

SIMS Analysis of Nitrogen in Various Metals and ZnO

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INTRODUCTION

- Zinc oxide is a II-VI based semiconductor with properties similar to GaN. Nitrogen is a p-type dopant in ZnO. The growth of ZnO for nanowire nanolasers was first reported in 2001 [1].
- Nickel and nickel nitride may be used as protective coatings and diffusion barriers for many semiconductor and high technology applications.
- The combination of Cu interconnects and low-k dielectric materials for new 90nm chip process have been reported [2].
- It can be seen that the ability to correctly measure nitrogen levels in these materials is an important issue.

What Are The Challenges for Measuring Nitrogen in Ni, Cu and ZnO?

- Nitrogen has a very high ionisation potential (14.53eV) and zero electron affinity [3]. As a result, both positive and negative secondary ion yields of nitrogen atomic ions are poor or absent.
- In Si, nitrogen is normally profiled with a Cs⁺ primary beam and monitored using negative molecular ions of (Si+N)⁻. In Al films, nitrogen can also be profiled by monitoring (Al+N)⁻ with Cs⁺ primary bombardment [4].
- For Ni and Cu films or layers, problems arise due to mass interferences among the various ions of interest: ⁶³Cu, ⁶⁵Cu, ⁵⁸Ni, ⁶⁰Ni, ¹²C, ¹⁴N, and ¹⁶O.
- The relative mass difference are 2 mass units: e.g., in Ni, (⁵⁸Ni+N)⁻ interferes with (⁶⁰Ni+C)⁻; in Cu, (¹⁴N+⁶³Cu) interferes with (¹²C+⁶⁵Cu), and (¹⁴N+⁶⁵Cu) will interfere with (¹⁶O+⁶³Cu).
- A mass resolution of m/Δm > 9500 to 15000, is needed to separate these interferences. For Ni and Cu, the C and O levels are often at comparable or higher levels than the N. In these cases, the SIMS analyst cannot be sure which molecular ions are being measured.

What Do We Focus On?

With a Cameca instrument, operating using Cs⁺ ion bombardment, Cs-attachment (i.e. CsM⁺ or Cs₂M⁺ normally has a reasonable ion yield and no major mass interferences from the matrix in Ni and Cu. Cs-attachment has been applied to the SIMS analyses of many elements in many materials, including nitrogen in Cu [5]. Cs-attachment may provide a good solution to profiling nitrogen in multi-layer structures such as Ni/Cu/Si.

In this paper, based on various ion-implanted standards, we report that nitrogen in ZnO can be measured using a Cs⁺ primary beam, monitoring (¹⁶O+¹⁴N)⁻. This is because the possible mass interference of (¹²C+¹⁸O)⁻ is normally weak since ¹⁸O is only about 1/500 of the abundance of ¹⁶O. We also report N profile measurements and the optimization of sensitivity in Cu and Ni films using a Cs⁺ primary ion beam monitoring (CsN)⁺ and (Cs₂N)⁺ cluster ions.

Comparisons between profiles measured by SIMS and profiles simulated by SRIM [6] will be discussed. Solutions for profiling multi-layer structures such as Ni/Cu/Si will be proposed. Limitation of the Cs-attachment method will also be discussed.

EXPERIMENTAL

- Samples:
 - 1000nm thick ECP (electrochemical plating) Cu,
 - 2000nm ECP Ni film
 - Commercially available polished Zinc Oxide wafer (n-type due to intrinsic defects and no nitrogen doping)
 These were used for the ion implantation. The initial nitrogen levels in the Ni and Cu prior to the implantation were about 2e17 atoms/cm³, and initial nitrogen level in ZnO prior to implantation was below 3e16 atoms/cm³.
- ¹⁵N was chosen for implantation into Ni and Cu films at an energy of 200keV and a dose of 5e14 atoms/cm², at room temperature.
- The ZnO was implanted with 100keV ¹⁴N⁺ to a dose of 5e14 atoms/cm², at room temperature.

SIMS Analysis

- Work carried out on a modified Cameca IMS-4f at Charles Evans & Associates in Sunnyvale, California.
- The Cs⁺ primary ions were accelerated to 10keV and the secondary ions were extracted at 4.5keV, resulting in a profiling energy of 14.5keV for negative secondary ions and a profiling energy of 5.5keV for positive secondary ions.
- The angle of incidence was 24.5° in negative ion mode and 42.5° in positive ion mode.
- The typical pressure in the main chamber during Cs⁺ primary beam analysis was in the mid 10⁻⁹ Torr range. It should be noted that since we focus on the implanted nitrogen concentration profiles here, no special vacuum improvement and sample preparation (such as short time baking and pre-sputtering) was involved in this work. No background subtraction was used for any profiles reported here.
- Depth calibration was done using a KLA-Tencor P-10 surface profiler.

