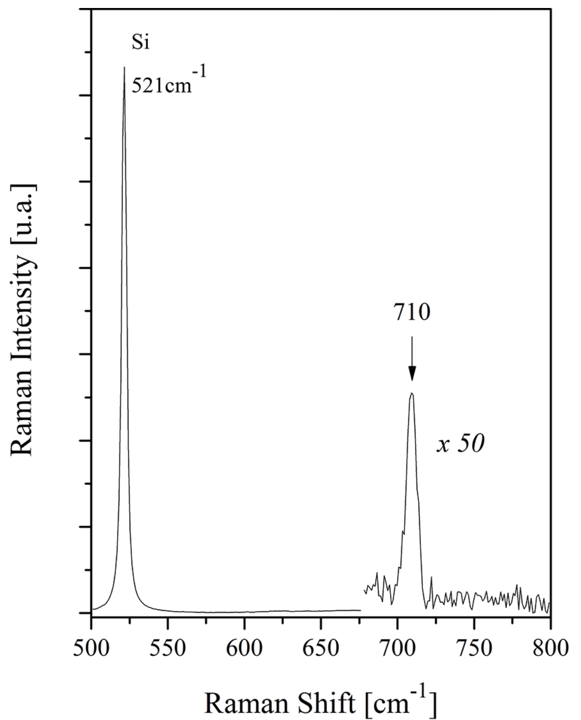

Figure 10. Raman spectra of GaN film grown on Si (111) substrate.

appreciation. This has been attributed to the longitudinal optical phonon of the GaN in wurtzite structure, A_1 (LO)[27,28]. Some authors previously reported on Raman mode shifts in GaN with a frequency lower than 734 cm^{-1}, the shift may arise from the presence of phonon confinement assuming the presence of nano-sized crystals suggesting a polycrystalline character of our films in accordance to XRD[4] results. We discard that this phonon is related to β-Ga_2O_3, because the β-Ga_2O_3 Raman signal is presented at 767 cm^{-1} [29].

4. Conclusions

We have processed and studied GaN films grown by PLD on Si (111) substrates, in a N_2 atmosphere inside the PLD-chamber growth. The XRD pattern reveals the polycrystalline character of the films due to the presence of the (100), (002) and (101) directions related to wurtzite phase of GaN. A small contribution of Ga-oxide phase is confirmed due to the presence of the (420) crystallographic direction. According to the SEM micrographs nanometric cauliflower-like structures are observed. PL signal depends on laser spot position on the surface of the sample, mainly the intensity of the NBE at 3.0 eV, as observed from the respective spectra. Temperature dependence of the PL signal was measured from 10 to 300 K at two different points on the same sample. At low temperature the PL spectra showed a high energy band at 3.36 eV, related to excitonic transition. At 10 K, the UVL band shows structures separated by 69 meV corresponds to the transversal optical phonon (TO) designated as E_1 with a frequency of 559 cm^{-1}. The Raman spectrum shows a peak centered at 710 cm^{-1}, which is associated to A_1 (LO) of GaN in wurtzite structure.

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