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In-depth Analysis of the Impurities in GaN

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Abstract

GaN epitaxial films were analyzed by Secondary Ion Mass Spectrometry (SIMS). Standard implanted samples were used to determine the appropriate analytical conditions for analysis of impurities. The dose and energy of implantation for selected elements (Mg, Al, Si, Zn, Cd, H, C and O) were chosen so the maximum impurity concentration was not more than 10^{20} atoms/cm^3. The optimum analysis conditions were ascertained from the standards for each element, and the detection limits were deduced from the background levels of the implantation profiles. We demonstate that lower detection limits of 10^{15} atoms/cm^3 with a dynamic range 10^3 - 10^5 are possible. Zn and Cd have low ion yields, so the minimum detection level for these elements is the background level of the detector. The detection limits of the other elements are determined by the contamination of an initial GaN matrix.

1. Introduction

The wide bandgap semiconductor GaN shows great promise for blue light emitting diodes and ultraviolet laser diodes. To realize such devices it is necessary to obtain thin films with controlled concentrations of impurities. The common dopants for GaN are Mg, Al, Si, Zn, Cd, and In [1]. Also, H, C, and O can be electrically active elements and the knowledge of their concentration is also of great interest [2]. It is therefore important to develop methods of analysis for all impurities which may affect device performance. Secondary Ion Mass Spectrometry (SIMS) is a powerful and convenient method for the determination of the distribution and concentration of impurities. It can perform quantitative analysis based on ion implanted standard samples [3] and is superior to other techniques with regard to the lateral and depth resolution.

In this study we optimized the analysis conditions to determine detection limits of impurities of interest for controlling the conductivity of GaN films. In-depth analyses of contaminants such as H, C, O is also shown.

2. Experiment

Standard samples were prepared by ion implantation into (0002) GaN films under the conditions listed in Table I. The implantation energy was chosen to obtain a maximum impurity concentration (R_p) depths between 100 - 150 nm to reduce the influence of sub-surface layers. The dose was selected to provide a maximum impurity concentration of ~1 atomic percent to insure a linear dependence of the impurity signal versus concentration (to within <1% [3]). The thickness of the GaN films were ≥2 µm to permit the measurement of the implantation distribution to $10\Delta R_p$.

A Cameca IMS 4f instrument was used. The analysis conditions were defined from empirically established principles for $A_{III}B_V$ semiconductors [4]. We selected 5.5 keV O_2^+ primary ions to analyze Mg, Al and In; positive secondary ions were recorded. Cs^+ primary ions (E = 5.5 keV) were used for Zn and Cd and CsX^+ ions (X= Zn, Cd) were detected. The Si, H, C, O signals were obtained using negative secondary ion registration. Primary current densities of 100 - 1000 µA/cm^2 were employed. The sputter rate for GaN was 2 - 10 Å/sec for the various of primary ions.

To eliminate a crater edge effects we chose the field and contrast diaphragms so that only a 60 µm diameter area

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centered in the 250 µm × 250 µm crater was analyzed.

3. Results and discussion.

3.1. Determination of Mg, Al, and In

The calibration characteristics $C = f(I_{impurity}/I_{matrix\ ion})$ obtained for each impurity from analyses of the implantation profiles are given in figure 1. The GaN^+ signal was chosen as the matrix reference ion. The raw data yielded ion counts per unit time which has been replotted in figure 1 once the total number of integrated counts was correlated with the implantation dose. In such graphs, the detection limit corresponds to the background level of the implantation profile. The main limitation to determining a detection limit in all the cases is bulk contamination of matrix by the analyzed impurity.

Some samples showed initial Mg matrix contamination which could be in the form of local inclusions revealed in our ion images of analyzed area. The detection limit for Mg presented in figure 1 corresponds to the "pure" matrix background level.

Local inclusions were more pronounced when we analyzed for Al (figure 2). We do not discuss the nature of the inclusions in this paper, but we believe their presence explains the high background signal level. Therefore, we believe that it is reasonable to expect that a 10^{15} atoms/cm^3 detection limit for Al (dotted line, figure 1) would be possible in the "pure" matrix case.

