Rutherford backscattering analysis of GaN decomposition

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The decomposition of GaN at temperatures ranging from 500 °C to 1100 °C has been studied by Rutherford backscattering (RBS), x-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). The development of a surface defect peak is a consequence of preferential N_2 loss at elevated temperatures. Additionally, broadening of the defect peak at 1100 °C, corresponding to a damage depth of approximately 0.25 μm beneath the surface, can be attributed to the diffusion of defects from the interface. At such temperatures, severe roughening of the surface is observed through AFM scans, which also correlated well with the damage depths estimated from RBS spectra. Nevertheless, Ga droplet formation is not detected from our samples as verified by XPS. Our results show that GaN remains thermally stable in N_2 up to 900 °C. At higher temperatures, significant decomposition occurs and gives rise to degradation to the structural and morphological properties of the film. © *2003 American Vacuum Society.* [DOI: 10.1116/1.1577570]

GaN and its alloys have virtually dominated the blue-green light-emission devices market[1] and their potential applications in high-power electronic devices have also been recognized. While GaN technology has gradually matured in recent years, many existing problems remain unsolved as challenges emerge, covering a wide spectrum of issues, including the growth and processing of device structures.

Annealing is an important step in the processing of GaN-based devices. It is employed for the activation of Mg dopants to achieve *p*-type doping,[2] the removal of processing-induced damage[3] and the alloying of ohmic contacts to both *n*-type and *p*-type GaN.[4] The temperatures involved in these processes may be sufficient to result in decomposition of the GaN surfaces. The preferential loss of N_2 at elevated temperatures is well known.[5] Additionally, Kuball *et al.*[6] have performed a thorough study on the thermal stability of GaN investigated by Raman scattering. Thermal damage at temperatures beyond 900 °C has resulted in the appearance of various defect modes in the Raman spectrum. A thermodynamical analysis of GaN decomposition has also been performed by Mayumi *et al.*,[7] which reveals the chemical reactions involved.

In this article, the thermal stability of GaN is investigated by Rutherford backscattering/channeling (RBS/C). Channeling offers the superior advantage of providing the depth profile of lattice damage in the material, such that the thickness of the damage region can be estimated accurately. The thermally disordered surface has also been studied by atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS).

A Si-doped epitaxial layer ($n \sim 3 \times 10^{18}$) of 1.5 μm thickness was grown in an EMCORE D125 metal organic chemical vapor deposition reactor on a sapphire (0001) substrate, with an undoped GaN 25 nm low-temperature-buffer layer sandwiched in between. 6 mm^2 samples were cleaved from the 2 in. wafer and subjected to rapid thermal annealing treatment at temperatures ranging from 600 °C to 1100 °C in flowing N_2. The duration of the anneals were fixed at 5 min.

The channeling experiments were conducted on the 3.5 MeV singleton accelerator at the Research Center for Nuclear Microscopy, National University of Singapore using a 2 MeV helium ion and proton beam. Ion channeling mea-

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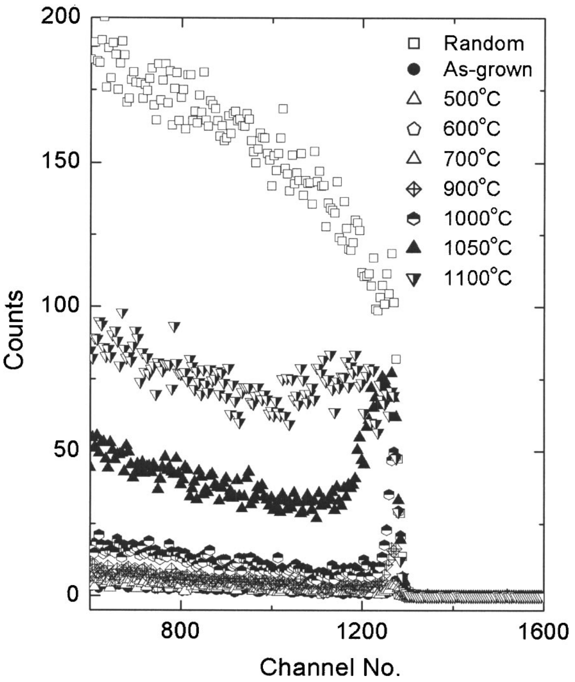

FIG. 1. RBS/C spectra illustrating the buildup of a surface defect peak as the annealing temperature rises from 500 °C to 1100 °C.

surements were carried out along the ⟨0001⟩ direction, and backscattered particles were measured using a 50 mm^2 Si surface barrier detector of 13 keV resolution. Charge integration of the incident beam was achieved by applying -500 V bias voltage in front of the samples in order to suppress the secondary electron emission. The total beam fluence used for each measurement was 5–10 μC. The chemical nature of the GaN surfaces was examined by XPS on a VG ESSCALAB 220I-XL system using an Al $K\alpha$ source of 1486.6 eV, while the surface morphology was imaged with a Digital Instrument DI3000 surface probe microprobe operated in the tapping mode.

