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Sensors and Actuators A 121 (2005) 131–135
SENSORS AND ACTUATORS A PHYSICAL
www.elsevier.com/locate/sna

Structural and composition analysis of GaN films deposited by cyclic-PLD at different substrate temperatures

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Received 25 February 2004; received in revised form 17 October 2004; accepted 27 December 2004
Available online 18 March 2005

Abstract

GaN films were deposited by cyclic pulsed laser deposition (cyclic-PLD) at different substrate temperatures between 400 and 600 °C. Alignment of the films along the *c*-axis, grain size, roughness and conductivity increased with temperature. Surface elemental ratio N/Ga was determined by X-ray photoelectron spectroscopy (XPS) and was smaller for films deposited at higher temperature. A decrease of the resistivity of the films agreed with higher metallic (Ga) surface concentration. Bulk elemental ratio N/Ga, determined by Rutherford backscattering spectroscopy (RBS), was higher than the XPS ratio and showed a very small tendency to decrease with deposition temperature. At 600 °C, there was evidence of contamination of the films by oxygen probably resulting from diffusion from the sapphire (Al_2O_3) substrate. These results suggest that adjustments in the deposition conditions are needed in order to have high crystal alignment, large grain size and good N/Ga ratio.

Keywords: GaN; PLD; XPS; X-ray diffraction; RBS

1. Introduction

The preparation of high quality semiconductor films of group-III nitrides (GaN, AlN, InN and their alloys) is a forefront task of the present technological research. The main reason is connected with the attractive applications of such films in "blue and UV" optoelectronic devices such as blue LEDs and blue laser diodes [1,2].

The pulsed laser deposition (PLD) is a promising alternative of the common metalorganic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE) techniques for preparation of these materials. One of the advantages of PLD is the possibility of deposition at lower temperature.

Substrate temperature is an important parameter for the growth of good GaN and it strongly determines the crystalline quality [3,4], electrical [5] and optical properties [6], growth rate [7] and even the impurities present in the films [8]. It has also been shown that very high deposition temperature may introduce impurities from the substrate into the film [9]. In this article we report results on characterization of GaN grown on pre-nitridated sapphire substrates at temperatures between 400 and 600 °C by applying a two-step cyclic-PLD process, previously developed by our research group. We compare them in terms of crystal structure, surface morphology, elemental (N/Ga) ratio and resistivity.

The growth rate was around 0.05 μm/h, which is smaller than reported by others.

2. Experimental details

All GaN films were deposited by cyclic-PLD on *c*-axis sapphire. Details of the deposition system can be found elsewhere [10]. Prior to growth, the substrates were immersed in phosphoric acid (85% dilution) for 5 min, rinsed in de-

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doi:10.1016/j.sna.2004.12.028

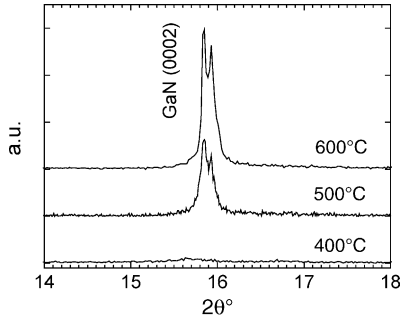

Fig. 1. θ–2θ XRD scans for three samples grown at 400, 500 and 600 °C on *c*-axis oriented sapphire. Only the GaN (0 0 0 2) peak is shown. The double peaks correspond to the splitting of $K_{\alpha 1}$ and $K_{\alpha 2}$ of the Mo X-ray source.

ionized water and finally degassed during 30 min at 700 °C under a pressure of 10^{-6} mbar. Radio frequency (13.56 MHz) nitrogen plasma was used to nitridate the sapphire surface in order to promote the creation of AlN nucleation islands or even monolayers. The creation of these islands or layers is not investigated in the present work. The 1 mbar nitrogen plasma was set to 4 W and the substrate temperature was kept at 700 °C during the 30 min of nitridation.

Each deposition cycle was composed of two steps. In the first one, the liquid Ga is laser ablated at a lower N_2 pressure of 0.2 mbar for 5 s. In the second step the laser is stopped, the N_2 pressure is raised to 1 mbar and the 3 W nitrogen plasma is switched on for 20 s. The cycle repeats until the pre-established deposition time is reached. Three GaN films were deposited at 400, 500 and 600 °C. The films were then characterized with various techniques.

Crystallite orientation was determined by θ–2θ X-ray diffraction scans using a Siemens D 5000 diffractometer with a molybdenum (Mo) source. Sample was oriented in order to maximize the (0 0 0 2) GaN peak. The maximum intensity of this peak was extracted for each sample from Fig. 1.