The detection limit of In is defined by the superposition of the matrix complex ions, such as $(^{71}Ga^{14}N_2{}^{16}O)^+$, $(^{71}Ga^{28}Si^{16}O)^+$ or $(^{71}Ga^{27}Al^{16}O^1H)^+$, and the $^{115}In^+$ signal. To minimize the influence of the complex ions it is possible to change the secondary accelerating voltage (offset ~ 90 V). This method allows one to discriminate complex ions by means of an energetic slit because they have a more narrow energetic distribution in comparison to monatomic ions. When complex ions are minimized, the In detection limit decreases by one order or magnitude (solid squares, figure 1).

3.2. Determination of Si, Zn and Cd

It is known [5] that the maximum ion yield of Zn and Cd in GaAs matrix is realized by using cesium primary beam with $CsZn^+$ and $CsCd^+$ secondary ion registration. We have determined that this is also true for the GaN matrix. Our measured detection limits are presented in figure 3, where the $^{147}CsN^+$ ion current was taken as the matrix signal. The use of $O_2{}^+$ ions on the same standard samples combined with monatomic $^{64}Zn^+$ and $^{114}Cd^+$ ion registration gave 5-10 times higher detection limits.

The determination for Si (figure 3) was realized by analyzing negative secondary ions ($^{28}Si^-$) with the aid of the high mass resolution mode ($\Delta M/M = 3000$). The $N_2{}^-$ matrix signal was taken as the reference. This is a traditional method for optimal Si determination in $A_{III}B_V$ semiconductors [6] [7]. The background signal appeared to be one order of magnitude above the detector background due to volume contamination of Si in the GaN matrix. The detection limit is actually much lower than the 10.5 x 10^{16} atoms/cm^3 represented by the dotted line in figure 3.

It must be mentioned that the high resolution mode is difficult to realize when one must record concentration profiles of several elements simultaneously. In-depth analysis of Si and Mg in GaN can serve as an example. We estimated the Si detection limit at optimal Mg analyzing conditions ($O_2{}^+$ primary beam and $^{44}SiO^+$ registration) to be only 10^{18} atoms/cm^3. Hence, if it is not necessary to detect very low Si concentrations, it is possible in normal mode operation ($\Delta M/M \sim 300$) to determine the position of a GaN pn junction directly.

3.3. Determination of H, C and O

The high electronegativity of these elements defines the choice of the analytical conditions. To have high sensitivity it is undoubtedly necessary to use Cs^+ primary ions to stimulate a high yield of negative secondary ions [4]. Our dynamic range (C_{max}/C_{min}) for concentrations of H, C and O is ≤2.1:1, even in experiments with optimal primary beam current density (~250 µA/cm^2). Therefore, we present the data most illustratively as implantation profiles (

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figure 4). The steady trend of the curve is defined by the background level corresponding to the volume contamination of the matrix by the analyzed impurity. We established that the maximum ion yields for H and O the monatomic negative ions, while for C the yield of CN^- ions is one order of magnitude higher than that of C^-.

The reason for the high background signal levels for the gaseous impurities is clearly illustrated in figure 5 which shows ion images of the analyzed areas. The images were obtained under conditions identical to those of the analyses over a 150 µm diamter. Segregation of these impurities to the crystallite boundaries is clearly observed. Carbon forms also incorporations with lack of H and O. We conclude that these impurities are incorporated during the crystal growth. We do not believe that it would be a problem to achieve detection limits for these elements of $\sim 10^{16}$ atoms/cm^3 because the background level corresponding to the impurity concentration in the matrix is three orders of magnitude higher than the ion detector noise level.

4. Conclusions

SIMS experiments were performed to determination appropriate analytical conditions for the analyses of elements commonly used for doping GaN. Analyses of standard implanted samples shows that detection limits down to 10^{15} atoms/cm^3 with dynamic ranges of 10^3 - 10^5 (Table II) are possible.