The buildup of thermal damage to GaN at various temperatures is well illustrated in the channeled RBS spectra of Fig. 1. While a single sharp surface peak is observed from all spectra below 1100 °C, a broad and significant peak can be noticed from the 1100 °C-annealed spectrum. The surface peak develops both in magnitude and width as the annealing temperature approaches 1100 °C, indicating a greater extent of surface disorder and a deeper penetration into the bulk. Significant surface disordering only starts to set in at temperatures above 1000 °C. The development of this surface peak is a consequence of the well-known phenomenon of preferential N_2 loss from GaN surfaces at elevated temperatures, as supported by the increasing Ga $2p^3$:N $1s$ ratios illustrated in Fig. 2. Defects in the form of vacancies and vacancy complexes are formed as a result, leading to surface disorder as measured by RBS/C (and also Raman scattering performed by Kuball *et al.*).[6] Nevertheless, the $\chi_{\min}$ parameter (ratio of aligned to random yield near the surface) for the 1100 °C-annealed sample is 51.5%, indicating that the surface is not completely amorphized despite such drastic heat conditions.

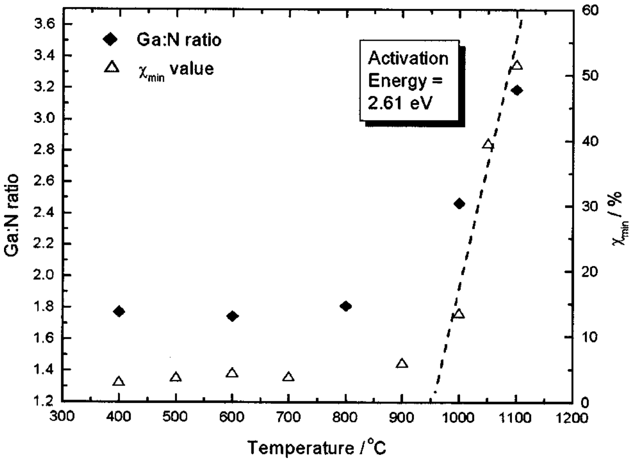

FIG. 2. Plot of Ga:N ratio and $\chi_{\min}$ as a function of annealing temperature.

A more unexpected observation is the emergence of a broad peak located between channel Nos. 1100 and 1300 in the 1100 °C-annealed spectrum, which corresponds to a damage depth of approximately 0.25 μm from the surface. Similar features have also been observed from ion-implanted GaN, which has been attributed to the buildup of extended defects and clusters resultant of energetic ion bombardments which penetrates into the lattice. However, the mechanism responsible for the generation of bulk defects is certainly different in this case, where an external ion source is absent. We believe that the defects are able to diffuse gradually from the surface toward the bulk at the temperature of 1100 °C as the density of defects (N_2 loss) saturates near the surface, giving rise to a broadening of the defect peak in the spectrum. The backscattering yield deeper into the material (at channel No. 800, say) also increases with annealing temperature, indicating increased dechanneling of the initial channeled beam. Hence, both the interaction components of direct backscattering and dechanneling are present.

From the Arrhenius plot of the $\chi_{\min}$ parameter in Fig. 2, the activation energy of GaN decomposition in the high-temperature region (>950 °C) can be derived. The activation energy is evaluated to be 2.61 eV, whereby it can be inferred that the reaction is limited by N_2 formation and desorption.[8] The decomposition of GaN under such conditions can be described by

$$2\mathrm{GaN(solid)} \rightarrow 2\mathrm{Ga(solid\ or\ gas)} + \mathrm{N_2(gas)}. \tag{1}$$

It can be seen that Ga may remain on the GaN surface as Ga droplets, or it may be desorbed as soon as it is formed. On our annealed samples, Ga droplets are not visually observable under an optical microscope. To verify this, XPS was employed to examine the chemical bonding states of the Ga atoms near the surface. XPS spectra of the Ga $2p^3$ core level for the samples annealed at different temperatures are shown in Fig. 3. The binding energies for the annealed samples ranges from 1116.8 to 1117.0 eV, slightly shifted from that of the as-grown sample at 1116.7 eV. The shift of the Ga $2p^3$

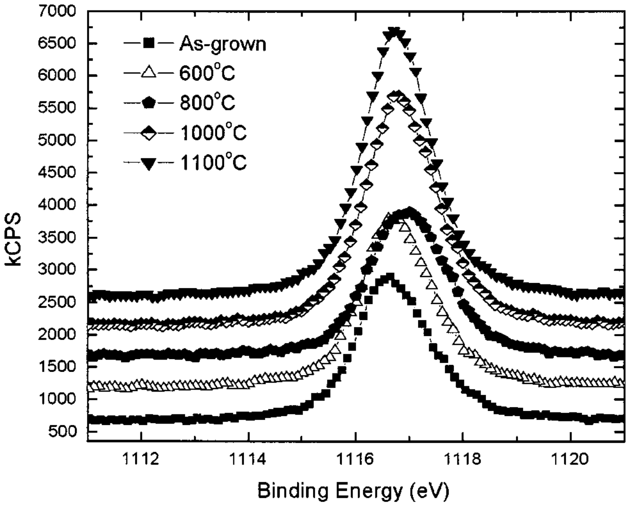

FIG. 3. XPS of the Ga $2p^3$ core level for various GaN samples annealed at different temperatures for 5 min.

peaks to higher energies can be attributed to enhanced oxidation of the decomposed surface due to the exposure of reactive dangling bonds (stronger O 1*s* peaks have also been detected from the annealed samples). Metal Ga droplets are not present on the surface, which would otherwise have resulted in a shift of the Ga $2p^3$ peak toward lower energies.

