Materials Science in Semiconductor Processing 89 (2019) 143–148

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

AlGaN nanowall network structure grown on sapphire (0001) substrate by laser molecular beam epitaxy

Prashant Tyagi[a,b], Ch. Ramesh[a,b], S.S. Kushvaha[a,b], M. Senthil Kumar[a,b,*]

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

ARTICLE INFO

Keywords:
AlGaN
Heteroepitaxy
High resolution x-ray diffraction
Surface morphology
Raman spectroscopy
Photoluminescence

ABSTRACT

Self-assembled AlGaN nanowall networks have been grown heteroepitaxially on sapphire (0001) substrate using laser molecular beam epitaxy (LMBE) technique. The effect of growth temperature on the formation of AlGaN nanowall network structure has been studied in the range of 500–700 °C. It is found that the growth of AlGaN under strong N-rich flux condition at a high growth temperature of 700 °C is conducive for the formation of self-assembled nanowall network. *In-situ* reflection high energy electron diffraction exhibits the three-dimensional growth of the AlGaN nanowall network structure oriented along c-axis. The nanowall width and pore size are measured to be 10–40 and 30–70 nm, respectively, by using field emission scanning electron microscopy. From room temperature photoluminescence measurement, a strong ultra-violet (UV) emission at about 3.52 eV due to band-to-band transition is obtained for the AlGaN nanowall structure with a high UV-to-yellow luminescence intensity ratio indicating a good optical quality. The grown AlGaN nanowall network is suitable for the applications in field emitters, photo-detectors and other nitride-based optoelectronic devices.

1. Introduction

Group-III nitrides are known for their application as optoelectronic devices active from infra-red (IR) to deep ultra-violet (UV) region of the electromagnetic spectrum due to their wide, tuneable band gap between 0.7 and 6.2 eV [1]. Moreover, AlGaN based ternary alloys are the key for high power and high efficient GaN-based UV light emitting diodes (LEDs), Schottky diodes and Laser diodes (LDs) that have major industrial and research applications such as three-dimensional (3D) printing technology, blue-ray technology, etc.[2–6]. AlGaN alloy also plays an inevitable role in the fabrication of AlGaN/GaN heterostructure based high electron mobility transistors (HEMTs) for high-temperature and high-power applications [7].

In recent time, III-nitride nanostructures have attracted the attention of many researchers around the globe due to their unique physical, electronic and optical properties as compared to their bulk counterpart [8,9]. Nanostructured materials are best suitable not only for understanding and study the fundamental physics but also in realizing nanoscale devices [10,11]. Among the nanostructures, nanowall networks have gained a special attention due to their high surface-to-volume ratio and electrical continuity in the lateral direction [12]. Several authors have reported the growth of GaN nanowall network structure on various substrates using molecular beam epitaxy (MBE) [13–15]. Recently, the evaluation of GaN nanowall network and their microstructure have been studied more systematically [16–18]. We have also reported on the low temperature growth of GaN nanowall network on GaN template using laser molecular beam epitaxy (LMBE) technique [19]. LMBE is a relatively less explored technique in the development of group-III nitrides. But, in LMBE, the laser used to ablate the target material assists the kinetic energy of precursor ad-atoms for surface mobility, which, in turn, helps to reduce the process temperature [20].

The growth of ternary alloy nanostructures is a very challenging task as one has to maintain material quality and specific alloy mole fraction simultaneously [21]. There are few reports on the growth of different kinds of AlGaN nanostructures like nanorods, nanocolumns, nanotowers etc. [22–24]. However, to the best of our knowledge, the growth of AlGaN nanowall network structure has not been reported in the literature yet. Here, we discuss the growth of self-assembled AlGaN nanowall network on c-plane sapphire by LMBE process and their physical properties.

