The effect of substrate nitridation temperature and buffer design on the quality of GaN epitaxial films

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ABSTRACT

A key issue for the entire field of III−Nitride materials growth is the unavailability of high quality lattice matched substrates. The most commonly used growth substrate, sapphire, still imposes constraints on the GaN film quality due to the lattice mismatch and control of polarity between sapphire and GaN . Therefore, the first stage of growth conditions (i.e. nitridation, types of buffer layers, growth ratio, annealing condition of buffer layer and so on) determines the characteristics (i.e. polarity, quality, and surface morphologies) of the subsequent GaN epitaxial layers. .Therefore, it is necessary to optimize the interface with the substrate and growth condition of buffer growth for the subsequent GaN epitaxial layer. In this work, we present the control of quality of GaN epitaxial layers with different nitridation temperatures. We present the dramatically improved structural quality of GaN epitaxial layers by optimized nitridation conditions.

INTRODUCTION

The development of a technology based on GaN and related alloys for LEDs and laser emitting in the green−blue−ultraviolet range has required a better understanding of heteroepitaxial growth of highly lattice−mismatched systems, such as GaN/sapphire. Surface reactions are important for thin film growth, and their knowledge is necessary for the control of growth process as well as material quality. In this context, many papers already underlined the importance of the substrate/epitaxial layer interface processing, such as nitridation of the sapphire substrate to have a few monolayer of AlN to reduce the lattice mismatch. Nitridation of the sapphire substrate generally precedes the buffer layer growth [5,6]. Nitridation parameters such as nitrogen precursor [7], nitridation time [8], and temperature [9,10] can strongly affect the properties of epilayers.

In this work, we present data on the effect of the substrate/GaN epitaxial layer engineering, i.e., the substrate nitridation temperature and buffer layer on the control of quality and polarity of GaN epitaxial layers grown by remote plasma assisted methods.

A r.f. (13.56 MHz) plasma source is used to integrate in an unique low temperature dry technology all the steps involved in the GaN growth, such as processes of substrate cleaning, substrate nitridation, and buffer and bulk layer growth. Specifically, a N_2 plasma is used to nitridize the sapphire surface. Various temperatures in the range 100 − 700 °C have been investigated and a temperature as low as 200°C has been found to yield high−quality GaN epilayers by plasma assisted methods. This is because the 200 °C of N_2 plasma nitridation is the temperature yielding a coherent and homogeneous AlN layer. In−situ real time monitoring and control of the chemical and structural surface modification is used to elucidate and control the chemistry of GaN epitaxial growth. The results obtained for GaN epilayers growth by RP−MOCVD are comparable to that obtained for GaN epitaxial layers growth by rf−MBE. Spectroscopic ellipsometry (SE), X−Ray diffraction (XRD), photoluminescence, atomic force microscopy (AFM), are provided to show the impact of the nitridation process and the growth conditions on the GaN film quality.

EXPERIMENTAL

GaN epitaxial layers with a thickness of ~ 1µm were grown on buffer layers on (0001) sapphire. In order to study the effect of the interface GaN/substrate preparation on the GaN bulk quality, ~ 30 nm GaN buffer layers were grown at 500 °C, 1 Torr and a TMGa flux of 38 µmol/min. The sapphire substrate was nitrided by a N_2 r.f. remote plasma to avoid any radiative damage and ion bombardment at the low temperature of 200°C and the high temperature of 700°C.

The GaN epitaxial layers were grown using a N_2 rf plasmas and trimethylgallium (TMGa) as precursor. The rf N_2

plasma was operated at 1 Torr, 400 W and at a flow rate of 1 slm. Because of the presence of methyl radicals from TMGa decomposition in the RP−MOCVD growth, H_2 was also added to the N_2 remote plasma in order to have H−atoms active in the carbon removal from the growing surface. GaN epilayers were grown at 750 °C varying the TMGa flux in the range 38−78 µmol/min.

Real time measurements of laser reflectance interferometry (LRI), spectroscopic ellipsometry (SE) were used to monitor the chemistry of the surface modification during growth. AFM, photoluminescence and XRD were used to evaluate epilayers quality. .

RESULTS AND DISCUSSION

Figure 1 shows the SE spectra of the real and imaginary parts of the sapphire pseudodielectric function recorded after N_2 rf remote plasma nitridation of sapphire at the different temperatures of 200°C and 700 °C. In particular, the increase of the real part and the decrease of the imaginary part of the sapphire pseudodielectric function to negative values in Fig. 1 are consistent with the formation of a very thin layer of AlN, as depicted from the model in the inset and described in detail in Ref [11]. In contrast, for nitridation the higher temperature of 700 °C, a strong increase of the and hence of the absorption of sapphire is found. This increase indicates that the layer forming by nitridation at high temperatures on sapphire is not a transparent AlN layer, but an absorbing specie accumulates on the sapphire surface. The SE data that were corroborated by the XPS analysis of the surface indicate the formation of a homogeneous 6Å thick AlN layer during sapphire nitridation at 200 °C, while 20Å thick discontinuous and inhomogeneous nitrided layer including both AlN and NO forms during nitridation at 700 °C in RP−MOCVD. This result is similar to what reported for GaN growth by MBE using a rf N_2 plasma source.

