Depth Profiles of Mg, Si, and Zn Implants in GaN by Trace Element Accelerator Mass Spectrometry


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Abstract. GaN is one of the most promising electronic materials for applications requiring high-power, high frequencies, or high-temperatures as well as opto-electronics in the blue to ultraviolet spectral region. We have recently measured depth profiles of Mg, Si, and Zn implants in GaN substrates by the TEAMS particle counting method for both matrix and trace elements, using a gas ionization chamber. Trace Element Accelerator Mass Spectrometry (TEAMS) is a combination of Secondary Ion Mass Spectrometry (SIMS) and Accelerator Mass Spectrometry (AMS) to measure trace elements at ppb levels. Negative ions from a SIMS like source are injected into a tandem accelerator. Molecular interferences inherent with the SIMS method are eliminated in the TEAMS method. Negative ion currents are extremely low with GaN as neither gallium nor nitrogen readily forms negative ions making the depth profile measurements more difficult. The energies of the measured ions are in the range of 4-8 MeV. A careful selection of mass/charge ratios of the detected ions combined with energy-loss behavior of the ions in the ionization chamber eliminated molecular interferences.

INTRODUCTION

The presence of impurities in semiconductors can dramatically affect the properties and behavior of the semiconductors. Impurities are purposefully introduced as n-type or p-type dopants, or sometimes accidentally introduced during processing. Detection and quantification of the implanted ions is necessary to correlate the behavior of an implanted/doped semiconductor. GaN is one of the most promising electronic materials for applications requiring high-power, high frequencies, or high-temperatures as well as opto-electronics in the blue to ultraviolet spectral region. GaN was studied in the late 1960s by Radio Corporation of America (RCA) researchers as a possible blue light-emitting diode (LED) for three-color television [1]. Red LEDs had already been developed from alloying GaAs with GaP [2] and yellow-green LEDs had been made by doping GaP with nitrogen [3]. Marusha and Tietjen made the first single-crystal film of GaN, however, the GaN films were n-type without intentional doping [1]. During attempts to make p-type GaN for pn junctions, heavy Zn doping was employed, which made the GaN films insulating. Subsequently, in 1989, p-type conducting GaN was produced by doping with Mg [4]. In 1995, blue and green heterostructure LEDs were produced [5]. Commercial GaN based LEDs and lasers are currently available. Currently, Si is a donor impurity in Ga and an acceptor impurity in N, Mg is a donor impurity in N and an acceptor impurity in Ga, and Zn is an acceptor impurity in Ga [6]. Secondary Ion Mass Spectrometry (SIMS) is one of the most widely used techniques for depth profile measurements [7,8]. However, in many cases, molecular interferences pose serious problems in identification and quantification of isotopes. Trace Element Accelerator Mass Spectrometry (TEAMS) [9], in many cases, is a more sensitive technique for depth profile measurement of implanted semiconductors because it allows removal of molecular interferences. Accelerator Mass Spectrometry (AMS) has already found wide applications in the fields of geology, archaeology, biomedicine, hydrology, environmental sciences and in many other branches of science [10]. TEAMS is a similar technique employed in the study of semiconductor materials. In this method, a SIMS
like source produces negative secondary ions from a sample, and many are in molecular form. These ions are injected into the tandem accelerator to produce MeV energy ions. The molecular ions break-up at the high voltage terminal of the tandem accelerator due to collisions with the stripper gas. The emerging positive ions with MeV energies are measured in a Faraday cup or in a detector. The TEAMS technique is proven to be more sensitive than SIMS for many elements [11-13].

**EXPERIMENTAL METHOD**

The 3MV NEC pelletron accelerator at the Ion Beam Modification and Analysis Laboratory (IBMAL) at the University of North Texas is designed for TEAMS experiments. The ion source for TEAMS measurements is an ultra-clean, cesium sputter source. The 9 keV Cs+ beam from the cesium gun is focused to ~100 µm size on the sample. The sample is an implanted semiconductor (e.g. 30Si in GaN etc.). The primary Cs+ beam current on target is about 100 nA. Secondary negative ion beams of 15 keV energy from the host matrix as well as the impurities are injected into the tandem accelerator at 1.7 MV terminal voltage for the TEAMS measurements. The rigidity of the analyzing magnet on the high-energy side of the accelerator sets an upper limit on the terminal voltage for heavy-ion counting. The high-energy magnet analyzes the momentum per charge of the transmitted ion. The TEAMS beam line is at 40° to the accelerator and has a 45° spherical-electrostatic analyzer (ESA) for energy per charge selection following the analyzing magnet. After the ESA, there is a Faraday cup and both a silicon surface barrier detector and a gas ionization chamber for particle counting.

In the case of implanted silicon wafers, the pilot beam current from the host matrix (e.g. Si+ ion current) is usually large enough to be measured in a Faraday cup. The trace impurity or implanted ion current is very low and therefore measured in the detector by the particle counting method. However, if the elements in the sample do not favor negative ion formation, the beam currents could be too small to be measured in a Faraday cup after acceleration. In such cases, even the pilot beam current has to be measured in the gas ionization chamber. Negative ion formation probability is a very important factor that determines the sensitivity of the measurement. GaN does not produce a good negative ion current. The typical Si+ current from a silicon target before injecting into the accelerator is ~5 nA, whereas for GaN it is only ~50 pA. The pilot beam and the trace beam are sequentially injected into the accelerator and the beam current or beam particles are measured to determine the concentration of trace elements. Since the concentration of host matrix atoms is the same throughout the measurement, the pilot beam current is used for normalizing the trace impurity count rate to include variations in beam currents during the experiment.