Surface morphology of the films (including mean roughness) was investigated by atomic force microscopy (AFM). Grain size was determined from the AFM scans.

Film resistivity was measured using van der Pauw 4-point-probe technique.

Surface chemical composition was extracted from ex situ X-ray photoelectron spectroscopy (XPS) data. Measurements were carried out in ultra high vacuum environment (10^{-10} mbar). The spectra were acquired using magnesium (Mg) Kα source (1253.6 eV), pass energy of 90 eV and a take-off angle of 90° (angle between sample surface and emitted photoelectrons). Shifting of the electrons binding energies due to charging of the sample was corrected assuming a binding energy for C 1s of 284.6 eV. Atomic sensitivity factors provided by Perkin-Elmer XPS Handbook were used to furnish semiquantitative analysis of the surface composition of the films. Areas of the N 1s, Ga 3d and Ga 3p peaks were calculated from high-resolution scans. Small windows for C 1s and O 1s were also taken. After taking into account the atomic sensitivity factors, the ratio of the calculated areas gives the corresponding elemental ratio. Based on the quality of the XPS peaks a 10% maximum error was assumed for the XPS N/Ga ratio.

The GaN films were further studied using Rutherford backscattering spectroscopy (RBS) with a collimated beam of 2 MeV He^+ ions. For each sample, elemental ratio (N/Ga) was obtained by measuring the height of the N and Ga peak (in the middle of the film) and normalizing by the scattering cross section for the respective element. The height of the Ga and N peaks was determined by making an average over a small window taken around the center of the peak and standard deviation was taken as the error of the measure.

3. Results and discussion

Fig. 1 shows the θ–2θ XRD scans for three GaN samples grown between 400 and 600 °C on *c*-axis oriented sapphire. As can be seen, the GaN (0 0 0 2) peak intensity decreases with lower substrate temperature. The slight variation in the thickness of the GaN films cannot explain the difference in the X-ray diffraction peak intensity. This is probably caused by the lower surface mobility of the deposited species at the reduced substrate temperature leading to randomly oriented crystallites. At the highest substrate temperature (600 °C), the growth of the films is clearly *c*-axis oriented. The magnitude of the (0 0 0 2) peak and the absence of the (10.0) and (10.1) peaks suggest a high degree of texture. Only the (0 0 0 2) family of planes is present in the X-ray pattern.

Fig. 2 shows the variation of surface film morphology with substrate temperature. Images are plotted in a 4 μm scale. The increase of the average domain size of the grains with deposition temperature is a clear indication of the transition from amorphous to polycrystalline material. This is in agreement with the XRD scans previously presented. The mean roughness (R_a) was measured to be 1, 3 and 10 nm for the substrate temperatures of 400, 500, and 600 °C respectively. The films are clearly polycrystalline even at 600 °C.

Film resistivity (Table 1), measured with 4-point-probe technique, showed an increase in the conductivity with the deposition temperature. This seemed to indicate an increase in the metallic composition of the films at higher temperatures

Table 1
Measured parameters for three GaN films deposited at different substrate temperatures

Characterization parameters	Deposition temperature (°C)		
	400	500	600
Normalized X-ray (0 0 0 2) intensity	0.05	0.5	1
Grain size (nm)	60	100	180
Mean roughness (nm)	1.2	3.1	9.8
Conductivity $(\Omega\,\mathrm{cm})^{-1}$	1	25	261
XPS N/Ga ratio (surface)	0.5	0.3	0.2
RBS N/Ga ratio (bulk)	1.08 ± 0.32	0.92 ± 0.36	0.89 ± 0.33

Insignificant measurement errors are not inserted.

