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Laser molecular beam epitaxy growth of porous GaN nanocolumn and nanowall network on sapphire (0001) for high responsivity ultraviolet photodetectors

Ch. Ramesh [a, b], P. Tyagi [a, b], Biplab Bhattacharyya [a, b], Sudhir Husale [a, b], K.K. Maurya [a, b], M. Senthil Kumar [a, b], S.S. Kushvaha [a, b, *]

[a] CSIR- National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi, 110012, India
[b] Academy of Scientific and Innovative Research (AcSIR), CSIR-NPL Campus, Dr. K.S. Krishnan Road, New Delhi, 110012, India

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We report on high-responsivity metal-semiconductor-metal (MSM) structure based ultraviolet (UV) GaN photodetectors fabricated on various GaN nanostructures such as porous nanocolumn network (PNCN), nanowall networks (NWNs), and granular and compact thin films. Different GaN nanostructures were hetero-epitaxially grown on c-sapphire using laser molecular beam epitaxy by tuning the AlN buffer layer growth parameters. High resolution x-ray rocking curve measurements indicate that the crystalline quality of GaN critically depends on the selection of AlN buffer layer growth conditions such as type of ablation target and growth temperature. The porous GaN nanostructures revealed a nearly stress-free wurtzite structure as deduced by Raman spectroscopy measurements. Room temperature photoluminescence spectroscopy showed that the GaN films possess a near band emission (NBE) peak at ~ 3.39 eV along with a broad yellow luminescence (YL) with maxima at 2.25 eV. For GaN PNCN and NWN structures, the NBE-to-YL emission ratio is more than an order higher compared to the GaN films. The fabricated MSM based UV-detector on GaN PNCN and NWN exhibited a high photo-responsivity of ~27.72 and 24.8 A/W, respectively, under 2 V applied bias at room temperature. The GaN PNCN and NWN nanostructures with excellent photo-responsivity and optical quality prove to be promising candidates for the fabrication of efficient UV photodetectors due to their continuity in lateral direction, high surface area-to-volume ratio and tailored surfaces.

1. Introduction

GaN and its alloys have drawn a special attention for various optoelectronic applications due to their exciting physical properties such as wide direct band gap, high mechanical strength, high saturation velocity, radiation hardness and stability at high temperature operation [1–5]. Some of the GaN based optoelectronic devices are high efficient light emitting diodes (LEDs), laser diodes (LDs), and ultraviolet (UV) photo-detectors (PDs), among others [6–10]. GaN devices are mostly fabricated on c-plane sapphire substrates due to their availability in large size, affordable cost and high temperature stability. However, GaN films grown on c-sapphire substrates possess high threading dislocation density and biaxial stress due to the large lattice mismatch between GaN and c-sapphire (14%), which strongly influences the structural and optical qualities of GaN films [11]. Various approaches such as nitridation of sapphire, intermediate AlN buffer layer and low temperature GaN buffer growth have been employed for improving GaN layer quality [12–17]. Apart from GaN film growth, researchers have also focused on growth of GaN nanostructures like nanorods, nanoflowers, nanocolumns, nanowalls, etc. due to their exciting physical properties such as high surface area-to-bulk volume ratio, low biaxial stress on lattice mismatched substrates and good optical response which are essential for the construction of nanoscale devices [18–20].

The UV-radiation detection is important for various applications like space communication, ozone layer monitoring, water purification, biological applications, flume detections, etc [21–25]. In last decade, researchers have developed UV- PD using various GaN

* Corresponding author. CSIR- National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi, 110012, India.
E-mail address: kushvahas@nplindia.org (S.S. Kushvaha).

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nanostructures due to several reasons such as high surface-to-volume ratio, effective light trapping, increased photoconductive gain and reduction of reflection loss [10,26–30]. Weng et al. fabricated PD based on GaN nanowires (NWs) grown on sapphire substrate and they obtained a photoresponsivity of 580 times higher than 2 μm thick GaN film [26]. Babichev et al. utilized transparent graphene contact to fabricate GaN NW UV-detector and obtained a photo responsivity of 25 A/W (357 nm) at 1 V applied bias [27]. Kang et al. presented the fabrication of high photo-responsive UV- and visible-light PDs by growing GaN and InGaN NWs at the side wall of GaN mesa through Au catalyst-assisted vapor-liquid-solid method [28]. Recently, GaN nanoflowers grown on Si (111) was utilized for the fabrication of UV-PD, in which, a photoresponsivity of 10.5 A/W at 1 V bias (325 nm light) was achieved [29]. Liu et al. observed high photoresponsivity and specific detectivity in the lateral meso-porous GaN UV-photodetector [30]. Among GaN nanostructures, nanocolumn (NC) and nanowall network (NWN) show added advantages for optoelectronic applications due to their enhanced light trapping and extraction behaviors, which can significantly improve the device efficiency. Moreover, the device integration with porous nanostructures is easier than NWs due to their continuity along the lateral direction. Yet, the fabrication of UV-PDs using porous nanocolumn network (PNCN) and NWN GaN have not been studied as per the available literature.