For depth profile measurements, the sample is raster scanned with the primary cesium beam over an area of 0.5 mm². Depth profiles can be measured more accurately by scanning as the profile is averaged over a finite area. The scan pattern is a rectangular spiral and the Cs+ beam forms a crater in the sample. The detection electronics are setup to count only the ions sputtered from the center (12 percent of the scan area) of the spiral. The center of the spiral corresponds to the flat bottom of the crater. Events arising from the walls of the crater distort the depth profile and are rejected.

**RESULTS**

We have measured the depth profiles of 30Si, 24Mg and 64Zn implanted in GaN. Details of the samples are given in Table 1. For 30Si measurements, the injected pilot beam is 69Ga+ and the trace beam is 30Si-.

| TABLE 1. Implanted ions in GaN wafers |
|-----------------|-----------------|-----------------|
| Implanted ion   | Energy (keV)    | Dose (at/cm²)   |
| 24Mg            | 150             | 1×10¹⁴          |
| 30Si            | 190             | 3×10¹⁴          |
| 64Zn            | 275             | 1×10¹⁵          |

After acceleration, 69Ga4+ and 30Si3+ beams were selected for detection. The 69Ga4+ current is too small to be measured in a Faraday cup, but produced a count rate of nearly 3000 counts per second in the gas ionization detector. On the other hand, by injecting (GaN)- ions, one can obtain measurable currents, typically around 10 pA.

However, for the case of 30Si implanted in GaN, extraneous noise affected the stability of the measured current in the Faraday cup and therefore we had to rely on the ionization chamber. Table 2 shows the injected and detected beams for the three samples.

<table>
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<tr>
<th>TABLE 2. Beam information</th>
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<tr>
<td>Injected ion</td>
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<tr>
<td>(24MgN)</td>
</tr>
<tr>
<td>(30Si)</td>
</tr>
<tr>
<td>(64ZnN)</td>
</tr>
<tr>
<td>(69GaN)</td>
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370
In the slow switching mode, Ga was injected for 5 seconds followed by Si for 15 seconds and the total counting was done for 50 cycles. The total time of measurement is approximately 2500 seconds per sample and was sufficient to measure the depth profile. Figure 1 shows the count rate versus time plot. A CAMAC based data acquisition system recorded the count rates of Ga$^{4+}$ and Si$^{3+}$ in the computer.

![Figure 1](image1.png)

**Figure 1.** Count rate versus time plot for $^{30}$Si implanted in GaN.

To determine the absolute concentration of implanted ions from the measured count rate of the implanted ion as a function of time, one must know the total implanted dose and the sputtering rate of the sample due to the cesium beam. The sputtering rate is determined by measuring the depth of the crater formed by Cs$^+$ beam. After the experiment, the sample is removed from the vacuum chamber and the crater depth is measured by an Alpha-Step 500 surface profiler. From the measured depth and total measured time, one can determine the sputtering rate, which is about 3 Å/sec. The normalization factor ($N$ in sec/cm$^3$) is given by the ratio of implanted dose ($\Phi$ in at/cm$^2$) to the product of sputtering rate ($S$ in Å/sec) and the area ($A$ in counts) under the cps vs. time curve.

$$N = \frac{\Phi}{(A \times S)}$$ (1)

The normalized concentration plot is shown in Fig. 2. Measurements of $^{24}$Mg and $^{64}$Zn are more difficult than that of $^{30}$Si, again due to poor negative ion formation probabilities. The molecular ion (MgN) was injected for magnesium measurements. We selected the $^{24}$Mg$^{3+}$ ion for measurement, as it doesn’t interfere with any other ion present in the system. The peak count rate was nearly 20 per second.

![Figure 2](image2.png)

**Figure 2.** $^{30}$Si depth profile in GaN.

The measured profile is shown in Fig. 3. We have also tried measuring the Mg$^{2+}$ ion due to its higher formation probability. The $^{54}$Mg$^{2+}$ ion does have an interference with $^{12}$C$^+$ because both ions have the same mass to charge ratio. Carbon contamination is ubiquitous at these detection levels. Surface carbon results in a very high-count rate and therefore pileup. Therefore, the first few cycles must be discarded. We observed that the Mg$^{2+}$ data also resulted in the same depth profile, though the rising part of the profile was distorted by surface carbon.

![Figure 3](image3.png)

**Figure 3.** $^{24}$Mg depth profile in GaN.

The measured profile is shown in Fig. 4. Since Zn is also not a good candidate for negative ion formation, we injected the molecular ion ($^{64}$ZN$^-$) and then measured $^{64}$Zn$^{3+}$. 

![Figure 4](image4.png)

**Figure 4.** $^{64}$Zn depth profile in GaN.
CONCLUSIONS

It is well known that dopants or impurities are known to alter the electronic properties of semiconductors. Mg, Si, and Zn are important dopant impurities for GaN and need to be quantified. Trace Element Accelerator Mass Spectrometry is a powerful technique that can perform these tasks for dopants in semiconductor materials. The TEAMS technique, in general, proved to be more sensitive than SIMS in many cases, because the molecular interferences are removed. This was more evident for samples that can produce prolific negative ions. Even in the case of those impurities that do not readily form negative ions, TEAMS can still offer the possibility of unambiguous identification and measurement of their absolute concentrations.

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REFERENCES