2. Experimental details

Self-assembled $Al_{1-x}Ga_xN$ nanowall network structure was grown on sapphire (0001) substrate by the ablation of Al_xGa_{1-x} alloy target under RF nitrogen plasma ambient. The role of growth temperature on the

* Corresponding author.
E-mail address: senthilmk@nplindia.org (M. Senthil Kumar).

https://doi.org/10.1016/j.mssp.2018.09.011
Received 19 July 2018; Received in revised form 6 September 2018; Accepted 13 September 2018
1369-8001/

formation of nanowall structure was studied in the range from 500 to 700 °C. The growth was carried out in an ultra-high vacuum (UHV) LMBE system equipped with KrF excimer laser (wavelength 248 nm with 25 ns pulse width), target carrousel, and radio-frequency (RF) nitrogen plasma source. The background pressure of the growth chamber was about 2×10^{-10} Torr. A micron thick molybdenum layer was coated on the back side of the sapphire substrate to achieve a uniform heating across the substrate. After the thermal cleaning at 850 °C under UHV condition, sapphire nitridation was carried out at 700 °C for 35 min by supplying RF nitrogen plasma. The RF power and the nitrogen partial pressure were kept constant at 400 W and 7.2×10^{-5} Torr, respectively. Due to sapphire nitridation, a few monolayers of AlN is expected to form on the surface, which has a close lattice match to $Al_xGa_{1-x}N$ and act as a buffer. After the nitridation, the desired growth temperature (500–700 °C) was achieved and the Al_xGa_{1-x} (x = 0.2) alloy target was ablated using the KrF excimer laser with an energy density of 3–5 J/cm^2 and a frequency of 45 Hz. The AlGa target was prepared by alloying high pure (> 6 N) elemental Ga and Al metals with an atomic ratio of 80:20. The details of alloy target preparation is discussed elsewhere [25]. The nitrogen partial pressure and the RF plasma power were tuned to $\sim 2 \times 10^{-5}$ Torr and 250 W, respectively, during the $Al_{1-x}Ga_xN$ growth and the growth was carried out for 2 h under a continuous supply of nitrogen plasma to maintain the N-rich growth condition. With the irradiation of each KrF excimer laser pulse, a plume is generated due to the absorption of laser energy by the alloy target. The RF nitrogen plasma is supplied continuously along with the target plume and it expands towards the substrate for the deposition. After the growth, the sample was gradually cooled down to room temperature. All the experimental parameters except growth temperature were kept constant for all the growth.

The grown samples were characterized for their surface morphology, structural, compositional, optical and electrical properties by using field emission scanning electron microscopy (FESEM), high resolution x-ray diffraction (HR-XRD), energy dispersive x-ray analysis (EDX), Raman spectroscopy, photoluminescence (PL) and current-voltage measurements. A Cu $K_{\alpha 1}$ x-ray source was used for HRXRD measurements (PANalytical X′pert PRO system). The FESEM mode of focused ion beam system (ZEISS, Germany) was used to obtain the surface morphology of the grown AlGaN samples, at an operating voltage of 5 kV. The PL data were recorded at room temperature with an excitation laser source of wavelength 266 nm.

3. Results and discussion

In the growth of III-nitrides by MBE/LMBE process, it is well-established that N-rich growth condition limits the surface mobility of group-III adatoms, due to which, a rough surface GaN is obtained (indicated by spotty RHEED pattern). On the other hand, in metal-rich flux condition, the layer grows two-dimensional (2D) with a smooth surface due to the high surface mobility of adatoms (indicated by streaky RHEED pattern). Thus, several researchers have employed *in-situ* RHEED as a tool to monitor the flux situation during GaN growth in MBE processes [26–29]. In this work, we have studied the growth of AlGaN under N-rich condition and the entire growth process was monitored *in-situ* using the RHEED observation. The sequence of LMBE process for AlGaN growth and the RHEED patterns recorded at different stages of the AlGaN growth process on sapphire substrate are shown in Fig. 1. A RHEED pattern of short streak with kikuchi lines was observed for the bare-sapphire substrate after thermal cleaning at 850 °C, which implies an atomically flat surface desirable for an epitaxial growth. After substrate nitridation at 700 °C, additional elongated streaks appeared along with sapphire RHEED pattern indicating the surface modification due to AlN formation, which is essential to improve the quality of group-III nitrides over sapphire as it reduces the lattice mismatch during heteroepitaxial growth. During AlGaN growth, the RHEED pattern turned into spotty features, which indicated the 3D growth normal to the substrate [29]. Previously, we had reported the growth of smooth surface AlGaN layer under metal-rich condition by the supply of modulated nitrogen plasma as monitored by streaky RHEED pattern [25].