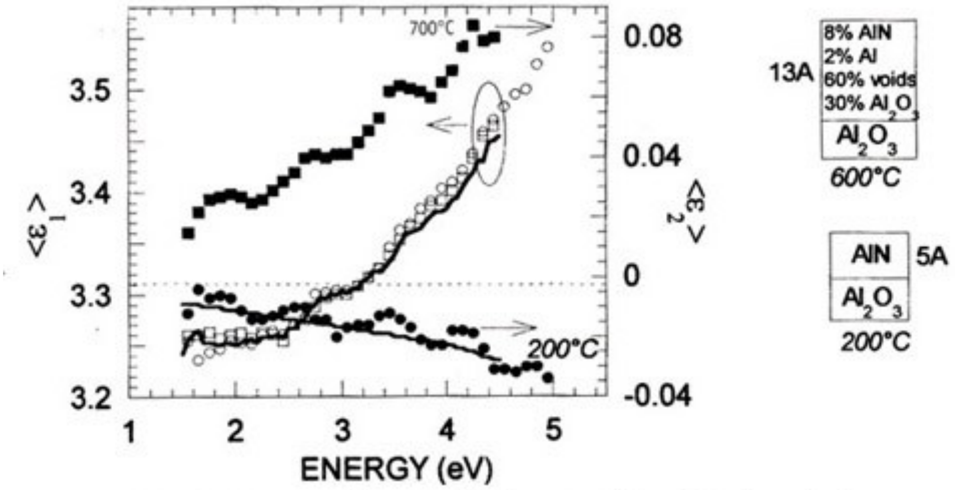

FIG. 1. SE spectra of the real, $\langle\epsilon_1\rangle$ (open symbols), and imaginary, $\langle\epsilon_2\rangle$ (filled symbols), parts of the α-Al_2O_3 (0001) pseudodielectric function after nitridation by a rf N_2 plasma at 200 °C (●, ○) and at 600 °C (□, ■). Continuous lines are the best-fit spectra corresponding to the best-fit models shown at the bottom. Other experimental conditions: rf power=200 W, P =0.2 Torr, N_2 flux=100 sccm.

Figure 2 show typical LRI traces of the reflectance intensity measured during the several stages involved in the GaN growth by RP−MOCVD: (AB) substrate cleaning and nitridation; (BC) deposition of about 30 nm of a buffer layer at low temperature (500°C); (CD) annealing of the buffer layer at T=750°C; (DE) growth of the GaN epilayer at T=750°C. Figure 2a is for a GaN growth carried out on sapphire nitrided at high temperature (700°C), while fig. 2b refers to GaN grown on sapphire nitrided at low temperature (200°C). During the steps of sapphire cleaning and nitridation (line AB), the reflectivity is constantly at the level of a bare and clean sapphire surface (R=7.7%).

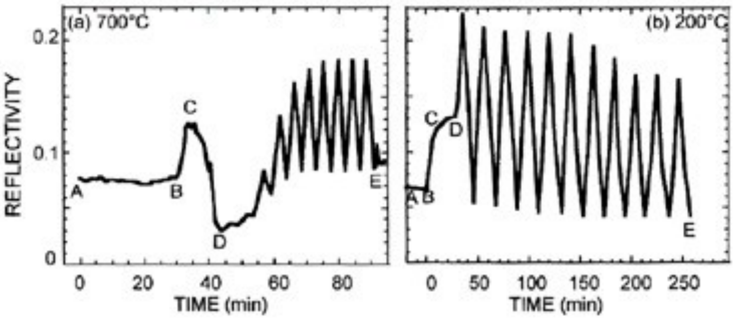

Fig. 2. Typical LRI traces recorded during the multistep growth of GaN in a RP-MOCVD system. (AB) is for substrate cleaning and nitridation, (BC) for 30 nm GaN buffer growth, (CD) for buffer annealing, and (DE) for GaN epilayer growth. GaN was grown on sapphire nitrided at a) 700 °C and b) 200 °C

