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GROWTH, MORPHOLOGICAL, STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF NITROGEN DOPED ZINC OXIDE THIN FILM ON POROUS GALLIUM NITRIDE TEMPLATE

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ABSTRACT
Gallium nitride (GaN) is susceptible of producing efficient display and lighting devices. Low cost hybrid heterostructured lighting devices are developed by combining zinc oxide (ZnO) with GaN that has gained much more research interest, nowadays. Porous GaN receives a great deal of attraction by its excellent and improved properties compared with its bulk counterpart. Several potential applications have been realized, including for serving as a strain-relaxed substrates for the growth of superior quality heteroepitaxial thin films and it is quite interesting. UV assisted photo electrochemical etching nanostructuring technique was utilized for the development of GaN porous structure in this study. Nitrogen is regarded as a good candidate for acceptor doping in zinc oxide by the availability of its gaseous state compared with the other available p-type doping sources. Nitrogen doped ZnO thin film was grown on the resultant porous GaN template using radio frequency magnetron sputtering technique at room temperature. The morphological, structural and optical properties of the fabricated porous nanostructure as well as the grown nitrogen doped ZnO thin films were studied. It was found that the grown nitrogen doped ZnO thin film exhibited p-type conductivity, determined by Hall measurements and the obtained results were presented.

KEYWORDS: GaN, Porosity, ZnO, X-ray diffraction, Raman Spectroscopy and Photoluminescence.

INTRODUCTION
Nitride based compound semiconductors, such as GaN, InGaN, AlGaN, and AlInGaN are very attractive and excellent candidates due to their superior material properties and versatility for use in a variety of optoelectronic applications such as light-emitting diodes (LEDs), solar cells, and laser diodes [1]. Among them, gallium nitride (GaN) is a ubiquitous semiconductor material which is especially, susceptible of producing efficient blue/ultraviolet to display and lighting devices. Notwithstanding its superiority in optoelectronic and electronic device performances, GaN LEDs and transistors are still facing the manufacturing cost related issues while goggling low-cost modified LED device structures. Therefore, the alternative findings are necessary and important to overcome this major issue faced by LED manufacturing technology. This would be achieved by fabricating cost effective hybrid heterostructured LED devices by combining zinc oxide (ZnO), as the other counter part of the fabricated heterostructured LED device with GaN. In the past few decades, ZnO receives much more attention for ultraviolet/blue LEDs and high temperature/transparent electronics. It is worth to mention that, ZnO and GaN have similar lattice structure and relatively small lattice mismatch, which is the most important and desirable property for the improvement of light extraction efficiency from the fabricated heterojunction LEDs [2]. Besides, it is one of the most frequently used semiconductor material by its excellent physicochemical, optical and relatively low production cost features [3]. Due to wide direct band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV), ZnO is dominated to be a promising luminance material for the next generation ultraviolet/blue optoelectronic devices.
Recently, porous semiconductors receive considerable attraction due to their excellent optical properties such as enhanced luminescence intensity, improved photo response, and band gap shift. Surface nanostructuring of GaN has been intensively studied by several researchers for its tremendous applications in various fields such as in

optoelectronics [4], chemical sensors [5-6] and growth templates [7-8]. Among them, it has gained a great deal of attraction by serving as a strain-relaxed substrate for the growth of superior quality epitaxial thin films [9-10]. It is important to mention that the strained substrates provide high density of dislocations which are severely limiting the electron mobility, doping efficiency and lifetime of the manufactured devices which are the most important device parameters. Nanoporous GaN has been synthesised by adapting several synthesise methods such as dry etching method [11], UV assisted photo electrochemical anodic etching method [12-14] and electroless chemical etching methods [15]. Among them, UV assisted photo electrochemical etching technique is considered a potential technique due to its simple and cost-effective natures for developing nanoporous structure and it is more suitable for GaN surface roughening which renders uniform and high density of pores. Besides, it also provides smoother surfaces compared with dry etching method that suffered subsurface damage by ion bombardment and also highly anisotropic. Whereas, UV assisted photo electrochemical etching is easily controlled by simply varying its bias parameters; it also provides negligible damage, highly selective nature, and it is relatively inexpensive. Thus; it is widely used for GaN surface modifications.

