Characterization of III nitride materials and devices by secondary ion mass spectrometry

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Secondary ion mass spectrometry (SIMS) is an excellent technique to characterize III nitride materials and devices (dopants, impurities, and composition). Using empirical standards, the ion yield trends are derived for III nitride matrices to enable quantitative and high precision characterization of both major and impurity elements. The technique can be employed to investigate the control of purity and doping, determine growth rate and composition, as well as reveal the structure of finished optoelectronic and electronic devices. SIMS is thus a powerful tool for failure analysis, reverse engineering, and concurrent engineering. © *1998 American Vacuum Society.* [S0734-211X(98)08001-9]

I. INTRODUCTION

III nitrides have recently been the subject of intense research on account of their promising applications in blue and ultraviolet optoelectronic devices as well as microwave and electronic devices.[1,2] The growth of epitaxial layers by metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) requires tight control on purity, doping, alloy composition, thickness, and interface quality. Secondary ion mass spectrometry (SIMS) is an excellent characterization technique because of its ability to depth profile with high sensitivity and good depth resolution.[3] SIMS complements electrical techniques as it detects dopants regardless of their site in the crystal lattice and provides a wealth of information to materials scientists and device engineers, e.g., in the study of impurity activation and dopant diffusion.

Using implanted materials and cross referencing to results obtained by techniques such as photoluminescence (PL) and Rutherford backscattering spectrometry (RBS), the ion yield trends of some of the important dopants and matrix elements in III nitrides are established. This fundamental study serves to provide accurate, precise, and reliable quantification of impurities and matrix composition. In this article, we will discuss the ion yield systematics and identify minor deviation from the trends. We will also describe the latest applications of SIMS to III nitrides with regard to purity control, layer thickness, stoichiometry, interface quality, as well as reverse engineering of finished devices.

II. EXPERIMENT

Secondary ion mass spectrometry measurements were performed with a magnetic sector based instrument (Cameca IMS-4*f*) and quadruple based instrument (PHI-6600). These two instruments are equipped with dual cesium and oxygen primary ion sources and complement each other in terms of performance. In general, a magnetic sector instrument provides lower detection limits and higher mass resolving power whereas a quadrupole instrument is capable of better depth resolution. Depth profiles were acquired on the Cameca IMS-4*f* using 8 keV primary O_2^+ ions with positive SIMS (monitoring positive secondary ions), 5.5 keV Cs^+ ions with positive SIMS (monitoring CsM^+ ions where M is the element of interest), or 14.5 keV Cs^+ ions with negative SIMS (measuring negative secondary ions). The primary bombardment energy varied from 1 keV to several keV for the PHI-6600. The primary beam was rastered over a square region 50–125 μm on one side, and secondary ions were collected from the central region of the sputtered craters by using a physical aperture 30 μm in diameter (Cameca IMS-4*f*) or electronic gating (PHI-6600). The sputtering rates were determined by measuring the analytical crater depths with a Tencor P10 stylus profilometer. The RBS data were acquired using a National Electrostatic Corporation 1 MeV terminal voltage accelerator (3 MeV maximum for alpha particles) equipped with a Charles Evans & Associates end station. The RBS analysis was carried out at a backscattering angle of 160° with the samples orthogonal to the incident ion beam. The RBS spectra were fitted using a theoretical model and iteratively adjusting elemental concentration until the theoretical curves agreed with the experimental spectra. The III nitride samples were grown by MOCVD. The reference materials were implanted with known doses of the elements of interest including Si, Mg, Zn, Cd, Se, B, H, C, O, Cl, Fe, Mo, Ni, Cu, and Mn.

III. RESULTS AND DISCUSSION

A. Ion yield trends

Our experimental results elucidate the variation in the ion yields in the AlGaInN system. The relative sensitivity factors (RSFs) used in quantification are typically measured with

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TABLE I. Trends in ion yields in (a) AlGaN, (b) AlInN, and (c) GaInN.