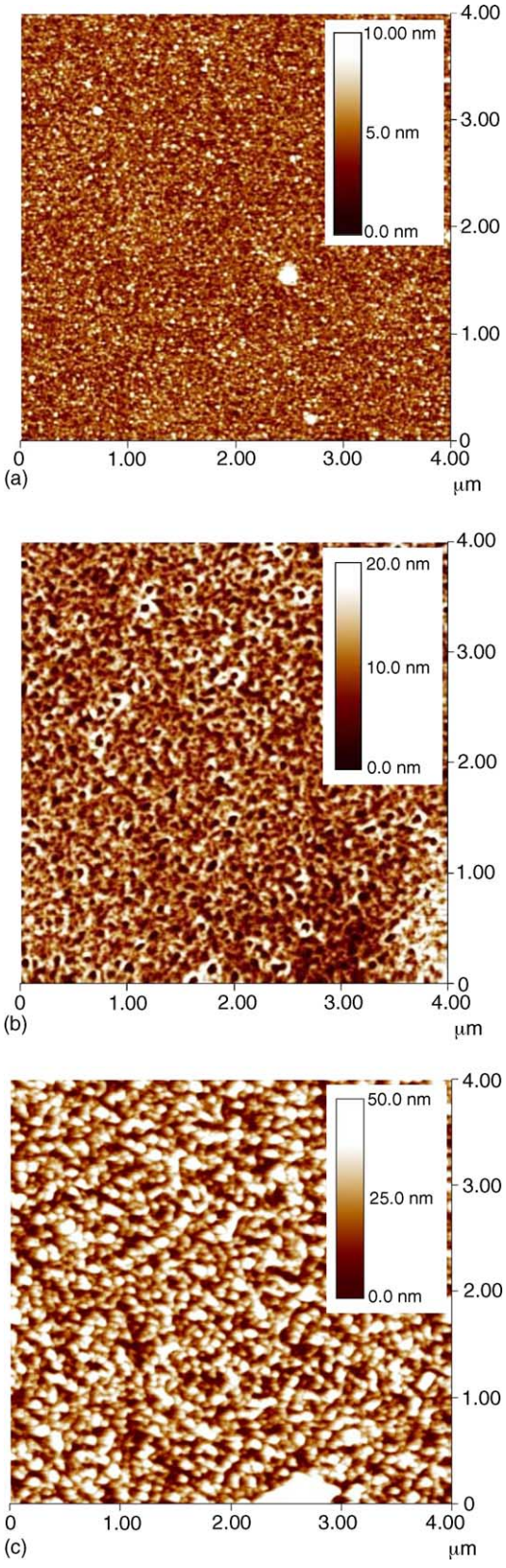

Fig. 2. Evolution of surface morphology of GaN samples deposited at (a) 400 °C, (b) 500 °C and (c) 600 °C. Pictures taken with AFM.

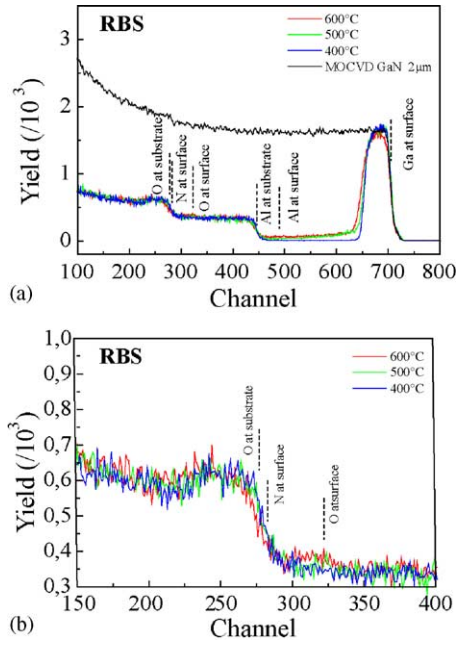

Fig. 3. 2.0 MeV He^+ RBS spectra for 3 GaN films deposited at 400, 500, and 600 °C. Films were deposited on sapphire (Al_2O_3) by PLD. Spectrum from MOCVD GaN sample was also taken for reference purposes (a). Detailed part of the spectrum shows possible contamination of the film deposited at 600 °C by oxygen (b).

due to loss of nitrogen. Results from surface compositional analysis, determined by XPS, agreed with this assumption (Table 1). The elemental ratio N/Ga at the surface of the film decreased with increasing substrate temperature (Fig. 4). At 400 °C, the amount of nitrogen is 0.5 the amount of gallium and at 600 °C this elemental ratio (N/Ga) is 0.2. This corresponds to 60% decrease of the XPS surface elemental ratio N/Ga.

XPS only gives us information on the composition of a small surface layer, typical 2 nm thickness. In order to establish if the elemental ratio N/Ga in the surface resembles the ratio in the bulk, RBS spectra were obtained for all the films (see Fig. 3).

Spectrum from one MOCVD GaN sample was also taken for reference purposes. An elemental (N/Ga) ratio of 1 was assumed for this 2 μm thick GaN film.

Due to the small thickness of the samples (∼80 nm) the peak corresponding to Ga in the GaN layer is well detached from the substrate signal (Al and O steps). Considering the error of the measurement, the height of this peak is the same for all the samples (including the MOCVD reference sample) and consequently they have the same bulk Ga concentration. Because of the low sensitivity of RBS for light elements, the backscattering peak corresponding to N in the GaN film is barely seen. In fact, the N peak appears superimposed on the O signal from the substrate. By mathematically removing the O background it was possible to determine the height of the N signal for all the samples. For these calculations, the dependence of the RBS yield on the square of the scattering