It is identified that ZnO is intrinsically n-type semiconductor due to its associated interstitial defects such as zinc interstitial, oxygen vacancies and other structural related defects [16]. However, group III elements (Al, Ga and In) are widely used to sucessfully achieve n-type doping which are easily replaced by Zn ions in the crystal structure and substantially improve the electron carrier concentration [17-19]. Conversely, it is more difficult to grow p-type ZnO because of the instability of the doping ions. However, it has been continuously attempted by using either group I elements (Li, Na, and K) for Zn sites [20-21] or group V elements (N, P, As, and Sb) for O sites [22] throughout the worldwide researchers. Nitrogen is identified as a good candidate for acceptor doping of zinc oxide and a lot of papers report on p-type ZnO obtained as a result of nitrogen doping [23-24]. Nitrogen is highly preferred compared with other available acceptors by its similar ionic radius compared to oxygen and the availability of gas source for achieving p-type doping in ZnO structure.

In this communication, porous nanostructure was developed on the surface of GaN substrate by using UV assisted photo electrochemical etching method. Nitrogen doped ZnO thin film was grown on the fabricated porous GaN template by employing radio frequency magnetron sputtering technique at room temperature. The morphological, structural, electrical and optical properties of the porous nanostructures as well as nitrogen doped ZnO thin films were studied and the obtained results were presented.

MATERIALS AND METHODS

In this experimental study, porous gallium nitride template was utilized as substrate for the growth of nitrogen doped ZnO thin films. The total process was executed in two different stages. In the first stage, porous gallium nitride growth template was prepared from the commercial 2-inch diameter GaN wafer (from Technologies and Devices International Inc., USA) by UV assisted photo electrochemical etching in a custom-made Teflon cell containing a mixture of sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) with a 3:1 volume ratio. Platinum wire and GaN substrates acted as the cathode and the anode, respectively. The porous gallium nitride was formed at a constant current density of 10 mA/cm^2, under the illumination of an UV lamp with 500W power for an etching period of 60 minutes to develop sufficient deep porous nanostructures. The etched template was thoroughly rinsed with deionized (DI) water and then dried with high purity nitrogen gas prior to the coating process.

In the second stage of the experiment, HHV A500 radio frequency (RF)-sputtering system was employed with zinc oxide (ZnO) target (99.999% purity) to deposite nitrogen doped ZnO thin film. The base pressure was 3×10^{-5} mbar, that was raised to 2×10^{-2} mbar by purging the chamber with high purity argon and nitrogen gases that served as the sputtering and doping gases such as 10 and 5 SCCM (SCCM denotes cubic centimeter per minute) respectively through mass-flow-controlled inlets on the prepared porous template and the maintained power of the sputtering was 150 W. One micron thick nitrogen doped ZnO thin film was deposited onto the developed porous gallium nitride substrate. The deposited film was subsequently annealed in a tube furnace for one hour at 500ºC under nitrogen atmosphere. Finally, the porous gallium nitride and the deposited p-ZnO thin film morphological features were visualized by empoloying field emission scanning electron microscopy (FESEM) (model FEI/NovaNanoSEM450). The crystalline structure and orientation of the nitrogen doped ZnO thin film were ascribed with X-ray diffraction (XRD) (PAN analytical X'Pert PROMRDPW3040) with CuK_α radiation wavelength of 0.154 nm. Electrical properties were measured at room temperature by Van der Pauw method (Hall effect measurement Model: Accent/HL 5500 PC). The optical properties of the porous template as well as the nitrogen doped ZnO thin film were analysed at room temperature with JobinYvon HR 800UV,Edison, NJ, USA equipment. He–Cd laser (325