(a) Relative ion yields of different species vs Al content in AlGaN

Al content	B^+ /Ga^+	Mg^+ /Ga^+	As^- /NGa^-	C^- /NGa^-	H^- /NGa^-	Si^- /NGa^-	B^- /NGa^-	O^- /NGa^-	$CdCs^+$ /NCs^+	$MgCs^+$ /NCs^+
0	0.10	3.0	7.0	9.0	30	40	80	500	800	1000
0.075	0.12	3.0	9.0	16	40	50	60	600	350	1000
0.125	0.07	3.0	10	15	30	50	40	600	200	1000
0.21	⋯	⋯	10	10	20	40	20	450	200	900

(b) Relative ion yields of different species vs Al content in AlInN

Al content	B^+ /In^+	Mg^+ /In^+	As^- /NIn^-	C^- /NIn^-	H^- /NIn^-	Si^- /NIn^-	B^- /NIn^-	O^- /NIn^-	$CdCs^+$ /NCs^+	$MgCs^+$ /NCs^+
0.6	0.10	2.5	80	150	1000	150	110	4000	100	1000
0.7	0.12	2.7	70	120	1500	150	45	3000	80	900
0.8	0.12	2.5	70	400	1000	120	45	4000	200	900

(c) Relative ion yields of different species vs In content in InGaN

In content	B^+ /Ga^+	Mg^+ /Ga^+	C^- /NGa^-	H^- /NGa^-	B^- /NGa^-	O^- /NGa^-	$CdCs^+$ /NCs^+	$MgCs^+$ /NCs^+
0	0.10	2.0	40	9.0	63	200	800	1000
0.14	0.09	2.0	40	8.0	63	250	800	1000

respect to various atomic or molecular matrix ions such as Al^+, Ga^+, In^+, NAl^-, NGa^-, or NIn^-. As multiple measurements were made under a range of different instrumental conditions in many cases, relative standard deviations in the RSFs can be estimated. The statistics suggest that calibration with respect to the matrix ion NM^- (where M is Al, Ga, or In) is preferable to the use of M^- in negative SIMS since the M^- ion intensity is more sensitive to the instrumental tuning conditions and produces a wider spread in the RSFs. Similar considerations were adopted to select the most stable matrix ions for normalization under the other SIMS analysis conditions.

SIMS data for the matrix elements can be calibrated with photoluminescence (PL) results but complications exist. For instance, the nominal wavelength of InGaN layer is not only related to the In content, but also to the dopant concentrations. A high concentration of Zn can shift the wavelength from the expected 400 nm for $In_{0.14}Ga_{0.86}N$ to 440 nm. Hence, care must be exercised in the correlation process, for example, by cross checking with an independent technique such as RBS. Complications aside, SIMS clearly can be calibrated against PL. If the PL results do indeed give the In concentration reliably within 0.1%, then the SIMS data are limited chiefly by the measurement precision which can reach about 0.5%. The converse relationship is also useful. SIMS plays an important role in calibrating the qualitative models employed to interpret optical data, especially when optical methods provide a relatively economical and nondestructive means to monitor epilayers on the production line.

Table I illustrates the trend in ion yields with matrix composition for the implanted elements, but it should be mentioned that RSFs tend to vary considerably among different SIMS instruments, particularly for molecular ions. Our data indicate that variations in the Al content tend to exert a larger effect on ion yields than variations in the Ga or In content. This can be attributed to the relative size, electronegativity, and polarizability of the Al cation compared to the Ga and In cations.

