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Improving the electrical properties of non-intentionally doped n-GaN by deuteration

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Here we report on the study of the effects on the charge transport properties of deuterium in-diffusion in non-intentionally doped *n*-GaN using a two steps process: a low temperature deuterium diffusion and then a thermal anneal at temperatures as high as 800 ºC, for driving the deuterium deeper into the material. The obtained results show that deuteration by this two steps process produces a decrease on the electron concentration of at least one order of magnitude and an increase of the same order on electron mobility. Such improvements are attributed, respectively, to the capture of free electrons by free deuterium acceptor and to the deuterium passivation of deep acceptor levels located at the dislocations core, decreasing their dispersive and recombination capability. The observed improvement remains stable at temperatures close to 800 ºC. This deep acceptor level passivation should positively impact the performance of electronic devices made with non-intentionally doped *n*-GaN layers.

Keywords: Deuteration; Gallium nitride; Passivation

1. Introduction

Gallium nitride and its alloys are the choice materials for a number of optolectronic and electronic applications which have already widely demonstrated their true capabilities producing high performance devices as high electron mobility transistors (HEMTs), ultraviolet and infrared detectors (UVD, IRD), non-linear optical (NLO) structures, and tera-hertz sources and detectors, among others [1-6]. Nevertheless, because of the lack of intrinsic substrates, until to now, most of the GaN layers used for electronic devices are epitaxially grown on foreign substrates such as sapphire, silicon carbide, silicon, and other materials, usually displaying a large lattice and thermal mismatch. The resulting material is highly defective with dislocation densities, N_T, in the range 10^7-10^{11} cm^{-2} with its physical properties strongly degraded, producing devices with lower than expected performances [7-11]. As examples of the deleterious effects introduced by dislocations on HEMTs can be mentioned; the drain current knee walk out and collapse, reduction of the break down voltage, gate lag and current leakage low frequency and 1/f noise increase [9-13]. In the case of UVD detectors, the persistence of photoconduction strongly limits their frequency response [14], etc. It has been established that in this material threading edge dislocations (TDs) contains acceptor levels, although, there is no established energy value in the band gap. Such levels capture free carriers constituting a negatively charged line. Assuming an acceptor level about every lattice constant along the *c* direction, a volumetric acceptor concentration on the order of $2x10^7 N_T$ cm^{-3} is expected [15, 16]. Although at room temperature not all of the available states in the TDs are charged, enough electrons are captured by these states to build up a barrier energy that is highly efficient at scattering carriers [15-18]. Moreover, recent studies demonstrate that there is an entire region around the dislocation core, constituting a negatively charged rod with a radius of several nanometers that might bear a charge density as high as 10^{20} cm^{-3} [19, 20]. This negative charge rod produces the so called "mobility collapse", which means that for layers with a free electron concentration lower than $\sim 10^{17}$ cm^{-3}, the electron mobility decreases to abnormally low values instead of increasing as the carrier concentration decreases. Such mobility behavior cannot be explained with the classical carrier scattering mechanisms and has been reasonable explained introducing the dispersive effect of the energy barriers due to the negatively charged TDs [8, 17, 18]. On the other hand, the ability of hydrogen to passivate a variety of deep and shallow levels in various semiconducting materials is well established now [21]. This is the reason why theoretical models have been developed to explore the hydrogen behavior in GaN [22], and experimental efforts have been realized attempting to take advantage of the possibility of improving the material and devices performance. Nevertheless, poor results have been obtained and long hydrogenation treatments are necessary to observe some improvements [23-25]. Notwithstanding the precedent attempts to improve the charge transport properties of GaN layers by hydrogen passivation of defects, it is interesting to study in a more detailed way the influence of the controlled introduction of deuterium on the physical properties of non-intentionally doped gallium nitride layers (nid-GaN). Here, we present a