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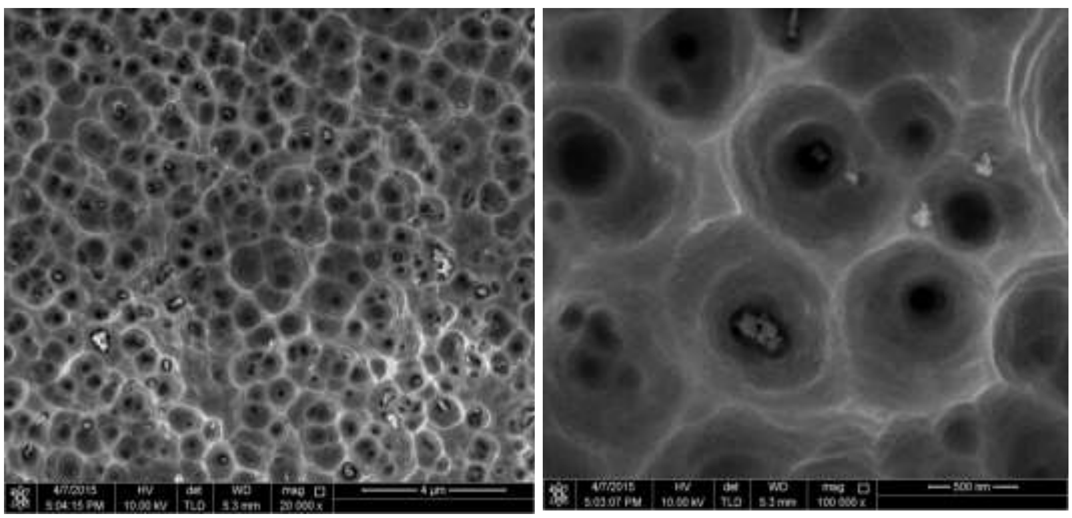
nm) and an argon ion laser (514.5 nm) were used as an excitation source for PL and Raman measurements, respectively.

RESULTS AND DISCUSSION

The involving mechanism of the photo electrochemical etching is, the associated semiconductor energy band bends towards downward direction [25] which depletes the electrons from GaN surface due to the applied bias. As a result, the accumulated holes are immediately injected into the GaN surface that oxidizes the surface due to the detachment of the bonding electrons and the resultant oxides are subsequently dissolved into the etchant by the etching reaction and eventually, porous structure was developed on the utilized GaN surface that was further improved by the illumination of UV light during etching. The microstructural features of the fabricated gallium nitride porous structures through UV assisted photo electrochemical etching were shown in figure 1 (a) and (b-enlarged image) respectively.



(a)

(b)

Figure 1: (a) FESEM micrograph of porous GaN template, (b) for high magnification

It is obvious that the pores are of spherical shape in contrast to other star, elongated, triangular and squarish type of pores that were previously reported [13] which implies that excellent porous network without any ridge morphology and distributed almost uniformly throughout the etching area of the studied semiconductor surface. Room temperature Raman analysis of pristine and the synthesised porous gallium nitride were carried out in the $z(x, \text{unpolarized})\,\bar{z}$ where x is in plane direction (perpendicular to the c-axis of the hexagonal crystal) as shown in figure 2. In this unpolarized scattering geometry, E_2(TO) and A_1(LO) Raman active phonon modes are only admitted by Raman selection rules and the corresponding modes were appeared in both pristine and porous GaN samples. In addition to that one more forbidden A_1(TO) Raman phonon mode appeared in porous GaN which clearly infers that the optical properties get modified by porosification process through the disordering of the crystalline structure that eventually alters the Raman scattering by the efficient coupling of the scattered radiation of the surface nano-building structure, i.e., fabricated nano porous structure.

It is interested to note that the allowed phonon modes in porous GaN film have higher Raman intensities compared to pristine GaN film due to the reduction of dislocations. In addition to that, these peaks get red shifted which has clearly confirmed the relaxation of the presenting compressive stress in the as grown GaN sample because of the quantum confinement effect of the porous structures [14]. The presence of the disorder-activated phonon mode of the porous structure in the recorded Raman spectra ensure the potential lighting applications. The optical properties of the synthesised porous structure was studied by recording room temperature photoluminescence (PL) spectra of the pre-etched and post-etched GaN samples was illustrated in fig.3. The obtained PL spectra clearly exhibit the substantially enhanced PL intensity of the porous structure than the pristine sample without any significant peak shift.