Figures 1(a)–1(c) depict the trends with changing composition for ion yields of the matrix species $AlCs^+$, $GaCs^+$, $InCs^+$, and NCs^+. The molecular MCs^+ secondary ions, where M is the matrix element, are often utilized to determine the stoichiometry of III–V compounds.[4] These ions tend to form in the gas phase away from the sample surface via a recombination mechanism involving the neutral atom M and the abundant Cs^+ ion sputtered from the cesiated surface during Cs ion bombardment. This formation mechanism reduces matrix effects on ion yields that are generally nonlinear and somewhat unpredictable. To further assess the accuracy of the results rendered by the MCs^+ ions, the SIMS data are plotted against RBS results (Fig. 2). It should be noted that by using the $AlCs^+/GaCs^+$ ratios, the sputtering yield dependence can be removed and the results show excellent linearity. Figures 1(d)–1(f) display the trend in ion yields with composition for dimer and trimer ions such as Al_2, Ga_2, In_2, Al_3, and Ga_3. Such dimer and trimer ions provide a means for very precise multivariate interpolation of stoichiometry with SIMS.

Two important observations can be made. First of all, the InN sample may actually be a subnitride. The $InCs^+/NCs^+$ ratios have been measured in four different InN samples, and vary more than tenfold. This is in contrast to the NCs^+ ion intensity which is relatively constant in all the GaN, AlN, AlGaN, and AlInN samples measured. The value measured in the implanted sample used in this work is somewhat high suggesting that the indium may not have been fully nitrided. Second, some heterogeneity was observed within the AlInN samples both laterally and as a function of depth. Generally, such lateral inhomogeneity can be ascribed to pinhole defects, and the compositional variation with depth amounts to only about 5% on average.