As mentioned, the strong surface defect peaks from the annealed samples correspond to a large extent to disorder near the surface. In order to visualize the roughening due to decomposition, AFM scans were taken from the surfaces. Figure 4 shows the AFM 20×20 μm surface scans for samples annealed at 600 °C, 900 °C, and 1100 °C. The measured root-mean-square (rms) roughnesses are 9.095 nm, 11.025 nm, and 156.98 nm, respectively. It is noticed that significant surface roughening occurs when the temperatures reach 1100 °C, a similar conclusion drawn from the RBS analysis. In fact, the rms roughnesses correlate well with the damage depths estimated from the RBS spectra, as shown in Table I.

TABLE I. Comparison of rms roughnesses as determined by AFM and damage depths as determined by RBS for GaN samples annealed at 600 °C, 900 °C, and 1100 °C.

Temperature (°C)	rms roughness (nm)	Damage depth (nm)
600	9.095	~30
900	11.025	~30
1100	156.98	~250

It is also worthwhile to correlate these results with the Raman scattering analysis of Kuball *et al.*[6] In their study, three thermal stability regions for GaN have been identified. No structural degradation is evident from the Raman spectra for annealing temperatures of up to 900 °C. This is consistent with our RBS data: The $\chi_{\min}$ value remains well below 10%. Between 900 °C and 1000 °C, a broad Raman peak centered at 610 cm^{-1} was observed, which has been assigned to disorder-induced Raman scattering. No obvious modifications in the surface morphology were visible after the thermal treatment, which again is consistent with our AFM data. At such temperatures, microscopic defects (vacancies and vacancy complexes) are formed which give rise to the Raman feature and a $\chi_{\min}$ value of ~13%. For temperature above 1100 °C, macroscopic lattice disordering becomes prominent, evident from the pitting of the sample surface (see Fig. 4). Additional Raman modes at 630, 656 and 770 cm^{-1} have emerged. Such macroscopic disorder can also be inferred from the high $\chi_{\min}$ value of more than 50% and the emergence of a bulk peak in the channeled spectrum from the 1100 °C-annealed sample.

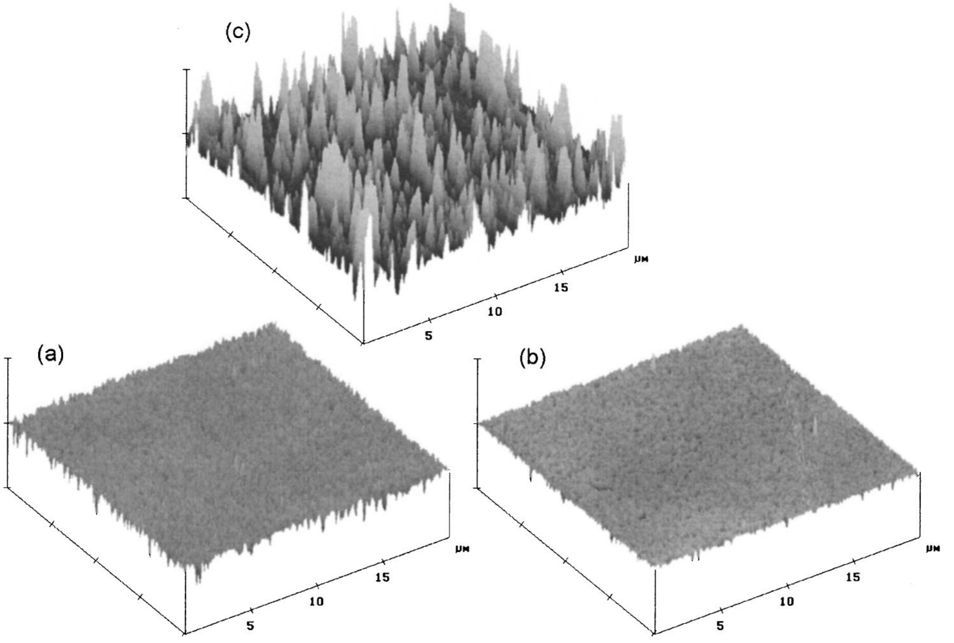

FIG. 4. AFM three-dimensional images of (a) as grown, (b) 900 °C annealed, and (c) 1100 °C annealed GaN surfaces. Note the severe roughening of the (c) due to surface decomposition.

In summary, a structural analysis of the decomposition of GaN has been presented. GaN remains thermally stable at temperatures of up to 900 °C. As the annealing temperature increases, a surface disorder peak develops in the RBS spectrum both in intensity and width. Lattice disordering on a macroscopic scale sets in at temperatures above 1050 °C, evident from the emergence of a broad defect peak and the severe pitting of the surface.

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