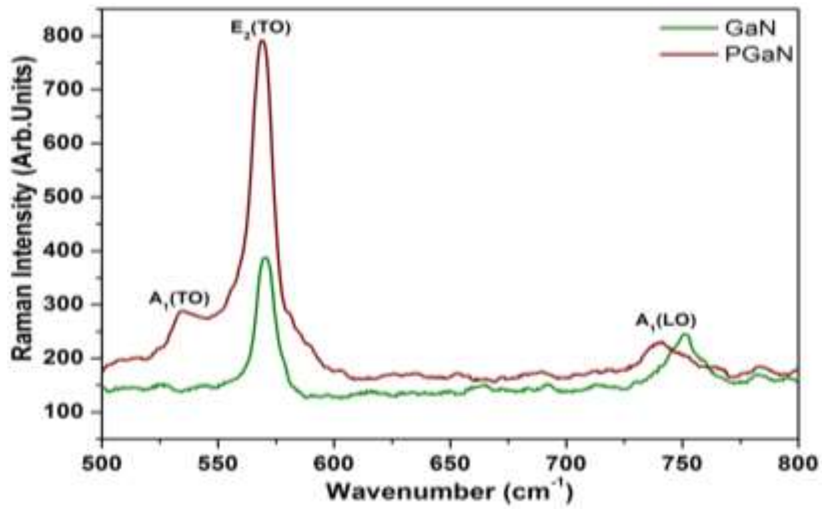


Figure 2: Raman spectra of Porous GaN and pristine (GaN) samples

The uniform PL line shape with the enormous improvement of the PL intensity was attributed to the reduction of the dislocation density and the effect of optical microcavity from the side walls of GaN porous crystallites compared to pristine GaN that provide the strong light scattering similar like Raman scattering. Moreover, higher surface to volume ratio of the porous structure enormously increase the number of participating electrons in the photoluminescence process, as a result of emitted photons was higher in porous GaN and the porosity has the dominant influence of the PL intensity enhancement that is highly desirable for lighting applications.

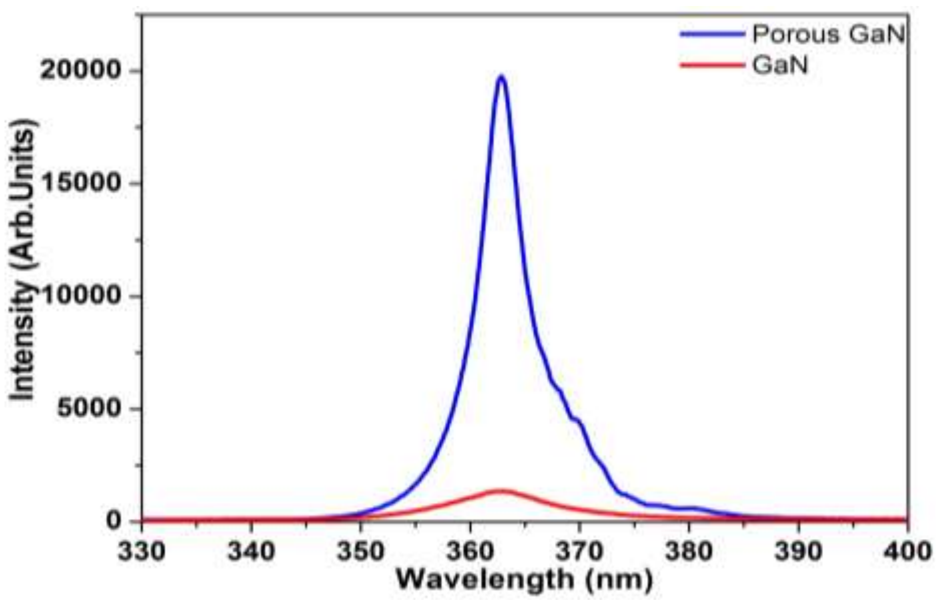
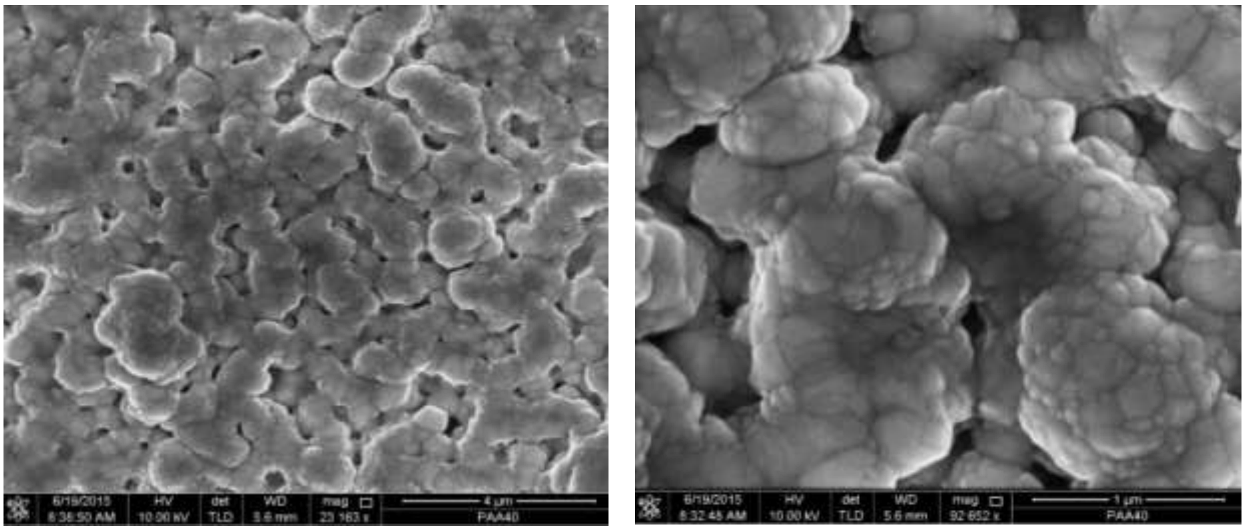