The ion yield trends provide the means for producing

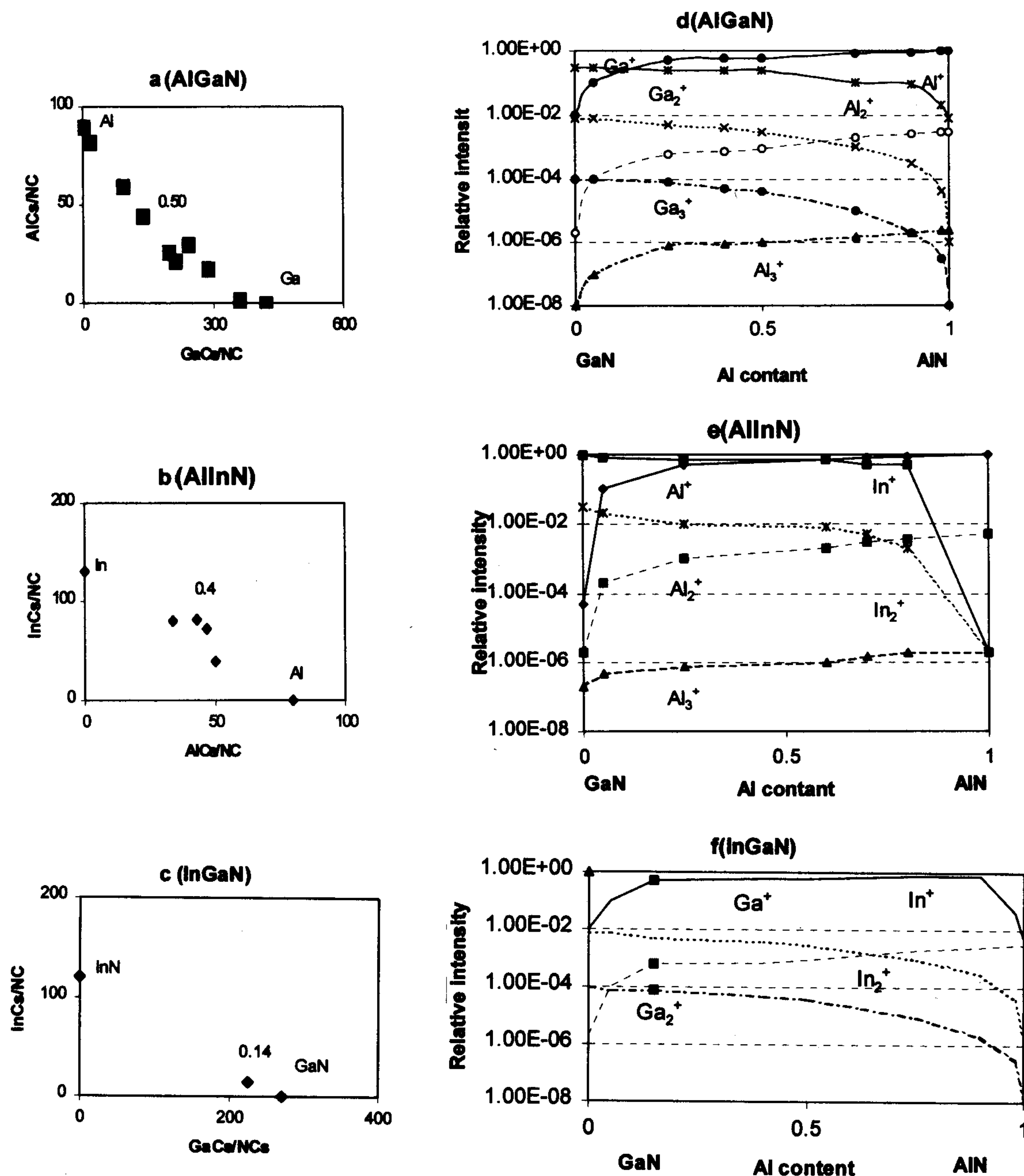


FIG. 1. Trends in ion yields are displayed for the matrix ion species: (a) and (d) AlGaN, (b) and (e) AlInN, and (c) and (f) GaInN. The curves in (a), (b), and (c) are for linear interpolation of stoichiometry from standards using MC^+ secondary ions where M is a matrix ion N, Al, Ga, or In. The curves in (d), (e), and (f) are for multivariate interpolation of stoichiometry from standards using Al^+, Ga^+, In^+, In_2^+, Ga_2^+, In_2^+, Al_3^+, and Ga_3^+ secondary ions.

more accurate SIMS data for R&D and production line purposes. For example, the trends within the AlGaInN system provide a basis for accurate inferences, interpolation, and extrapolation to compositions not represented among the standards. The ion yield systematics of this small set of implanted elements allow one to infer conversion factors for many other elements to an accuracy of better than a factor of 2. The results can provide some insight into the chemical nature of the III nitride materials itself or the detailed physical structure of epilayers. Some information pertaining to the bond ionicity in the materials is present in the flux of the secondary ions. For example, the Al–N and Ga–N bond ionicities appear to differ with consequences for the NCs^+ ion yield based on the nonlinearity displayed in Fig. 1(a). Since it is well known that the corresponding diagram for AlGaAs has a more linear nature, the Al–As and Ga–As bond ionicities in AlGaAs seem more similar than do the Al–N and Ga–N ionicities in AlGaN. Likewise, the trend for electropositive B to form more negative ions and electronegative As to form fewer negative ions, with increasing Al content in AlGaN, suggests that the local electronic structure is changing.