Unfortunately, attempts to achieve low detection limits for N, C and O have failed. We postulate that the measured minimum sensitivities of $C_{min} \approx 10^{18}$ - 10^{19} atoms/cm^3 are caused by the segregation of these impurities on crystallite boundaries.

Finally, we mentioned that our data collection was complicated by sample charging during the ion bombardment and methods must be employed to minimize this effect.

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Table I

Ion implantation data for the GaN samples

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Sample#	Isotope	Dose [cm^{-2}]	Energy [keV]
43	^{24}Mg	3e15	200
63	^{24}Mg	1e15	200
65	^{24}Mg	1e15	200
62	^{27}Al	1e15	200
64	^{27}Al	1e15	200
15	^{115}In	5e14	100
24	^{28}Si	1e15	100
41	^{28}Si	5e15	200
61	^{28}Si	1e15	200
50	^{64}Zn	6e14	200
53	^{114}Cd	3e15	200
60	^{114}Cd	3e14	200
31	^{16}O	1e15	100
23	^{12}C	1e15	100
32	^{12}C	1e15	100
33	^{1}H	1e15	50

Table II

Dynamic range and detection limit of analyzed impurities.

Mg	Al	Si	Zn	Cd	In	H	C	O	
I_{max}/I_{min}	5e4	1e4	1e3	1e3	1e3	1e4	5-7	10	10
C_{min}, at./cm^3	2e15	2e16	1e17	3e16	5e16	1e16	1e19	3e18	5e18

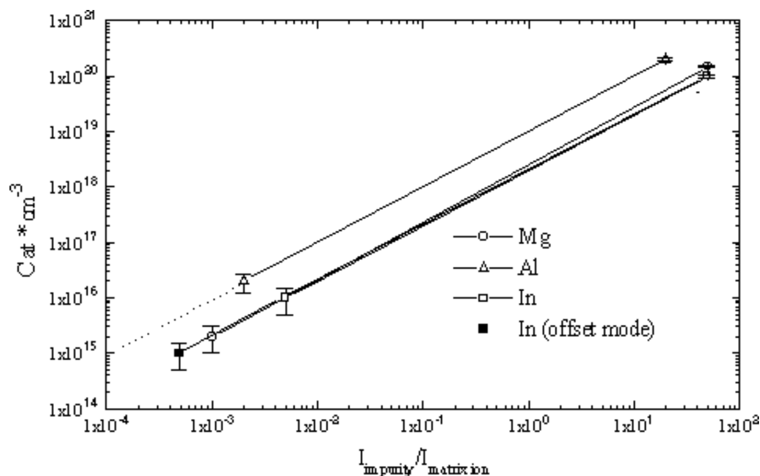

Figure 1. Calibration characteristics of Mg, Al and In impurities in GaN.

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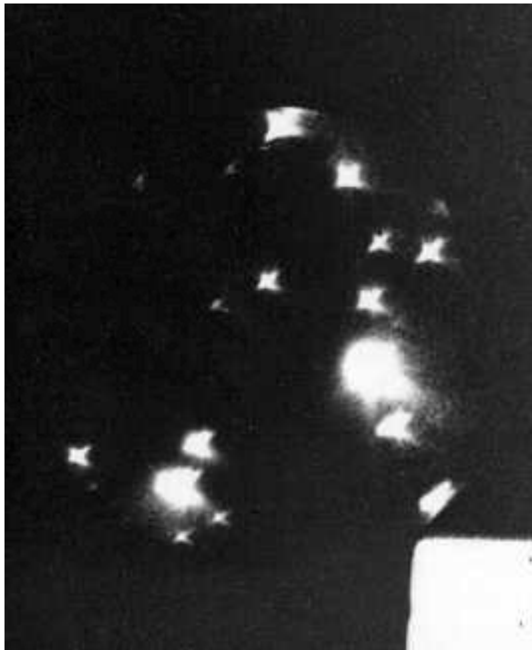

Figure 2. Ion image ($^{27}Al^{+}$) of Al contamination in the GaN-matrix (image field is 150μm).

