



Observation of the early stages of GaN thermal decomposition at 1200 °C under N₂



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ABSTRACT

We investigated the partial decomposition of GaN layers grown in an atmospheric pressure metal organic vapor phase epitaxy (AP-MOVPE) vertical reactor at 1200 °C under N₂ ambient. In these conditions, the early stages of GaN thermal decomposition were studied. The GaN decomposition was monitored by in-situ laser reflectometry (LR). The properties of the as grown and decomposed GaN samples were analyzed by scanning electron microscope (SEM). We show that GaN decomposition starts by the formation of GaN nano-grains at the early stages. Then, due to the anisotropy of the decomposition, the GaN nano-grains are more easily etched than the GaN (00.2) surface. The lateral etching may results in local smooth GaN surface formation. After that the depth etching starts again on the etched pits. Room temperature cathodoluminescence (CL) study revealed better optical properties of the GaN grains when compared to the whole GaN surface.

1. Introduction

Due to their wide band gap and high thermal conductivity, III-nitrides materials have been employed for high-power and high temperature applications [1,2]. Among III nitrides group, gallium nitride (GaN) has received considerable attention because of its significant band gap value of 3.43 eV at 300 K. The structural, optical and electrical properties are critical for device performance and all these properties depend on the process temperature [3,4]. High temperature treatment of GaN is an essential processing part in device fabrication such as p-GaN doping (by Mg acceptors) activation and ohmic contacts realization for GaN based devices [5–10]. Thermal annealing process is also used to reduce the defects density in GaN [4,11]. Considerable improvements in surface morphology and PL intensity have been achieved by high temperature rapid thermal annealing of GaN [3]. The knowledge of the critical temperature, below which the GaN epitaxial layers remains stable under the high temperature annealing conditions, is of great interest. Most of the works on annealing of GaN showed that GaN properties are affected when the processing temperature exceeds 900 °C [5–7,11]. However, thermal treatments should be performed in thermodynamic conditions that avoid film decomposition. Several studies showed that the annealing of GaN at temperature beyond 1000 °C even in nitrogen causes decomposition in the near GaN surface region [12–14]. In previous works, we demonstrated that GaN decomposition starts from critical temperature beyond 700 °C under H₂ and 1100 °C

under N₂ [15–17]. Bchetnia et al. [17] studied the annealing temperature on GaN decomposition rate in the range of 1000–1200 °C under N₂ environment in AP-MOVPE reactor. The GaN thermal decomposition has been studied by others groups versus several parameters that relates to decomposition environment such as temperature, pressure, carrier gas and geometry reactor [15–21]. However, little attention has been devoted to the effect of initial surface morphology on the partial GaN decomposition process. Recently, we investigated the relationships between the initial coalescence degree of GaN and its decomposition kinetic at 1200 °C under N₂ [22]. We demonstrated that decomposition of complete coalesced GaN can be performed nearly layer by layer and decomposition of incomplete coalesced GaN leads to anisotropy etching with high surface degradation [22]. The decomposed GaN layer until 0.6 μm of thickness loss showed crystalline property comparable to the as grown GaN layer. To the best of our knowledge, there is no work on the early stage of GaN thermal decomposition under N₂.

In this work, by using a coalesced GaN layer we investigated the different stages of GaN thermal decomposition at a fixed annealing temperature close to 1200 °C under N₂. We used the in situ time-reflectance and SEM to study the evolution of GaN surface state versus the early stages of its decomposition.

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2. Experimental details

The GaN layers were grown by AP-MOVPE on sapphire substrates at 1120 °C using the standard SiN treatment [23]. Trimethylgallium (TMGa), and ammonia (NH₃) were used as Ga, and N precursors, respectively. A mixture of H₂ and N₂ was used as carrier gas in MOVPE process. The heated reaction zone is obtained through induction heating and the backside temperature is monitored by S-type thermocouple and feedback system. The standard growth experiments start with the sapphire substrate nitridation under NH₃ at 1080 °C for 10 min. Then, the SiN treatment is carried out at the same temperature during 75 s under NH₃ and silane (SiH₄) flows. Then, the temperature is decreased down to 600 °C to grow nominal 30 nm thick GaN buffer layer. Afterwards, the temperature is increased to 1120 °C to grow the GaN sublayer. Firstly, the GaN growth starts by three-dimensional (3D) mode with a large surface roughness. Due to a coalescence process the GaN layer progressively undergoes a transition from 3D to 2D growth mode that finally leads to smooth surface. The as grown GaN sample is referenced as A₀. Four cut up GaN samples were annealed at 1200 °C in AP-MOVPE reactor under pure N₂ (2 slm). After their partial decomposition the samples are labeled A₁, A₂, A₃ and A₄. The annealing treatment of each sample was stopped at different stages corresponding to thickness loss in the range of 0–0.6 μm. The growth and decomposition processes were in situ controlled by He-Ne-laser reflectometry (λ = 632.8 nm) at normal incidence light. The surfaces of the annealed samples were ex-situ examined by SEM and CL at room temperature using 3 keV electrons beam.