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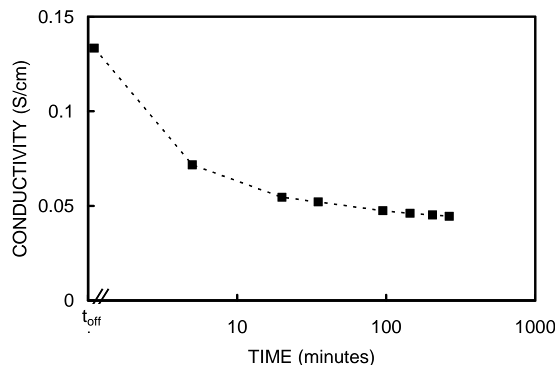

Figure 1. Photoconductivity observed on an as grown nid-GaN sample, illuminated with photons from a green light emitting diode biased at a power 1 mW, t_{off} means the time at which the light is turned off.

study of the effects of deuteration of nid-GaN on a two steps process; a pre-diffusion step, where deuterium is introduced at low temperature by a short diffusion time but high plasma power and then its in-diffusion, explored at various temperatures and durations. The main results are, more than an order of magnitude increase on the room temperature electron mobility of the nid-GaN layers, accompanied by a decrease on their electron concentration of more than a decade. Improvements that remain stable at temperatures, close to 800 ºC and that should allow a better device performance.

2. Experimental details and results

The nid-GaN layers used in this study were grown by low pressure metal-organic chemical vapor deposition (LPMOCVD), using trimethylgallium as group III and ammonia (NH_3) as group V precursors and hydrogen as carrier gas. Layers were grown on the c plane of two inches in diameter sapphire substrates, featuring a thickness of 3.0 µm, the whole layer presented a mirror like surface. All the samples studied were taken from the same wafer. The layers were electrically characterized by measuring their room temperature electron concentrations and mobilities. Quantitative deuterium profiles were obtained by secondary ion mass spectrometry (SIMS) measurements using a Cameca ims-4f instrument, having a deuterium detection limit of $5x10^{15}$ cm^{-3} with a Cs^+ primary beam and ion implanted calibration standards. For electrical measurements, ohmic contacts were formed depositing, by sputtering, 20 nm Ti and 200 nm Al, and thermally annealed at 780 ºC. The Ti and Al were deposited through a thin square patterned metal mask bearing holes at each corner of a diameter close to 0.4 mm. Electrical contacts ohmicity was verified by current voltage measurements using an HP 4145 Semiconductor Parameters Analyzer after the first thermal anneal to obtain ohmic behavior, as well as after each sample thermal anneal. Hall data were collected using the van der Pauw method on 4x4 mm^2 samples and employing a magnetic field of 5 KGauss. The electrical measurements were made on as-grown samples, after deuteration, and after each step of thermal anneal. After the as-grown measurements some samples were

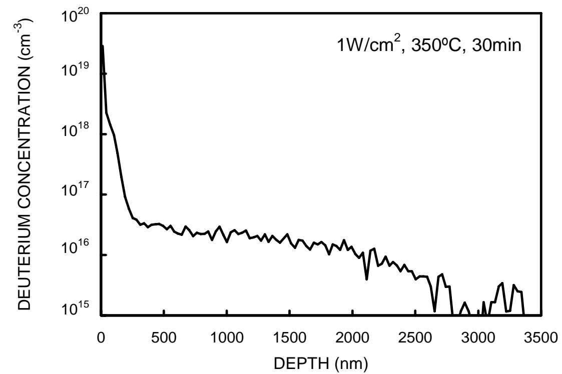

Figure 2. Secondary ion mass spectroscopy deuterium profile in a LPMOCVD nid-GaN 3.0 µm thick.

thermally annealed at temperatures as high as 800ºC for 15 minutes, assessing that the thermal treatment by itself does not modify the electrical properties of the layers. Measurements show that in obscurity and at room temperature, the as-grown samples measured by Hall presented electron concentration and mobilities around 10^{17} cm^{-3} and 10 cm^2 $V^{-1}s^{-1}$, respectively. All the studied samples, when illuminated with photons of energy smaller than the GaN band gap, displayed a strong photoconduction, as shown in Fig. 1. The light source used was a green light emitting diode having its peak emission at 2.6 eV with a full width at half maximum of 0.14 eV and biased at 1mW.