RESULTS & DISCUSSION

3.1 Analysis of ¹⁵N-implanted Ni and Cu films

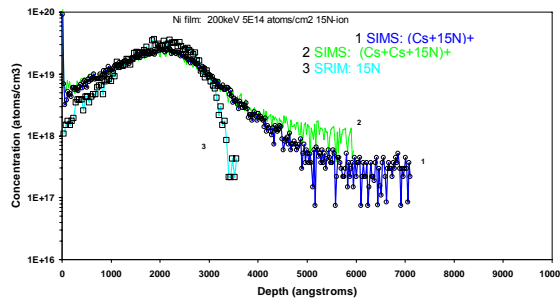


Fig. 1 SIMS depth profiles of implanted ¹⁵N in Ni, Line 1: quantified from (CsN)⁺ signal; Line 2: from (Cs₂N)⁺ signal; Line 3: simulated ¹⁵N Profile.

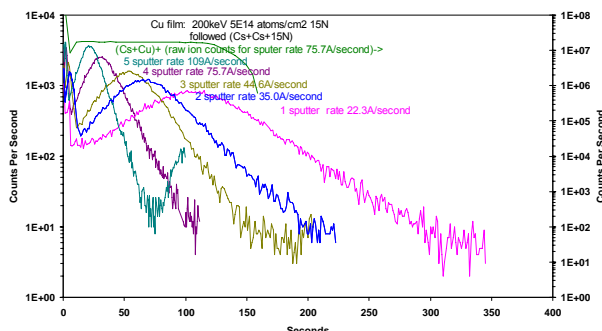


Fig. 2 The raw data [(Cs₂N)⁺ ion count vs the time] of five Cs-attachment SIMS measurements on the ¹⁵N implanted Cu.

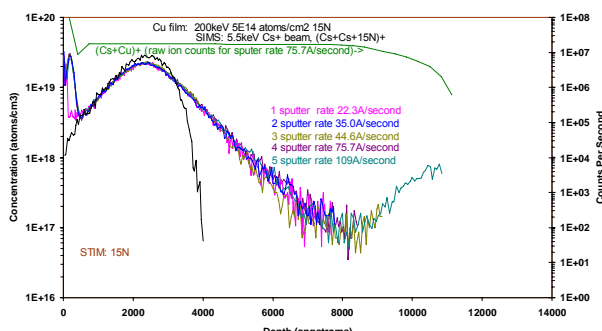


Fig. 3 The calibrated ¹⁵N depth profiles corresponding to the raw data shown in Fig 2 (lines 1 to 5). Line 7 is (CsCu)⁺ raw ion counts.

SIMS Quantification [7,8]

- With the implanted sample as a STANDARD of known composition:

$$RSF = \frac{C_a}{I_a} \times I_m$$

C_a - is the known concentration of element "a"
I_a - is the measured intensity of element "a"
I_m - is the measured intensity of matrix element "m"
(Here we used O⁻ for ZnO, (Cs₂)⁺ for Ni and Cu)

- CONCENTRATION:

$$C_a = I_a \times \frac{RSF}{I_m}$$

C_a = concentration of element "a"
I_a = intensity of element "a"
RSF = relative sensitivity factor
I_m = intensity of matrix element "m"

No significant variations of the RSFs were observed over a wide range of sputter rates.

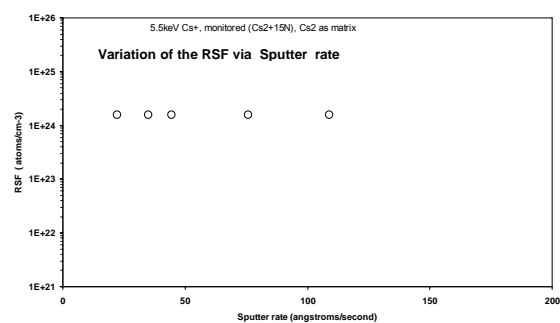


Fig. 4 The variation of the RSFs with the sputter rate for this case of nitrogen in Cu (5.5keV Cs⁺, (Cs₂N)⁺ and using Cs₂ as matrix.

The Cs-attachment method also works in Si, although the detection limit is much worse than for (Si+N)⁻.

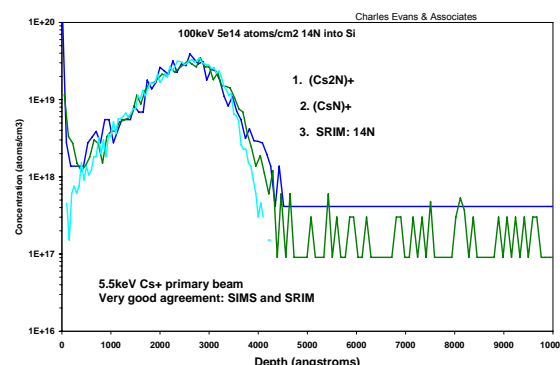


Fig. 5 SIMS and SRIM profiles in ¹⁴N-implanted Si sample.