The nitridation does not significantly affect the reflectivity, since a very thin nitrided layer is formed. During deposition of 30 nm of the GaN buffer layer (line BC), an increase of the reflectivity is observed. This increase depends on the thickness of the buffer layer; however, for a thickness of about 32 nm, the value of ~16% expected for GaN should be reached. During the annealing (line CD) at T = 800°C of the buffer layer, different phenomena are observed depending on the initial nitridation temperature. In particular, fig. 2b shows a slight increase of the reflectivity, indicating that the annealing causes a rearrangement and a material densification without inducing any roughening of the growth surface. Additionally, during RP−MOCVD growth on sapphire nitrided at 200°C, no drop in the reflectivity is observed after the buffer/annealing steps, while other authors, operating GaN growth in conventional MOCVD systems, reported a drastic decrease of reflectivity to values as low as 1−2% upon annealing, as found when sapphire nitridation is operated at 700°C (see line CD in fig. 2a). Hence, a flat and high−quality nucleation template layer for the GaN epilayer is formed by 200°C nitridation. The drop in reflectivity for the case in fig. 2a requires the subsequent growth of about 1mm of GaN to recover the reflectivity value characteristic of GaN, so that high GaN thickness have to be grown to have good quality and smooth materials. In contrast, under the present RP−MOCVD conditions and, specifically using low temperature sapphire nitridation, smooth GaN epilayer grows from the beginning. Therefore, data indicates that 200°C plasma nitridation promotes 2D−dimensional layer−by−layer growth, while inhomogeneous 700°C plasma nitridation results in 3D−island growth. This result applies not only to RP−MOCVD but also to r.f. N_2 plasma MBE growth as already demonstrated in previous papers.

The high quality of RP−MOCVD GaN epilayers grown on the 200 °C nitrided sapphire substrate has been also deduced by structural and optical measurements. The GaN crystal quality was characterized by omega scans of symmetric (0004) and asymmetric (10−5) reflecting planes. The GaN films grown on sapphire nitrided at 200°C lead to lower FWHM of 152 arcsec (0004) and 313 arcsec (10−5), while values of FWHM of 350 arcsec (0004) and 520 arcsec (10−5) were measured for the GaN film grown on sapphire nitrided at 700°C. A dislocation density of about 1×10^8 cm^{-2} and 5×10^8 cm^{-2} that was calculated from dislocation pits of AFM images has been measured for GaN epilayers grown on sapphire nitrided at 200 °C and 700 °C, respectively. This reduction in dislocation density could be related to growth conditions resulting in 2D growth (see Fig. 2). Therefore, it is clear that the GaN crystal quality improves with decreasing nitridation temperature of the sapphire substrate. Evidence of an improvement in material quality for GaN on sapphire nitrided at 200 °C is also obtained from photoluminescence spectra shown in Fig. 3. The normalized intensity of the near band edge (I_B) emission to that of the yellow band (I_Y) is maximized at he 200 °C sapphire nitridation temperature.

Concerning the surface morphology, all films have uniform and very smooth morphologies with a surface roughness of RMS = 0.4 nm for the GaN epitaxial layer grown on sapphire nitrided at 200°C and a RMS = 3.4 nm for the GaN epitaxial layer grown on sapphire nitrided at 700°C.

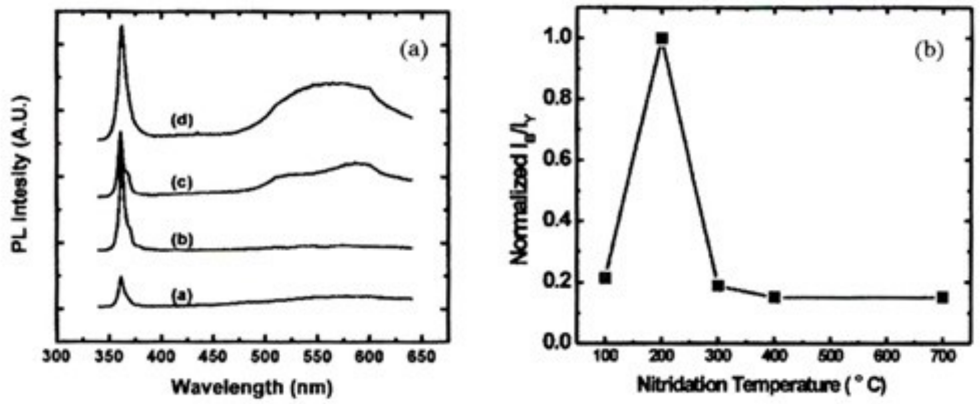

Fig. 3. a) Typical PL spectra of GaN epilayers grown by N_2 rf plasma-assisted MBE on sapphire nitrided at (a) 100 °C, (b) 200 °C, (c) 400 °C, and (d) 700 °C. b) Normalized intensity of the band edge (I_B) to yellow luminescence (I_Y) at room temperature for GaN films grown on sapphire nitrided at various temperatures

These values are typical of Ga−polar surfaces, as also confirmed by the NaOH etching polarity test performed on the same GaN samples. However, surface potential images recorded for GaN epitaxial layers grown on sapphire nitrided at 200°C and 700°C have shown that a higher density of N−polar domains characterizes the sample nitrided at low temperature, while the sample nitrided at higher temperature is Ga−polar but with a larger density of dislocations.

CONCLUSION

Kinetic and chemical aspects related to the use of N_2 plasma activated rf−plasma assisted RP−MOCVD have been presented and discussed. The in situ real time monitoring results have shown that the use of low temperature (200°C) rf N_2 plasma nitridation is beneficial to GaN epitaxial growth resulting in a 2D−like growth mode. Low temperature nitridation also results in higher PL intensity and better structural properties.

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