After being characterized in their as-grown condition, the nid-GaN layers were deuterated using a RF remote plasma procedure at a constant deuterium pressure of 1.0 mbar, a power density of 1 W/cm^2 and a sample temperature of 350 °C, for 20 minutes. Figure 2 shows a typical deuterium SIMS profile obtained on a deuterated sample. Deuterium profiles as this one have been discussed in detail before [23], however, is important to underline here that the deuterium profile has two distinguishable regions, one with a 10^{18} cm^{-3} concentration within the first 250 nm from the surface, and the second region below this depth with a 10^{16} cm^{-3} concentration almost constant that continues through out the entire layer thickness, situation that is observed even for deuteration durations as short as 5 minutes. This behavior has been explained assuming that the deuterium diffuses extremely fast through edge dislocations, which should, thus, contain a high deuterium concentration. Although the layers were grown using hydrogen as carrier gas, we were no able to detect any hydrogen in the samples, that might be due to the fact that the hydrogen detection limit of the used SIMS is around 10^{17} cm^{-3}.

After the deuteration, the samples were once again electrically characterized as described before. The obtained results reveal that the electron concentration was systematically reduced by half of its as-grown value, however, the mobility remained almost unchanged, or even, is slightly reduced. Then, the layers were thermally treated on a step by step basis and their electrical properties

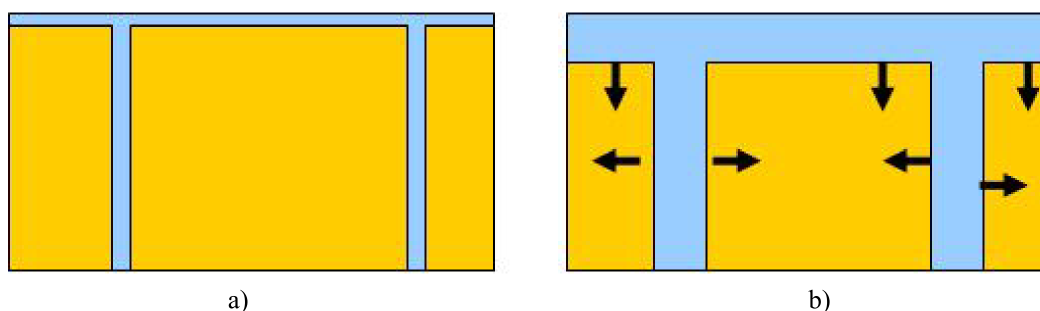

Figure 3. (a) Proposed deuterium distributions (blue), (a) for the first diffusion step at low temperature, short diffusion time and high plasma power, (b) after the second diffusion step at high temperature and short diffusion time, here the deuterium reach deeper into the grain bulk away from the dislocation edge and surface layer, the arrows indicate the way deuterium in-diffuses.

were measured after each thermal treatment. The thermal treatments started at a temperature close to the one used to deuterate the samples; 370 ºC, five equal duration treatments were realized for a total annealing time of 500 minutes. The whole thermal treatment produced a further reduction of the electron concentration, although a small one, with an equally slight increase on their mobility. The thermal anneal continued with the same samples, at an annealing temperature of 550 ºC, now for nine equal duration treatments for a total annealing time of 1100 minutes. In this case, the carrier concentration continued to systematically decrease after each thermal treatment reaching a minimum value of $3x10^{16}$ cm^{-3}, a decade lower than the as-grown value. Simultaneously, the mobility systematically increased until reached a value of 140 $cm^2V^{-1}s^{-1}$, 14 times higher than the as-grown value. However, for the last two annealing steps both properties reached saturation. The next anneal temperatures used were; 600 ºC, 650 ºC, 700 ºC and 750 ºC, for total annealing durations of 100, 40, 30 and 10 minutes, respectively. For each attempted anneal temperature, the electron mobility continued to increase each time that the anneal temperature was increased, to a final value close to 200 cm^2 $V^{-1}s^{-1}$, i.e., almost 20 times its as-grown value, although the electron concentration did not change any more from the lowest value already given. This behavior was observed for all the samples deuterated and heat treated by the same way. It is important to underline that for the as-grown samples, although taken from the same wafer, the electron concentration and mobility values measured, were quite different; ±100 % from already given values, revealing an important inhomogeneity of the electrical properties throughout the wafer. Independently of the electron concentration and mobility values measured for the as-grown samples, the after deuteration and thermally treated corresponding ones, lied very close to each other for all the treated samples, clearly improving the homogeneity of the electrical properties among the samples. Additionally, the strong photoconductive effect observed on the as-grown samples had almost disappeared.

