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Influence of growth temperature on laser molecular beam epitaxy and properties of GaN layers grown on c-plane sapphire

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ABSTRACT

We have investigated the influence of growth temperature on the in-plane strain, structural, optical and mechanical properties of heteroepitaxially grown GaN layers on sapphire (0001) substrate by laser molecular beam epitaxy (LMBE) technique in the temperature range 500–700 °C. The GaN epitaxial layers are found to have a large in-plane compressive stress of about 1 GPa for low growth temperatures but the strain drastically reduced in the layer grown at 700 °C. The nature of the in-plane strain has been analyzed using high resolution x-ray diffraction, atomic force microscopy (AFM), Raman spectroscopy and photoluminescence (PL) measurements. From AFM, a change in GaN growth mode from grain to island is observed at the high growth temperature above 600 °C. A blue shift of 20–30 meV in near band edge PL emission line has been noticed for the GaN layers containing the large in-plane strain. These observations indicate that the in-plane strain in the GaN layers is dominated by a biaxial strain. Using nanoindentation, it is found that the indentation hardness and Young's modulus of the GaN layers increases with increasing growth temperature. The results disclose the critical role of growth mode in determining the in-plane strain and mechanical properties of the GaN layers grown by LMBE technique.

1. Introduction

In the last two decades, group III-nitride materials have derived keen research interests and been highly successful in proving their cutting-edge applications in optoelectronics and high power, high frequency electronics due to its wide direct bandgap, high mobility and high breakdown field [1–5]. The performance of group III-nitride devices highly depends on crystal quality and strain of epitaxial layers that are building the device structure. Due to the difficulty in achieving bulk GaN growth, III-nitride layers are normally grown hetero-epitaxially on foreign substrates that lead to generation of a high density of crystalline defects and high strain in the grown epitaxial layers. The crystalline defects play a key role in determining the efficiency of devices, and there are numerous reports related to the studies of quantitative analysis of defect concentrations [6–8]. Thus, the minimization of defects and growth of high quality epitaxial layers are required to promote the production of reliable and high performance devices. The conventional techniques for GaN growth are metal organic chemical vapor deposition (MOCVD), hydride vapor phase epitaxy (HVPE), and plasma assisted molecular beam epitaxy (PAMBE). Laser molecular beam epitaxy (LMBE) is a relatively new and least explored technique for III-nitride growth. But, LMBE has an advantage over other conventional techniques that the growth of GaN films can occur at low temperatures due to the high kinetic energy of film precursors produced by laser ablation [9–11]. Low temperature growth process is critical to further improve GaN epilayer quality by employing thermally vulnerable but closely lattice-matched substrates like ZnO, $LiGa_2O_3$, etc. and also to develop high quality In-rich III-nitride materials.

III-nitrides are grown hetero-epitaxially on different substrates like sapphire, silicon, silicon carbide, etc. But, due to the fact that

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sapphire has a good epitaxial symmetry, high thermal stability, affordable cost and its availability in large wafers, most of the GaN devices are fabricated on sapphire. However, sapphire has a large lattice constant and thermal expansion coefficient mismatch with GaN. Consequently, the grown GaN epitaxial layers are characterized for a high level of in-plane strain and structural defects like dislocations, stacking faults, etc. In general, nitridation of sapphire substrate is carried out before GaN growth as pre-nitridation helps in formation of an intermediate AlN layer for the growth of high quality GaN layers [12,13]. In addition, growth temperature plays a key role in determining the properties of GaN epitaxial layers [14,15]. The reports on LMBE growth of GaN on sapphire substrates are very limited in literature, and the effect of LMBE growth parameters on the physical properties of grown GaN layers is not well understood yet. Particularly, there is no data reported on the mechanical properties of LMBE grown GaN layers using nanoindentation. Considering the advantages of LMBE growth technique in developing III-nitride materials, it is vital to systematically study the effect of experimental parameters on the GaN layer properties. Especially, the in-plane strain in GaN/sapphire lattice mismatched structure determines the characteristics of the grown epilayers and heterostructures [16]. In this paper, we report on the growth temperature dependant in-plane strain, structural, optical and mechanical properties of GaN layers on sapphire (0001) grown by the laser ablation of a HVPE grown GaN solid target using LMBE technique. The properties of GaN layers are found to improve with increasing growth temperature and good quality GaN epitaxial layers have been obtained by growing them above 600 °C.