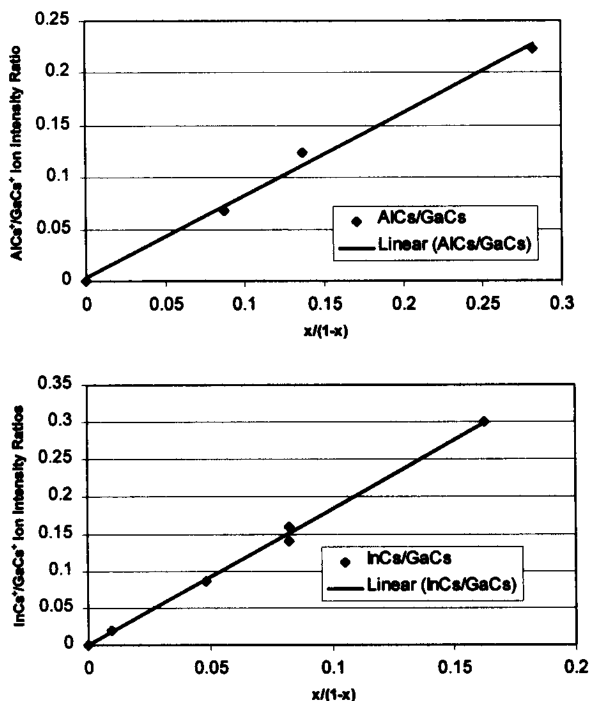


FIG. 2. (a) $AlCs^+/GaCs^+$ ion intensity ratios in SIMS analysis vs composition ratios $x/(1-x)$ for $Al_xGa_{1-x}N$ samples where the x value was determined by RBS (top); (b) $InCs^+/GaCs^+$ ion intensity ratios in SIMS analysis vs composition ratios $x/(1-x)$ for $In_xGa_{1-x}N$ samples where the x value was determined by RBS (bottom).

Information related to the local composition is also present in the secondary ion flux. For instance, if the III nitride is heterogeneous, with a nominal composition of $Al_{0.1}Ga_{0.9}N$ but actually composed of microscopically distinct regions containing pure AlN and GaN, the intensities of the Al and Ga dimer and trimer ions will be significantly higher than the values exhibited in Figs. 1(d)–1(f). These dimers and trimers can potentially be used to study a kind of interfacial defect in which the interface is atomically abrupt but contains some topographical roughness. This could be of use, for example, in checking epilayer flatness in heterojunction devices.

It is also worth mentioning that several InN samples measured by us have unusually high $InCs^+/NCs^+$ ratios (or low NCs^+ ion intensities), suggesting that these matrices are probably not fully nitrided. Last but not least, SIMS complements many optical nondestructive techniques. Photoluminescence (PL) and x-ray data can be correlated with SIMS results to better understand a particular sample. This is especially important for III nitrides because dopants can alter the lattice constant by means of strain and consequently the PL spectrum.

B. Latest applications to III nitride semiconductors

A better understanding of the ion yield systematics and improvement in the experimental techniques have enabled quantitative characterization of III nitride materials and devices by SIMS. Figure 3 illustrates the role of SIMS in a typical GaN MOCVD LED process. The applications in-

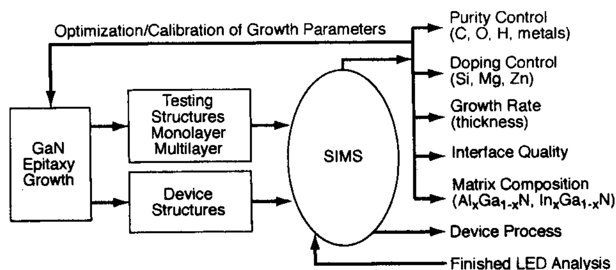


FIG. 3. SIMS applications to the characterization of GaN based materials.

clude the depth profiling of dopants (Mg, Zn, and Si), common impurities (atmospheric and metallic ions), and compositions. These specific applications will be described in the following sections and a measurement on a finished LED device will also be included to demonstrate the latest attempt in using SIMS in the fields of failure analysis, reverse engineering, and concurrent engineering. The wealth of information obtainable by SIMS has proven extremely valuable in solving practical problems as well as in a research and development environment.

1. Purity and doping control

Control of purity in the epilayer requires very low detection limits because the concentration range of interest is usually below 10^{16} atoms/cm^3. The setup of the experimental conditions for such analysis is not trivial and depends on the combination of the impurities to be analyzed and the matrix. Although the choice of the primary ions is most important, the appropriate detection techniques for secondary ions, such as energy discrimination and detection of molecular ions, can improve the detection limits further. Table II summarizes the typical detection limits by SIMS for some of the important elements in GaN.

