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# Direct SIMS Determination of the $In_xGa_{1-x}N$ Mole Fraction

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We demonstrate that our secondary mass ion spectroscopy (SIMS) method for the determination of the mole fraction in solid $In_xGa_{1-x}N$ solutions is accurate and reproduceable *without need of reference samples*. The method is based on measuring relative current values of $CsM^+$ (M=Ga, In) secondary ions. The claim of reliable SIMS determination without reference samples was confirmed by four independent analytical methods on the same samples with a relative error in the InN mole fraction determination below 15%.

## 1 Introduction

III-V nitride semiconductor heterostructures are useful for light-emitting devices, especially at shorter wavelengths than are reachable with conventional compound semiconductors. The device properties depend critically on the metal cation composition of the emitting layer, i.e. generally the $In_xGa_{1-x}N$ mole fraction [1]. The accurate determination of the alloy composition in InGaN solid solutions is a difficult but important task, especially in the presence of phase segregation effects.

Secondary ion mass spectrometry (SIMS) is a widely used method for the analysis of layer compositions in semiconductors and semiconductor devices [2]. SIMS is complementary to photoluminescence and x-ray diffraction for InGaN mole fraction determination because it measures an overall In/Ga ratio insensitive to phase segregation into In-rich and In-poor regions. However, the calibration of SIMS data for elements present in greater than 1 atomic percent (at. %) is complicated by non-linearities in the signal vs. at. % dependence in many experimental configurations. Furthermore, each SIMS measurement generally requires a standard of known and similar composition to the sample under interrogation to permit quantitative determination of elemental concentrations.

Here we show that a SIMS determination in $In_xGa_{1-x}N$ composition is accurate over a wide range of InN mole fractions. The determination of this mole fraction can be done with relative intensities of the analytical signals MCs+ of matrix cations, as has been shown by Gnaser [3] [4] who used molecular secondary ions to determine relative sensitivity factors (RSF) in the AlGaAs/GaAs system. Once the RSFs for a given apparatus are known over an appropriate alloy range, the SIMS process is calibrated and produces the alloy mole fraction. In our system, the In and Ga RSFs are equal and stable over time, permitting us to reproduceably determine the $In_xGa_{1-x}N$ mole fraction to within a relative accuracy of 15% without the need of a reference layer. The SIMS data were verified by four independent measurement techniques.

## 2 Experimental

### 2.1 Samples

Four III-nitride thin film samples were studied. Two heteroepitaxial GaN/SiC halide vapor phase epitaxy deposited samples were ion implanted with 100 keV and 200 keV $In^+$ ions at doses of $1x10^{14}$ atoms/cm$^2$ and $1x10^{15}$ atoms/cm$^2$, respectively. In addition, two $In_xGa_{1-x}N$/glass films (denoted as P1 and P2) deposited by plasma-enhanced molecular beam epitaxy (PEMBE) were studied. The details of the PEMBE deposition of InGaN have been described elsewhere [5]. Sample P1 had an estimated InN mole fraction of 30% and thickness of 700±70 nm based on prior PEMBE flux calibrations. Sample P2 had an estimated InN mole fraction of 40% and thickness of 1000±100 nm based on the same calibrations.


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### 2.2 SIMS

A CAMECA IMS4f SIMS instrument operating at a pressure of $2x10^{-9}$ mbar was used. A $Cs^+$ primary beam focussed to a 70 µm diameter at a current of ~100 nA with an 5.5 keV impact energy scanned over an area of $250x250\ \mu m^2$. Positive secondary ions of $CsM^+$ (M = In,Ga) were accepted from circular area 60 µm in diameter by means of ion optical system. A mass resolution of $M/\Delta M$=300 and an energy window of 130 eV were used during data collection.

### 2.3 X-ray Diffraction

X-ray diffraction was performed using the Cu $K_\alpha$ line on a Geigerflex D/max.-RC diffraction system manufactured by Rigaku Corporation. The InN mole fraction was determined from Vegard's law.

### 2.4 Energy Dispersive X-ray Fluorescence Spectroscopy

Energy dispersive x-ray fluorescence (EDXRF) spectroscopy of the Ga $K_\alpha$ and In $K_\alpha$ lines was carried out using a Spectrace 5000 instrument manufactured by Tracor Corporation. The calculation of the InN mole fraction in samples P1 and P2 was done using the standardless variant of the fundamental parameters method.

### 2.5 Electron Probe Microanalysis

Electron probe microanalysis (EMPA) was performed using a CAMSCAN-4DV scanning electron microscope with an energy dispersive analyzer AN-10000 manufactured by Link Analytical Corporation. Energy dispersive analysis was employed for the In $L_\alpha$, Ga $L_\alpha$ and Ga $K_\alpha$ lines. Systemic errors were avoided by analyzing the samples at 10 kV and 20 kV using two sets of standards: monocrystals of InP and GaP and thin films of InN and GaN. The InN mole fraction was determined by the intensity ratio of the standard samples versus P1 and P2.

### 2.6 Secondary Neutral Mass Spectrometry

Secondary neutral mass spectrometry (SNMS) measurements were performed using a Leybold-Heraeus INA-3 instrument. In this technique, sputtered neutral species from the thin film being interrogated are positively ionized in the same low pressure ($4x10^{-3}$ mbar) rf Ar-plasma producing the sputtering ions. An $Ar^+$ ion impact energy of 520 eV was chosen to permit the measurement of Ga and In signals at current densities ~10 $mA/cm^2$ emanating from a sputtered field ~5 mm in diameter. A relative sensitivity factor (RSF) between In and Ga of $RSF_{In}=0.9RSF_{Ga}$ was determined using pure InN and GaN films, and applied to determine the InN mole fractions of samples P1 and P2.