RESULTS & DISCUSSION

Nitrogen in Ni and Cu:

For Ni: monitoring CsN⁺ is more sensitive.

For Cu, monitoring Cs₂N⁺ and CsN⁺ are similar but Cs₂N⁺ is slight better.

The RSFs are dependent on the matrix materials. e.g. when monitoring Cs₂N⁺ and using Cs₂ as the "matrix" reference, the following RSF order is observed:

$$RSF(Cu) < RSF(Si) < RSF(Ni).$$

The measured and simulated profiles by SRIM [6] are both Gaussian-like distributions and are in good agreement each other. But, the measured N profile is about 20% to 25% wider than the simulated profile and so the measured N peak concentration is lower than the simulated N peak concentration. For Au-implanted YBaCuO samples it has been reported that the Au profile measured by SIMS is about 20% wider than the simulated Au profile from SRIM [7]. We think that mixing effects from the primary ion beam during SIMS profiling [8] may partially induce the widening of the measured profiles.

Cs-attachment works well for Ni and Cu and would clearly be useful on multi-layer structures such as Ni/Cu/Si.

It has been found that using an O₂ primary beam while monitoring N⁺ atomic ions is an alternative method of measuring N in Cu and Ni, however the detection limits up 5 times poorer than with the optimized Cs-attachment method.

3.2 Analysis of ¹⁴N-implanted ZnO

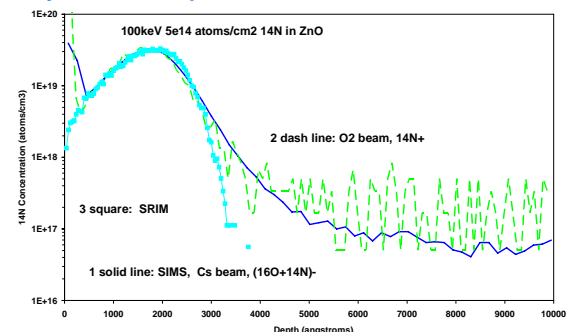


Fig. 6 SIMS depth profiles of implanted ¹⁴N in ZnO, 1. solid line: using 14.5keV Cs⁺ and monitoring (O+N)⁻ signal; 2. dashed line: using 8keV O₂⁺ beam and monitoring ¹⁴N⁺ signal; 3. square line: simulated ¹⁴N profile from SRIM.

Nitrogen in ZnO:

The Cs-attachment method discussed above is poor for profiling nitrogen in ZnO. This is because the matrix molecular ions of (⁶⁶Zn+⁶⁷Zn) cause a strong mass interference with ¹³³Cs, and thus CsN⁺ or Cs₂N⁺ cannot clearly show the implanted N distribution. Thus for nitrogen measurement, the Cs-attachment method only works on selected matrices with the following necessary condition: No molecular/cluster ions formed from the matrix should have a nominal mass the same as ¹³³Cs.

It should be noted that ¹⁸O is 1/500 of the abundance ¹⁶O and so the interference of (¹⁸O+¹²C)⁻ with (¹⁶O+¹⁴N)⁻ is normally very low in ZnO. In fact, a very high mass resolving power, i.e. m/Δm > 25000 is needed to separate these (unreachable using a Cameca).

If the C level in the test ZnO sample is very high, the measured (¹⁶O+¹⁴N)⁻ signal will be significantly interfered with (¹⁸O+¹²C)⁻. We have initially estimated that, a 6e19 atoms/cm³ level of C will contribute a 3e17 atoms/cm³ false level of N through the interference since both (¹⁶O+¹⁴N)⁻ plus (¹⁸O+¹²C)⁻ would be measured. In this case, nitrogen may have to be measured by using an O₂⁺ beam.

CONCLUSION

- For Cu and Ni, the optimised way to measure nitrogen is using a Cs⁺ primary beam and Cs ion attachment: monitoring (Cs₂N)⁺ in Cu and (CsN)⁺ in Ni. No significant variation in the RSFs was observed for the range of the selected sputter conditions. The RSFs are dependent on the matrix materials. The Cs-attachment method can clearly work on the multi-layer structures such as Ni/Cu/Si.
- The optimized way to measure nitrogen in ZnO is using a Cs⁺ primary beam, monitoring (O+N)⁻. For multi-layer structures, or for ZnO containing a high level of C, nitrogen can be measured using an O₂⁺ primary beam and measuring ¹⁴N⁺ directly, however with a poorer detection limit than the (O+N)⁻ method under Cs⁺ profiling.
- The range data measured by SIMS are compared with the simulated data from SRIM. The agreements are found to be very good in ZnO, and good in Cu and Ni films.

Acknowledgements

The authors gratefully acknowledge the support of the SIMS group of Charles Evans & Associates, and our other colleagues at CE&A.

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