The elements Si, Zn, and Mg are currently used as n and p dopants for the GaN system. For doping control, there is a need for an accurate and rapid technique to calibrate the dopant sources, and when using ion-implanted standards, SIMS can provide a means of measuring the concentration of impurity with an accuracy of better than 10%. By comparing the atomic concentration of the dopant with electrical carriers determined by Hall measurements and $C-V$ profiling, the doping efficiency can be readily deduced. Moreover, with a multilayer structure of different doping levels, a single measurement of the depth profile allows a calibration curve to be determined. Figure 4 shows a p-n homojunction in GaN using Mg and Si as p- and n-type dopants. Common contaminants in GaN such as O and C and some transition metals such as Fe, Mo, Cr, and Ni are also measured. The oxygen and carbon concentrations in this sample are above the detection limits while the metallic contaminants are at or below the SIMS detection limits.

TABLE II. Typical detection limits (atoms cm^{-3}) obtained with SIMS in GaN.

Common dopants	Detection limits
Si	1×10^{15}
Mg	1×10^{15}
Zn	5×10^{15}
Cd	1×10^{16}
Se	1×10^{14}
Common contaminants	**Detection limits**
H	1×10^{17}
C	5×10^{15}
O	1×10^{16}
Cl	1×10^{15}
Al	1×10^{16}
In	1×10^{16}
Metal contaminants	**Detection limits**
Cr	5×10^{14}
Fe	5×10^{15}
Mo	5×10^{15}
Ni	2×10^{16}
Cu	2×10^{16}
Mn	5×10^{15}
Na	1×10^{14}
K	5×10^{13}

2. Layer thickness, matrix composition, and interface quality

When combined with postbombardment crater depth measurements, SIMS can easily provide the thickness of very thin films with good accuracy. However, for heterostructure samples, a calibration curve for the dependence of the sputtering rates on matrix composition will be needed for an accurate determination of layer thickness.

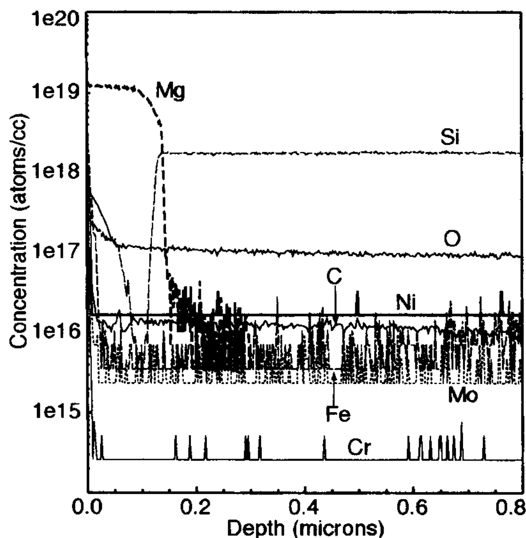


FIG. 4. SIMS depth profile of a p-n homojunction in GaN using Mg and Si as p- and n-type dopants. Common dopants in GaN such as O and C and some transition metals such as Fe, Mo, Cr, and Ni are also measured.