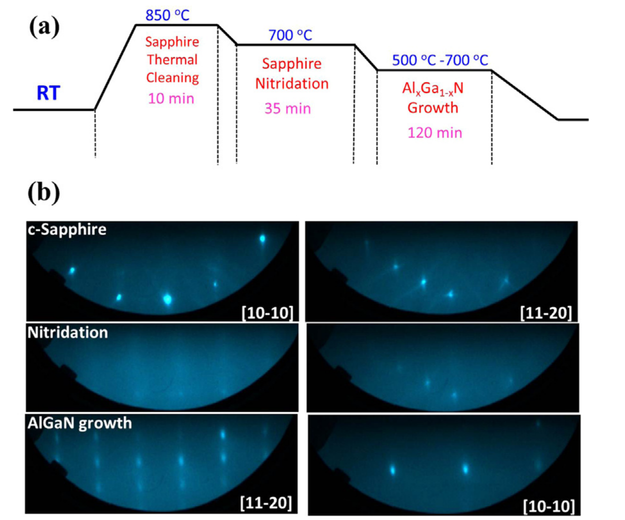

Fig. 1. (a) Growth sequence of AlGaN by LMBE process, (b) Typical *in-situ* RHEED patterns observed at difference stages of AlGaN growth process.

It is observed that the quality of AlGaN grown below 600 °C was inferior with a strong alloy fluctuation. Therefore, the samples grown at 600 and 700 °C are considered for the analysis here. The HR-XRD 2Θ-ω scans of AlGaN samples grown at 600 and 700 °C are presented in Fig. 2(a). The XRD spectra reveal a set of (0001) plane peaks for AlGaN and sapphire substrates indicating that the AlGaN grows along c-axis on sapphire with wurtzite hexagonal structure, as noticed by the RHEED observations. A shift in XRD peak position of AlGaN samples is observed towards higher angle as compared to GaN peak position. This indicates a decrease in the GaN lattice parameter due to the incorporation of Al into the GaN lattice. Also, the XRD peak positions shifted further to the higher angle when the growth temperature was increased from 600 to 700 °C, which implies more Al incorporation with increasing growth temperature. The overall shift in AlGaN peak position is minimal since the lattice mismatch between GaN and AlN is small about 2.4%. Furthermore, from the peak shift of (0004) plane, we estimated the Al composition by using Vegard's law [30], which turned out to be about 3% and 8.7% for the AlGaN grown at 600 and 700 °C, respectively. Here, it is presumed that the grown samples are relaxed with negligible inherent strain since the layers are thick consisting of deep surface pits / porous nanostructure. The Al composition increases at higher temperature AlGaN growth due to an increase of Al/Ga flux ratio on the growth surface resulting from pronounced Ga desorption at 700 °C. Masuyama et al. studied the AlGaN film growth by dual-beam pulsed laser deposition (PLD) using Ga and Al metal targets ablated under nitrogen gas pressure of 5 Pa [31]. They observed that the Al composition in the grown film increased with the increase in the growth temperature from 720 to 775 °C due to Ga re-evaporation. Rupp et al. employed the laser-induced reactive epitaxy to grow AlGaN films using laser ablation of AlGa alloy target under a nitrogen gas pressure of 0.1–0.13 mbar, in which, the Al content drastically increased in the grown film once the growth temperature increased above 800 °C [32]. In the earlier report by Willmott et al. on AlGaN growth by pulsed reactive crossed-beam laser ablation using liquid $Al_{0.50}Ga_{0.50}$ alloy and gas pulse of nitrogen, it is observed that the Al content strongly increased in the film above 96% for the growth temperature ≥ 700 °C [32]. The vapour pressure of Ga at this typical substrate temperature is two orders of magnitude higher than that of Al, which leads to higher Al/Ga ratio due to Ga re-evaporation [31,33].