3. Results and discussion

Fig. 1 shows a typical record of the in situ laser reflectivity signal obtained during growth (steps a–c) and decomposition (step d) of GaN. The reflectivity signal during growth and decomposition is normalized with respect to the last and first maxima, respectively. During the temperature ramp to 1200 °C, we found that when the temperature reach a 1100 °C value, as indicated by the arrow 2 in Fig. 1, the reflectivity signal shows an abrupt increase before it start to oscillate. This behavior occurred for all GaN decomposition experiments in the same conditions. This can indicate firstly a critical temperature of GaN decomposition under N₂ about 1100 °C and secondly a high reflective GaN

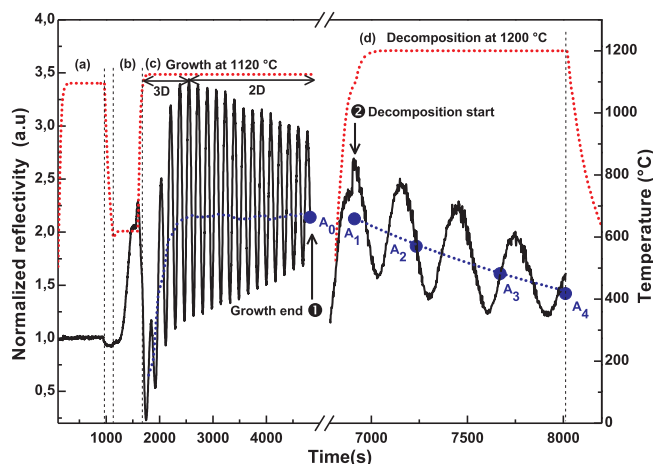


Fig. 1. In situ laser reflectivity measurements during growth and partial decomposition of GaN. The growth steps shown in this figure are: (a) nitridation during 10 min followed by short time (75 s) SiN treatment of sapphire substrate at 1100 °C, (b) low temperature (600 °C) GaN buffer layer growth, (c) temperature ramp from 600 °C to 1120 °C, (d) growth of high temperature (1120 °C) GaN sub-layer starting by 3D growth mode and followed by 3D-2D transient mode until complete coalescence. The step (d) corresponds to GaN decomposition at 1200 °C under pure N₂. The arrows 1 and 2 indicate growth end and decomposition start, respectively. The points labelled (A₁–A₄) indicate the stage at which the decomposition was interrupted.

surface due to formation of Ga rich GaN surface originating in a preferential evaporation of N₂ [24]. When the temperature reaches a constant value of 1200 °C, the GaN decomposition takes place and the reflectivity signal oscillations indicate a GaN thickness loss. From the oscillation period (T) of in situ time-reflectance ($R(t)$), the growth rate and decomposition rate (V) were calculated by using the following equation: $V = \frac{\lambda}{2nT}$ (Eq. (1)). Where n is the refractive index for the used wavelength. Then the layer thickness (d) can be calculated from the equation: $d = V \cdot \Delta t$ (Eq. (2)). Where, Δt is the duration of process. For the buffer layer thickness control, we used the ratio ($r = \frac{R_b}{R_s}$) (Eq. (3)) of buffer layer reflectance (R_b) by the substrate one (R_s). For the growth of sample A₀, we measured these growth rate values 0.34 μm/h and 2.77 μm/h for GaN buffer layer and GaN sublayer, respectively. The as grown GaN sublayer presents a total thickness close to 2.48 μm, where 0.73 μm is reached in 3D growth step and 1.75 μm is reached in 2D growth step. From the in situ time-reflectance recorded during the decomposition process, if we have several oscillation periods, by using Eq. (1) and Eq. (2) we can calculate an average value of decomposition rate. In case of sample A₄, the calculus gives an average decomposition rate close to 1.61 μm/h. In case of lower thickness loss such as stages A₂ and A₃, for which the oscillations numbers are insufficient, the ex-situ multi wave reflectance ($R(\lambda)$) technic gives more accurate measurements of decomposed GaN thickness. The measurements of thickness are detailed in Table 1 and Table 2. In these experiments, because the maximum thickness loss is 0.60 μm, we will discuss about partial decomposition of 2D GaN layer.

Fig. 2 shows the multi-wave reflectance spectra for samples A₀–A₄ measured in wavelength range of 200–1100 nm at normal incidence. The reflectance spectra show that for wavelengths higher than the corresponding GaN gap (365 nm), the GaN film is transparent and multiple optical interferences take place within the epitaxial layer. This explains the observed reflectance oscillations with a magnitude and period that are related to thickness and optical constants (n and k) film. Smooth and flat GaN surface and GaN/substrate interface give very pronounced oscillations. From spectra in Fig. 2, the film thickness (d) can be calculated in each period by the following equation [25]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (\text{Eq. (4)})$$

where λ_1 and λ_2 are the wavelengths for two adjacent same type of extreme (max or min) and n_1 and n_2 are their corresponding refractive index values. The variation of GaN refractive index versus wavelength was taken from Ref. [26]. By summing over all periods of pronounced oscillations an average (\bar{d}) was calculated and taken as the film thickness. In Table 1 we give as example the sample A₄ thickness calculus using this method. The thickness loss ($d_l = d_i - \bar{d}$) (Eq. (5)) is given by the difference between the thickness of the as grown GaN layer (d_i) and the average decomposed thickness (\bar{d}). Table 2 gives the surface roughness values (derived from average reflectivity) of samples A₀–A₁ as well as their corresponding thickness values calculated using time-reflectance and multi-waves reflectance spectra. The values of thickness given by the two methods are in good agreement. The sample A₁ was annealed until 1100 °C, so its thickness remains close to that of sample A₀.

Fig. 3 shows the SEM images of the top surface of sample A₂, where it can be seen some flower-like particles, with an average size of around 5 μm, surrounded by a high density of GaN nano-grains. The flower-like particles (with the same size) are present in other decomposition stages.

Fig. 4 shows high magnification SEM images corresponding to the as grown GaN (A₀) and the region between GaN nano grains for the decomposed samples (A₁–A₄). For the as grown sample we observed a smooth and flat GaN surface which is in good agreement with the high reflectivity contrast corresponding to a coalesced GaN layer. The SEM image of sample A₁ shows homogenous structure formed by nano-grains. The presence of nano-grains could indicate the beginning of GaN

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