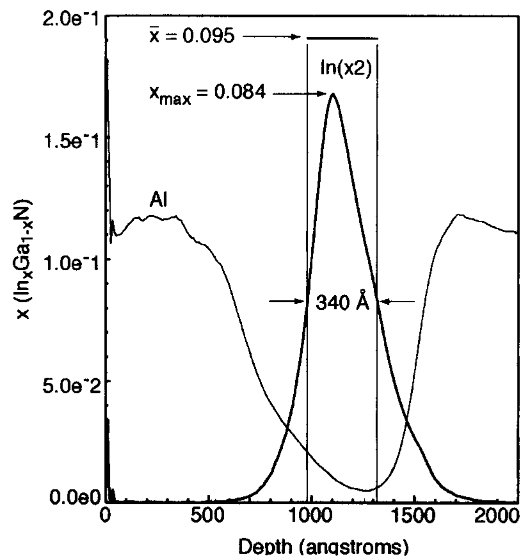
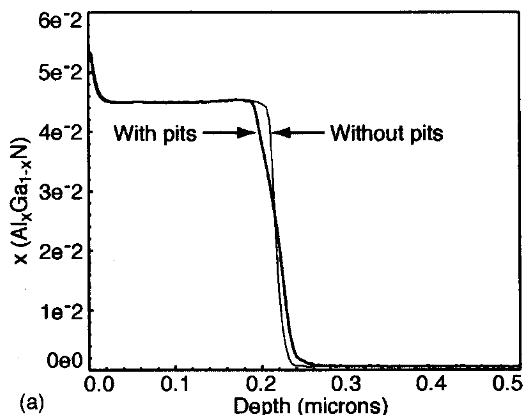
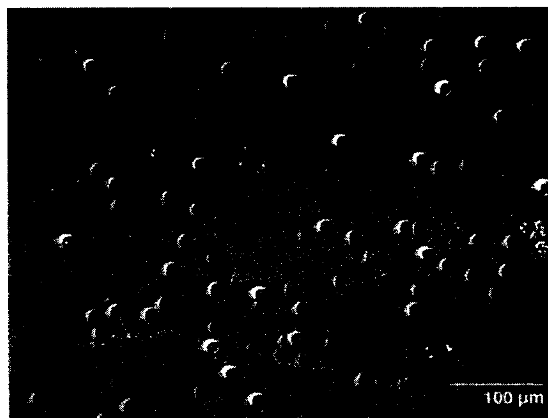


FIG. 5. Composition depth profile by SIMS of a GaN/InGaN/GaN quantum well structure. The quantum well is nominally 40 nm thick.

As described in the previous section, SIMS quantification of matrix elements is complicated because a variation in matrix composition changes the secondary ion yield and leads to a nonlinear calibration curve. One technique for circumventing the matrix effect is to detect the molecular ion MCs^+ (M is the matrix element to be analyzed) under Cs^+ bombardment. This technique allows the use of some other well-defined III–V compounds such as AlGaAs and InGaAs as the SIMS standards for III nitrides. Comparing the usual compositional techniques such as PL and x-ray diffraction measurements, SIMS can unambiguously provide a chemical composition profile of device structures in addition to dopant profiles. Figure 5 shows the depth profiles of a GaN/InGaN/GaN quantum well structure by SIMS. Since the depth resolution (about 15 nm) is not high enough to totally resolve the well in this case, the In profile does not show a flat top in the InGaN well, which is necessary to give a single value characteristic of this layer. Consequently, the In concentration value indicated (x_{max}=0.084) in the figure underestimates the real In concentration. However, a correction can be made. The areal density of In can be calculated by integrating the In profile across the quantum well. An upper limit to the In composition of $x=0.095$ is obtained by assuming that the quantum well is a perfect delta function with a width of 34 nm (the full width at half-maximum for the In peak). Therefore, the real In concentration should be between 0.084 and 0.095.

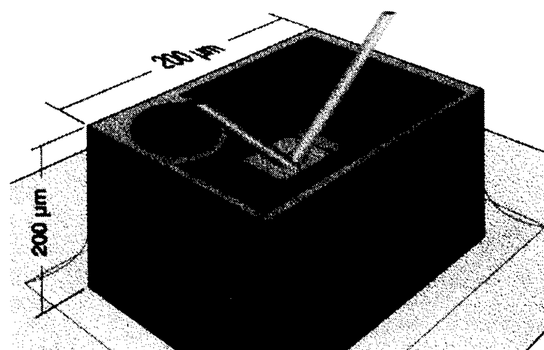
The depth resolution in SIMS is determined by several physical processes induced by ion bombardment (cascade atomic mixing, preferential sputtering, etc.) as well as by the initial surface roughness.[5] Generally speaking, one can achieve depth resolution no better than the initial surface roughness of the sample. For specimens with a very smooth surface such as GaAs and Si, the depth resolution is limited by ion mixing and by the roughness that is induced by ion





(b)

FIG. 6. (a) Al depth profiles at the interface of an AlGaN/GaN sample. One profile was acquired on a sample with a high density of visible surface pits, whereas the other curve was obtained on a sample with few if any visible pits. (b) Optical micrograph depicting the surface morphology of this sample.