## 3 Results and Discussion

SIMS measurements performed on the In-implanted GaN samples confirmed that the $CsIn^+/CsGa^+$ signal intensity ratio is equal to the actual atomic concentration ratio of In in GaN at relatively low In concentrations. One SIMS measurement is shown in Figure 1. In these data, the $CsN^+$ reference signal is normalized to unity, and the observed $CsIn^+$ and $CsGa^+$ count rates are plotted on this scale. For simplicity, the $^{71}Ga$ signal having a relative abundance of 0.396 is plotted. The $^{69}Ga$ data were parallel to the $^{71}Ga$ data. Taking into account the observed $CsIn^+$ and $CsGa^+$ count rates and the $^{69}Ga$ relative abundance, we find that the ratio of In/Ga counts is: $2.7/(2.8x10^2 \div 0.396) = 0.0038$. The InN concentration at the maximum of the implantation distribution determined from the implantation dose is $(1.8 + 0.1)\times10^{20}$ $at/cm^{-3}$. The accepted atomic density of Ga at GaN is $4.4\times10^{22}$ $at/cm^{-3}$. Hence, the mole fraction of In at maximum point of concentration is 0.004. The known In concentration from the implantation conditions is $In_{0.004}Ga_{0.996}N$. Therefore, the signal intensities observed in our SIMS experiment provide us with a calibration within 10% of the true In concentration in InGaN samples at low In content [6].

To determine if our technique extrapolates to higher InN mole fractions, we investigated the PEMBE samples using SIMS, and then verified those measurements using four independent techniques. These results are shown in Table 1. The five independently measured values shown permit us to determine the InN mole fraction to within $P1=In_{0.30\pm0.04}Ga_{0.70}N$ and $P2=In_{0.375\pm0.045}Ga_{0.625}N$, which corresponds to an absolute InN mole fraction measurement uncertainty of 12-13%.

Furthermore, the independent mole fraction measurements performed on P1 and P2 show a consistent trend. For example, x-ray and SIMS correspond closely. EDXRF and SNMS both measure several percent lower InN mole fraction and EMPA measures several percent higher InN content with respect to SIMS. These correlations suggest that given an expanded sample set which would provide us with improved statistics, the experimental uncertainty of the InN mole fraction determination could be narrowed considerably from our present worst case relative mole fraction uncertainty of 13%. Furthermore, any one of these measurement techniques, depending on which is most convenient and reproduceable, might be applicable towards the routine determination of the InN mole fraction of InGaN, even in the abscence of a standard.


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## 4 Conclusion

We have presented a SIMS-based method for the accurate determination of InN mole fraction in InGaN solid solutions without need of a reference sample, and verified this claim by independent measurements of the InN mole fraction. The method is based on comparing the relative $CsIn^+/CsGa^+$ signal intensity ratios. Comparisons with an ion implanted standard show that the SIMS signal intensity ratio reflects the actual In/Ga composition of In-implanted GaN films to within 10%. The method was successfully extended to higher InN mole fraction alloys indicating that non-linear signal intensity effects are not present in our SIMS measurement. The SIMS data are sufficiently stable that we can reproduceably measure absolute InN mole fractions with a relative accuracy of 13% or below.

## REFERENCES


[1] H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, M. Burns , *J. Appl. Phys.* ***76***, 1363-1398 (1994).

[2] A. Benninghoven, F. G. Rudenauer, H. V. Werner, Secondary Ion Mass Spectrometry: Basic Concepts, Application and Trends, Wiley, New York (1987)

[3] H. Gnaser, *J. Vac. Sci. Technol. A* ***12***, p452-456 (1994).

[4] H.Gnaser, “Quantification of SIMS depth profiling using MCs+ secondary ions”, in Proc. 10th Int. Conf. on SIMS, A. Beninghoven, B. Hagenhoff, H. W. Werner. Eds., J. Wiley & Sons, Chichester, pp.207-210 (1997)

[5] Tilman Beierlein , S. Strite, A. Dommann, D. J. Smith, *MRS Internet J. Nitride Semicond. Res.* ***2***, 29 (1997).

[6] A. P. Kovarsky, Yu. A. Kudriavtsev, V. S. Strykanov, M. P. Vatnik, "Quantitative in-depth SIMS analysis of impurities in GaN with implanted standard samples," presented at 11th Intl. Conf. SIMS, Orlando, Florida, Sept. 7-12, 1997


## FIGURES

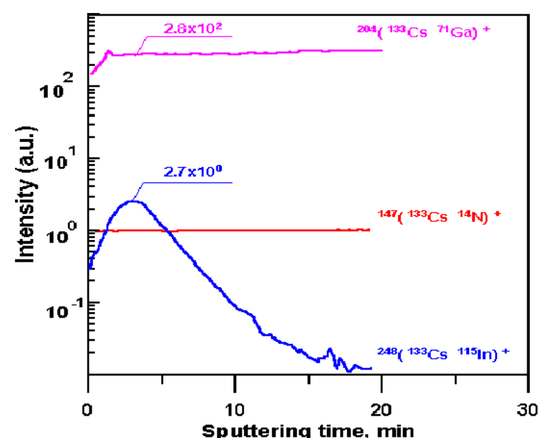


Figure 1. Depth profile In implanted in GaN with energy 200 keV and dose $1x10^{15}$ $cm^{-2}$. The $^{147}(^{133}Cs^{14}N)^+$ reference signal is normalized to unity.

## TABLES

| Technique/Samples | P1 | P2 |
|---|---|---|
| SIMS | x=0.3 | x=0.375 |
| X-ray | x=0.3 | x=0.38 |
| EDXRF | x=0.275 | x=0.345 |
| EMPA | x=0.35 | x=0.42 |
| SNMS | x=0.26 | x=0.33 |


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