Figure 3: PL intensity of the pristine and porous samples

The grown nitrogen doped ZnO film obtained after being annealed at 500 ºC under nitrogen atmosphere was shown in fig.4 (a) and ((b- magnified image). It was found that the deposited nitrogen doped ZnO thin film was well adhered with the porous GaN substrate due to filling of the pores and producing of labyrinth patterns. It was ascribed that the sputtered nitrogen doped ZnO film has been deposited on top of the porous structure by keeping the air filled pores which was released during the annealing process and forming such kinds of growth patterns [26].



(a) **(b)**

Figure 4: (a) FESEM images of the nitrogen doped ZnO, (b) for high magnification

Furthermore, it has observed that the coated ZnO thin film is well closely connected with the porous GaN template. This may be owing to the occurrence of the replacement of etched portions by the deposited nitrogen doped ZnO thin film and it was believed that should effectively improve the stability of the fabricated porous structuring pattern. This kind of stress free growth templates, effectively reduce the dislocations of the depositing thin film and ensures the high crystalline quality of the grown thin films on top on it and was further confirmed through high resolution X-ray diffraction (HRXRD) analysis.

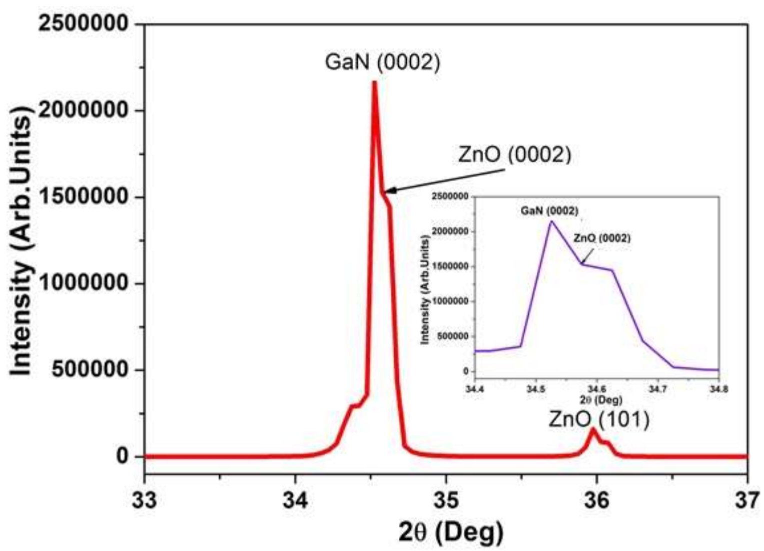


Figure 5: HRXRD patterns of the nitrogen doped ZnO on porous GaN template

The resultant HRXRD pattern of the grown nitrogen doped ZnO film was shown in figure 5. It is observed from that, the grown epitaxial thin film is oriented along (0002) crystal plane. Besides, the grown nitrogen doped ZnO thin film (2θ = 34.5750º) and the utilized porous GaN template (2θ = 34.5250º) having very high diffraction intensities towards the same crystal orientation. However, higher diffraction intensity of the grown ZnO layer compared to growth template undoubtedly ensures the excellent crystal quality due to the stress free as well as having lower crystalline defects of the porous GaN substrate. Electrical properties of the grown nitrogen doped ZnO film was measured at room temperature through Hall measurements with Van der Pauw method, in this measuring configuration, silver is used for metal contacts at the four corners of the square sample between the deposited nitrogen doped ZnO thin film of thickness around one micron and the measuring probe. It was found that the grown nitrogen doped ZnO thin film having p- type conductivity and the obtained values of carrier concentration and mobility were 6.14 x 10^{17} cm-3 and 0.126 cm^2/Vs, respectively.