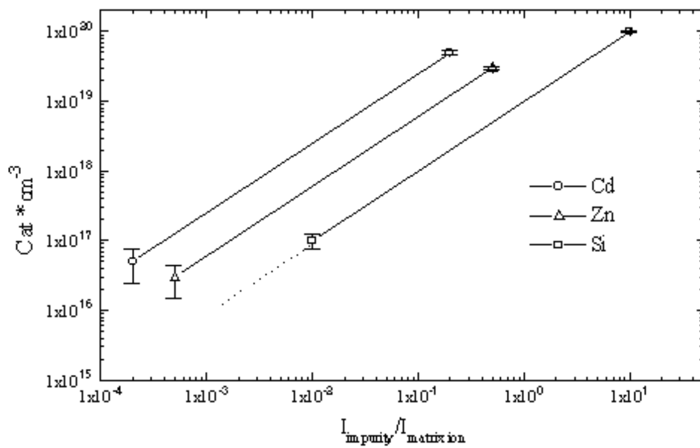

Figure 3. Calibration characteristics of Cd,Zn and Si impurities in GaN.

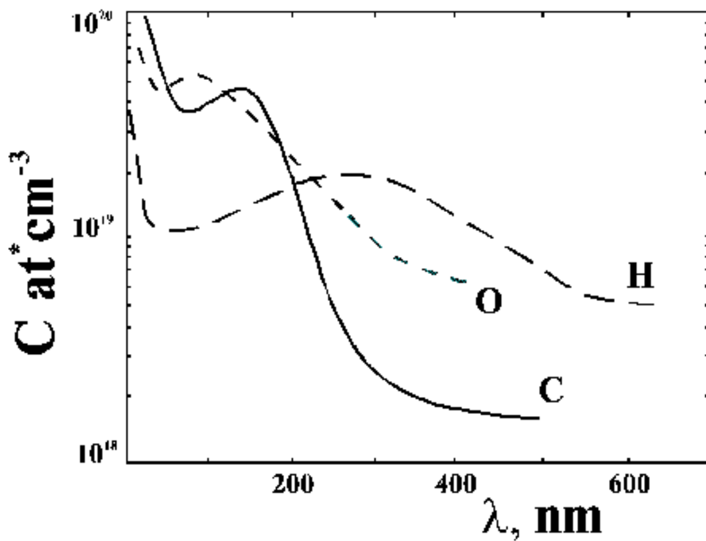

Figure 4. Depth profiles of H, C and O in implanted samples.

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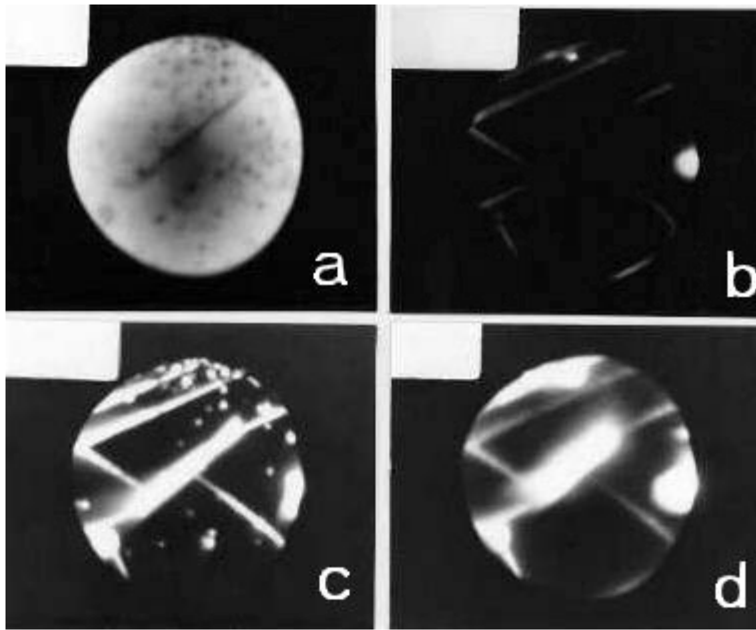

Figure 5. Ion images of H, C and O contaminations in the GaN matrix (a -GaN^-, b - H^-, c - CN^-, d - O^-).

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