2. Experimental details

The growth of epitaxial GaN layers were carried out on pre-nitridated sapphire (0001) substrate in a LMBE system equipped with *in-situ* reflection high energy electron diffraction (RHEED), and a radio frequency (RF) nitrogen plasma source. The base pressure of growth chamber was 2×10^{-10} Torr. The low background pressure minimizes the presence of impurities or residual contaminations. The back side of sapphire substrate was coated with 1 μm thick molybdenum layer to increase the absorption of heat and uniform heat distribution. The substrates were cleaned by organic solvents and de-ionized water before loading into the load lock chamber. Prior to growth, the substrate was degassed for several hours at 250 °C in the load-lock chamber of the LMBE system followed by a thermal cleaning at 850 °C for 10 min in the UHV chamber. After thermal cleaning of sapphire substrate, nitridation process was performed at 700 °C with an RF plasma power of 400 W and nitrogen gas flow of 1.2 sccm for 35 min. A high pure HVPE grown GaN solid target (6 N) was ablated using a KrF excimer Laser (248-nm wavelength, 25 ns pulse) with an energy density of about 5 J/cm^2 and a laser frequency of 10 Hz. In the system, nitrogen radicals were supplied through RF nitrogen plasma cell for stoichiometric GaN growth. The nitrogen gas flow and the r.f. power were tuned to 0.4 sccm and 250 W during GaN growth. GaN films were grown for a fixed duration of 2 h on nitridated sapphire substrate at various temperatures in the range 500–700 °C keeping all the other experimental parameters constant. The entire growth sequence was monitored through *in-situ* RHEED observations. From the thickness measurement of grown GaN layers, a growth rate of 120–140 nm/h is obtained in the growth temperature range employed in this study.

The irradiation of each KrF laser pulse with GaN target generates plasma plume due to strong absorption of laser energy by the GaN target. The plasma plume is generated continuously as per the designated laser frequency and expands towards the substrate for film deposition. The laser ablated plume contains GaN, GaN_{1-x}, and Ga species [17]. The nitrogen plasma constituents diffuse into the growth zone from the r.f. cell due to pressure gradient and contribute for the growth by supplying additional flux to maintain film stoichiometry. The epitaxial GaN layer growth is achieved by the reaction between the laser plume and the supplied nitrogen radicals on the sapphire substrate under a growth pressure of ~2×10^{-5} Torr [15].

The LMBE grown GaN epitaxial layers have been characterized for their structural properties by high resolution x-ray diffraction (HRXRD) and Raman scattering spectroscopy using a PANalytical HR-XRD system with Cu Kα_1 source and a triple monochromator spectrometer (T-64000, Jobin-Yvon/Horiba group) with an excitation source of 514.5 nm wavelength, respectively. A multimode-V Veeco atomic force microscopy (AFM) was used to image the surface morphology of the GaN layers while the photoluminescence (PL) characterization was performed using a 266 nm laser line at room temperature to examine their optical emission properties.

The nanoindentation measurements of GaN films deposited on sapphire substrates were performed by high resolution IBIS-nanoindenter (Fischer-Cripps Laboratories Pty. Limited, Australia) equipped with a diamond Berkovich indenter. All measurements were performed with a fixed load of 1 mN. In order to perform the nanoindentation measurements, the samples were mounted with the help of crystal bond wax on a metallic specimen holder with a magnetic base. Extreme care was taken to maintain parallelism while mounting the specimen to the sample holder. The entire system is left for four hours to attain thermal equilibrium before test to eliminate the error due to thermal drift. It is very important to use accurate dimensions of the indenter for the analysis of the results. For the Berkovich indenter, the radius of the tip can vary depending on the quality of the manufacture. To account for these variations in indenter geometry, an area function is applied to the result, which is a ratio expressed as a function of the plastic depth. For best results, a series of indentations were made on the sample and the average values used for the calculation of harness and Young's modulus.

3. Results and discussion

The *in-situ* RHEED showed an epitaxial growth of GaN over sapphire (0001) substrate with a 30° in-plane rotation with respect to the sapphire substrate. The patterns were spotty in all the growth runs exhibiting a three-dimensional growth of GaN layer, which indicated the N-rich flux condition at the growth surface. The ω-2θ XRD scans of the GaN epitaxial layers grown on pre-nitridated sapphire at various temperatures are presented in Fig. 1. The spectra show diffraction peaks only from {0001} family of crystal planes of wurzite GaN and sapphire indicating that single crystalline GaN layers are grown along c-axis. The intensity of GaN (0002) peak increased and the full width at half maximum (FWHM) of the GaN (0002) peak decreased significantly when the growth temperature was raised from 500 to 700 °C. The peak height and width generally depend on the thickness and the mosaic structure of the grown films. Considering the small variation of layer thickness among all samples, i.e. 240–280 nm, the change of XRD peak parameters can be largely related to the crystalline quality of the layers as confirmed by Raman and PL data as discussed below. The sharp and intense XRD peak observed for 700 °C implies that the higher growth temperature improves the crystalline property of the LMBE grown GaN layer. At higher growth temperatures, there is an increase in the kinetic energy of precursor atoms in addition to the laser power which further increases their surface mobility enabling the precursor atoms to find the proper lattice site to get incorporated into the growing layer. As a result, not only the crystalline quality but also the grain size of the GaN crystallites is