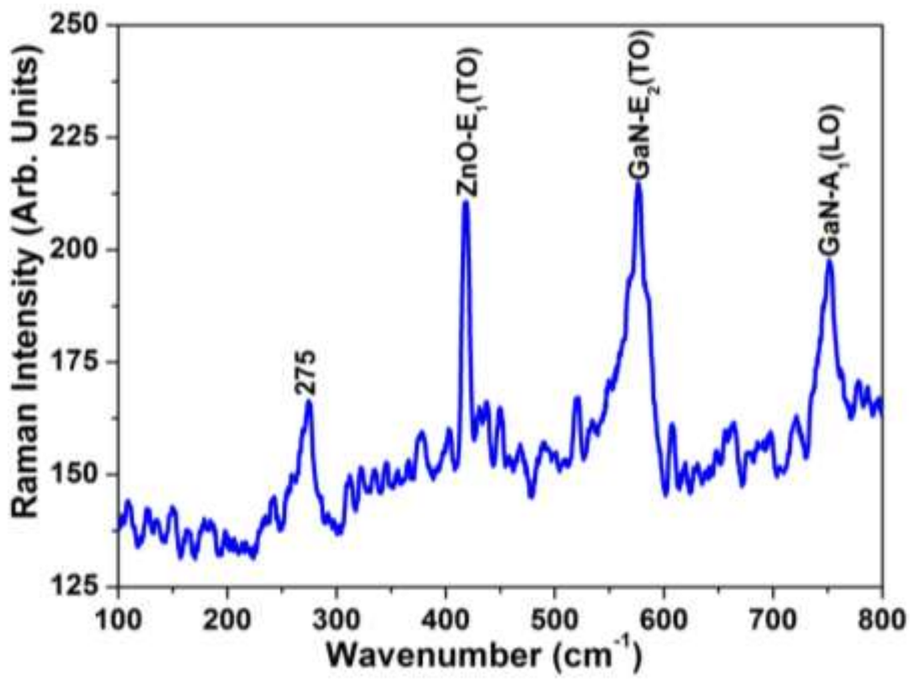


Figure 6: Raman spectra of the the nitrogen doped ZnO on porous GaN template

The optical features of the nitrogen doped p-type ZnO film then are studied with Raman spectral analysis under the same geometry as we did for porous GaN sample and the corresponding recorded Raman spectrum is shown in fig.6. We obtained two more ZnOs Raman peaks along with GaN related Raman modes, the unusual one is obtained at 275 cm-1, while the second is pointed out at 416 cm-1 that is ascribed by the allowed E1 (TO) phonon mode of ZnO thin film [27]. The peak at 275 cm-1 may be attributed due to the effect of nitrogen doping in the grown ZnO thin film [28]. The Raman study confirmed the presence of the nitrogen in the grown ZnO crystal lattices.

CONCLUSION

Porous nanostructure was developed on the surface of GaN substrates by UV assisted photo electrochemical etching technique. Nitrogen doped ZnO thin film was grown on the fabricated porous GaN template using radio frequency magnetron sputtering method at room temperature. The obtained FESEM micrographs reveal the developed pores are in spherical shape having excellent porous network without any ridge morphology and the deposited nitrogen doped ZnO thin film was well adhered with the porous GaN substrate due to filling of the pores and producing of labyrinth patterns. The recorded HRXRD pattern of the grown nitrogen doped ZnO film have very high diffraction intensity towards (0002) crystalline orientation along with GaN porous template. The appeared forbidden A_1(TO) phonon mode in porous GaN implied that the optical properties get modified by prosification process which, was further ascertained with the enormous improvement of the obtained PL intensity. Besides, the allowed phonon modes get red shifted ascertains the relaxation of the presenting compressive stress in the utilized GaN sample. The effect of nitrogen doping incorporated one more additional Raman mode, which was observed from Raman spectra of the grown ZnO thin film over the porous GaN substrate. The electrical measurement ensured the p-type doping of the grown nitrogen doped ZnO thin film. We believed that the presented work should help the new kind of heterostructure lighting devices in near future.

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