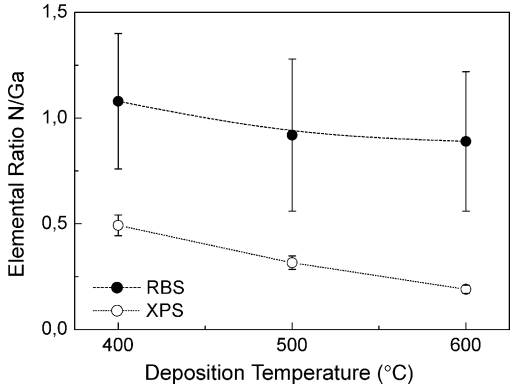

Fig. 4. Elemental ratio N/Ga calculated from RBS (bulk ratio) and XPS (surface ratio) data for 3 GaN films deposited at different temperatures. The dotted lines are just guides to the eye.

cross section was taken into account. Nevertheless, the low sensitivity of the RBS technique to light elements does not allow us to obtain a good signal to noise ratio for the N backscattering peak. On the other hand, the determination of the height of the Ga peak is much more accurate. The bulk elemental ratio N/Ga, obtained by dividing the peak heights of N and Ga (normalized by the corresponding scattering cross sections), is plotted in Fig. 4. Considering the large error associated with the calculation of the N peak height, all the films have more or less the same elemental ratio N/Ga. Still we can say that, there is a tendency similar to the one found in the XPS (see Fig. 4), showing a decrease of the N/Ga ratio with increasing temperature, although much less accentuated.

Despite the large error associated with the determination of the RBS N/Ga ratio for the bulk of the film, the XPS surface elemental ratio (N/Ga) is clearly outside the error bars of the RBS calculation. The surface composition of the films shows a smaller N/Ga ratio than the bulk of the films. Furthermore, this ratio decreases with deposition temperature. This may be caused by loss of nitrogen from the surface of the film during the cooling down process. Such effect should be stronger when starting the cooling process from a higher temperature. Therefore, samples deposited at lower temperature should present less deficiency in nitrogen.

Apart from the elemental ratio N/Ga, the RBS also shows another interesting feature. The backscattering spectrum for the sample deposited with a substrate temperature of 600 °C presents a small step at channel 325, which was identified as oxygen inside the thin GaN film. This is not evident on the other samples grown at lower temperature. We attribute this contamination to diffusion of oxygen from the hotter sapphire substrate (Al_2O_3) into the GaN film [9]. This process should increase with temperature and that is why we do not see oxygen steps on the films deposited at 400 and 500 °C. Nevertheless, further investigation is necessary to clarify this assumption.

4. Conclusion

We have studied the structural, electrical and compositional changes in GaN films deposited at three different temperatures by cyclic pulsed laser deposition (PLD). Deposition at the highest temperature improved the orientation of crystal grains along the *c*-axis and increased the grain size of the polycrystalline material. On the other hand, the film roughness and dark conductivity increased. XPS surface compositional analysis showed a decrease of the N/Ga elemental ratio with temperature that could explain the larger dark conductivity for the films deposited at higher substrate temperature. Within the error of the measurement, bulk composition determined by RBS did not show any variation with deposition temperature. Bulk Ga concentration of the PLD GaN films was found to be similar to the Ga concentration of MOCVD GaN reference sample. Nevertheless, the bulk RBS elemental ratio N/Ga was higher than the surface ratio extracted with XPS. We attribute the higher relative concentration of Ga at the surface of the film to the loss of nitrogen during the cooling down under vacuum after growth. This loss was stronger for the films deposited at higher temperatures.

Comparison of these results, obtained for samples produced under different conditions, suggests adjustments in the deposition parameters in order improve the quality of the PLD GaN films.

Acknowledgments

We would like to thanks Isabel Cabaço for allowing us to access the X-ray facility, to Oliver Ambacher for the MOCVD GaN sample, and Luis Melo for the AFM pictures. P. Sanguino acknowledges support from a grant given by Fundação para a Ciência e a Tecnologia (FCT). The work at IST is supported through project PRAXIS/P/FIS/10178/1998 and POCTI/FAT/42185/2001.

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Biographies

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R. Schwarz received a first degree in Physics and Mathematics from the University of Stuttgart, Germany, in 1977, and a Ph.D. degree from the University of Neuchâtel, Switzerland, in 1982. After his post-doc at Princeton University, USA, he joined the Physics Department of the Technical University of Munich, Germany, between 1986 and 1996. There he headed a number of research projects in the field of amorphous silicon, a topic he continued since then in Portugal, first as an invited professor at the Instituto Superior Técnico, IST, in Lisbon, then as Coordinator Professor at the Engineering Institute of Lisbon. Since 2003 he is Associated Professor at the Physics Department at IST focussing on GaN-based semiconductor research.