(a)

(b)

FIG. 7. (a) SIMS analysis of a finished LED chip after de-encapsulation (top). (b) Optical micrograph depicting the post-SIMS measurement crater on the lower left-hand side and the remnant of the setup crater on the upper right-hand side of the device (bottom).

bombardment. The ultimate depth resolution by SIMS can be less than 1 nm if careful choices are made on the primary ion species, primary ion energy, and bombardment angle.[6] However, for present day GaN samples, the depth resolution is mostly limited by the initial surface roughness. Even though surfaces are locally smooth on an atomic scale, the density of surface pits is great enough that the SIMS analytical area (from 10^2 to 10^3 cm^2) almost always includes some pits. These pits degrade the depth resolution to an extent which depends on their size and nature. Figure 6 shows the Al depth profiles at the interface of an AlGaN/GaN sample. In one case, some pits are visible at the surface, while in the other sample, the pits are far less numerous and invisible. Evidently, the width of the interface is broadened by the surface roughness associated with these pits. The loss of depth resolution will make the SIMS composition analysis of quantum well structures much more difficult, because secondary ion intensities characteristic of each thin layer must be measured to allow the composition to be determined accurately. Nonetheless, given the reasonably good depth resolution provided by SIMS, it can provide a straightforward means of identifying diffusion-related degradation mechanisms. Concurrent engineering principles typically prescribe a high-temperature testing routine through a series of annealing treatments at temperatures above that of the intended operating environment. The SIMS technique permits the quick analysis of a batch of such devices annealed at various temperatures and times in order to more swiftly develop robust packaging, contacts, and device designs.

3. Finished device analysis

In spite of the small size (total surface area of about 200 μm$\times$200 μm) of a finished LED device and the requirement for high sensitivity, SIMS analysis is possible but relatively difficult. Figure 7 shows a post-SIMS measurement crater on a GaN LED device after de-encapsulation (lower left corner) and the depth profiling results consisting of both dopant and matrix ion information are exhibited in Fig. 8. The ability of carrying out the analysis on finished devices makes SIMS technique a powerful tool for failure analysis, reverse engineering, and concurrent engineering (e.g., early identification of failure mechanisms expected in high-temperature operation).

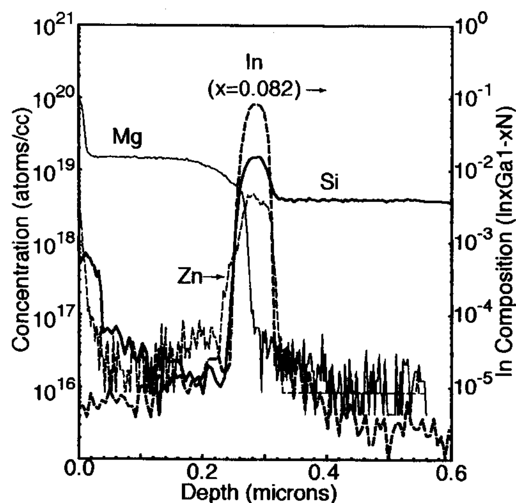


FIG. 8. SIMS depth profiles of dopants compositional profile for the GaN/InGaN/GaN LED device shown in Fig. 7.

IV. CONCLUSION

We have performed a comprehensive study on the complete characterization of III nitride materials and devices using SIMS. The ion yields of dopant and matrix species have been measured, making possible more accurate and precise measurement for these compounds. With a single technique, SIMS provides the quantitative analysis for both trace and major elements (concentration ranging from 10^{15} to 10^{22} atoms/cm^3) to investigate dopant diffusion, impurity concentrations and distributions, as well as layer composition. Information on thickness and interface quality can also be obtained with the same measurement. Offering excellent sensitivity and depth resolution, SIMS is a very powerful characterization technique in both R&D and production environments.

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