Here, we present the effect of growth temperature and ablation target employed for AlN buffer on the formation and the properties of GaN nanostructures grown on c-sapphire using laser molecular beam epitaxy (LMBE). A compact GaN film was obtained for AlN buffer grown using Al metal target whereas porous GaN nanostructures were grown when solid AlN target was employed for buffer AlN growth at similar growth conditions. The metal-semiconductor-metal (MSM) structure based UV PDs were fabricated on various GaN films (granular and compact thin films) and porous nanostructures (PNCN and NWN) grown by LMBE technique and compares their photo-response properties. We have observed high photo-responsivity and external quantum efficiency for the GaN nanostructures over the film, ascertaining the possibility of fabrication of high responsive PDs using PNCN and NWNs. The possible mechanisms for growth and high responsivity of porous nanostructures have been discussed in more details and it was found that the PNCN structure has the advantage over film for PD devices.

2. Experimental

The epitaxial GaN nanostructures were grown on pre-nitrided c-sapphire substrate using ultra-high vacuum (UHV) LMBE growth technique (base pressure: 2×10^{-10} Torr) by varying the AlN buffer layer growth conditions. Initially sapphire substrate was cleaned with standard organic solvents and degassed at 250 °C in a load lock chamber for few hours. The thermal cleaning of sapphire substrate was performed in the main UHV growth chamber by slowly raising the temperature to 850 °C for 10 min. The thermally cleaned sapphire substrate was nitridated at 700 °C in presence of active nitrogen species generated by rf-nitrogen plasma source which is operated at 400 W forward power with 1.1 sccm of semiconductor grade nitrogen flow. We have grown two sets of GaN samples by varying the AlN buffer layer growth targets [31]. The schematic diagram of sapphire nitridation, AlN buffer layer and main GaN growth sequences of samples S1, S2, S3 and S4 is shown in Fig. 1. In first set, the AlN buffer layer was grown on nitrided sapphire at 600 (S1) and 700 °C (S2) by ablating high purity Al metal target in presence of active nitrogen plasma. In second set, an AlN solid target was ablated in presence of additional nitrogen plasma for the growth of the AlN buffer layer at 700 (S3) and 800 °C (S4). Finally, the main-GaN was grown at 700 °C on AlN buffer grown pre-nitrided sapphire substrate by ablating a high purity solid GaN (99.9999%) target. A KrF excimer pulsed laser (wavelength = 248 nm; pulse = 20 ns) was used to ablate the solid Al, AlN and GaN targets. Additional active N radicals were supplied during AlN and main-GaN growth by an r.f. N_2 plasma source (250 W power, 0.4 sccm N_2 gas flow). The entire growth sequence was monitored *in-situ* by using reflection high energy electron diffraction (RHEED) with 25 kV operating voltage.

The surface morphology and structural property of the LMBE grown GaN samples have been investigated using field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), high resolution X-ray diffraction (HR-XRD) and Raman spectroscopy. The plan- and 45° tilt-view images of the GaN nanostructures were taken using a FE-SEM (FIB, ZEISS, Germany) operated at 5 KV. The AFM in tapping mode was employed to study the surface topography of AlN buffer layers, GaN S1 and S2 using Si tip of radii less than 10 nm. The crystalline quality of the LMBE grown GaN nanostructures were deduced by X-ray rocking curve (XRC) measurements along (0002) and (10–12) diffraction planes by a PANalytical HR-XRD system using $CuK_{\alpha1}$ source with the wavelength of 0.15406 nm. The structural properties were also analyzed by performing Raman spectroscopy in backscattering geometry by optically exciting the GaN samples with a laser source of wavelength 514.5 nm. The optical property was characterized by photoluminescence (PL) spectroscopy using He-Cd laser source with a wavelength of 325 nm at room temperature. The MSM structure based UV-PDs were fabricated on all LMBE grown GaN samples (S1-S4) by depositing gold contacts (thickness ~ 100 nm) using patterned mask by sputtering technique. The active area of the GaN PDs devices is ~4×10^4 μm^2. Electrical properties of the fabricated GaN PD devices were characterized by current-voltage (I-V) measurements at room temperature. The sheet resistance of the samples (S1-S4) measured at room temperature are 8380, 3100, 78 and 42 Ω /cm^2, respectively. The time dependent photoresponse of device was investigated with probe station (Cascade Microtech EPS150TRIAX) in shield enclosure by illumination of UV-laser source with a wavelength of 325 nm and a power density of 13 mW/cm^2 under 20 s ON/OFF time intervals.

3. Results and discussion

3.1. Structural and optical properties of LMBE grown GaN nanostructures

Fig. 2(a) shows the FESEM image of LMBE grown GaN on low temperature (600 °C) AlN buffer layer grown using Al target on nitridated sapphire substrate. The FESEM image reveals that agglomerated GaN islands were grown with grain sizes of 60–120 nm. On the basis of the morphology, we defined it as granular GaN thin film [sample S1]. When the AlN buffer layer growth temperature increased from 600 to 700 °C, the GaN surface morphology changed from granular to nearly compact film structure with large grain sizes of 80–160 nm as shown in Fig. 2(b) [sample S2]. Furthermore, the root mean square (RMS) surface roughness of LMBE grown S1 and S2 samples were measured using AFM images [Fig. 2 (c–d)] of scan area 2 μm × 2 μm. The analyzed RMS roughness values are 15.45 and 13.97 nm corresponding to granular (S1) and compact (S2) GaN film samples, respectively. Here, the little higher surface roughness of S1 is attributed due to the presence of voids as revealed by AFM and FESEM images. The three-dimensional (3D) GaN growth was also supported by *in-situ* RHEED image taken during the GaN growth. The RHEED patterns of S1 and S2 samples along [11–20] direction are shown in the inset of