3. Discussion

The above results can be explained as follows. The low mobility measured on our samples has been explained in the literature by the carrier scattering dominated by negatively charged threading dislocations which in these samples their concentration seems to be between 10^{10} - 10^{11} cm^{-2} [8, 15, 16]. The observed initial decrease of the electron concentration and mobility on the as-deuterated samples has been explained by the capture of free electrons by free neutral D becoming D^-, because the acceptor nature of free deuterium in n-GaN [23], constituting additional dispersion centers, slightly decreasing the mobility. Then, as a heat treatment is done at a given temperature below 800 ºC, the deuterium located in the edge dislocation in-diffuses into the GaN columns bulk, or at least in the dislocation core where it might form complexes with initially ionized acceptors, decreasing the negative charge in the dislocation, decreasing, as well as, its associated barrier height and its carriers scattering properties. Then, for a given anneal temperature as the heat treatment time t continues to increase, the charge transport properties saturate because the diffusion depth being proportional to $(Dt)^{1/2}$, where D is the deuterium thermal diffusion coefficient, increases slowly and almost saturate. When the anneal temperature is increased the thermal diffusion coefficient increases driving the deuterium deeper into the dislocation stress region passivating more ionized acceptors, decreasing even more the dislocation dispersive capability and reaching a maximum for the electron mobility when annealed at 750 ºC for 10 minutes. The proposed deuterium diffusion is illustrated by Fig. 3, where the blue color corresponds to the deuterium rich regions and the arrows indicate the way it in-diffuses into dislocation stress region and crystalline bulk. Considering that the observed passivation is stable at temperatures as high as 750 ºC, it is reasonable to expect that the above observed improvements will remain unchanged at usual device operating temperatures. The observed photoconductivity might be produced by the electrons contained in the acceptor states located on the core of threading dislocations that are excited into the conduction band. Its disappearance after the drive in of the deuterium, using the same light intensity, is due to the fact that the

available electrons in the acceptors energy gap states have been strongly decreased as the acceptors have been deuterium passivated. Finally, although it has been reported a high stability of hydrogen in GaN, because of the strong bond with the acceptors, at an anneal temperature of 800 ºC or higher, the acceptor-deuterium complexes already formed are broken and the deuterium out-diffuses from the sample, returning to its as grown condition [26].

4. Conclusions

In conclusion, we have shown that in nid-GaN layers displaying a threading dislocation density around 10^{10} cm^{-2}, deuterium can be introduced through out the entire layer thickness by a low temperature and short duration but high plasma power deuteration process, and then being in-diffused by a short heat treatment at an optimal temperature of 750 ºC resulting on a decrease on the nid-GaN electron concentration from an initial value of 10^{17} cm^{-3} to the low of 10^{16} cm^{-3}, and boosting the electron mobility from ~10 cm^2 $V^{-1}s^{-1}$ to 200 cm^2 $V^{-1}s^{-1}$. Clearly the strong electrical activity of the dislocations has been passivated. Thus, all the draw backs of nid-GaN now associated to the deleterious electrical activity of the dislocations should be decreased. These improvements, stable at temperatures close to 800 ºC, might be useful to reach better performances of electronic devices based on this material that should remain stable at ordinary device operating temperatures.

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