Impurity measurements in semiconductor materials using trace element accelerator mass spectrometry

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Abstract

Accelerator mass spectrometry (AMS) is commonly used to determine the abundance ratios of long-lived isotopes such as $^{10}$B, $^{14}$C, $^{36}$Cl, $^{129}$I, etc. to their stable counterparts at levels as low as $10^{-16}$. Secondary ion mass spectrometry (SIMS) is routinely used to determine impurity levels in materials by depth profiling techniques. Trace-element accelerator mass spectrometry (TEAMS) is a combination of AMS and SIMS, presently being used at the University of North Texas, for high-sensitivity (ppb) impurity analyses of stable isotopes in semiconductor materials. The molecular break-up characteristics of AMS are used with TEAMS to remove the molecular interferences present in SIMS. Measurements made with different substrate/impurity combinations demonstrate that TEAMS has higher sensitivity for many elements than other techniques such as SIMS and can assist with materials characterization issues. For example, measurements of implanted As in the presence of Ge in Ge$_x$Si$_{1-x}$/Si is difficult with SIMS because of molecular interferences from $^{74}$GeH, $^{29}$Si$^{30}$Si$^{16}$O, etc. With TEAMS, the molecular interferences are removed and higher sensitivities are obtained. Measured substrates include Si, SiGe, CoSi$_2$, GaAs and GaN. Measured impurities include B, N, F, Mg, P, Cl, Cr, Fe, Ni, Co, Cu, Zn, Ge, As, Se, Mo, Sn and Sb. A number of measurements will be presented to illustrate the range and power of TEAMS.

PACS: 61.72.Ss; 61.72.Tt; 71.55; 82.80.Ms

Keywords: Trace element analysis; TEAMS; Accelerator mass spectrometry; Secondary ion mass spectrometry; SIMS

1. Introduction

In the many processing steps necessary for the fabrication of electronic devices, elemental impurities may be purposely introduced as n- and p-type dopants (e.g. As and B) or accidentally introduced during the manufacturing process (e.g. V, Fe, Cu). The presence of impurities even at trace levels of $10^{-6}$ to $10^{-12}$/cm$^3$ can affect device performance [1]. The scaling of device speed and operating voltage has made these devices especially sensitive to the presence of impurities.
A number of impurity characterization techniques are presently used by the semiconductor industry to monitor contaminants and intentionally introduced impurities, but many are limited in their range of application. For example, secondary ion mass spectrometry (SIMS) is one of the most commonly used techniques for impurity characterization in electronic materials, but is limited by molecular interferences [2,3]. Common molecular interferences with SIMS are: $^{28}\text{SiH}_3$, $^{29}\text{SiH}_2$, or $^{30}\text{SiH}$ for $^{31}\text{P}$; $(^{16}\text{O})_2$ for $^{32}\text{S}$; $^{28}\text{Si}^{12}\text{C}$ for $^{40}\text{Ca}$; $^{24}\text{Mg}^{28}\text{Si}$ for $^{52}\text{Cr}$; $(^{28}\text{Si})_2$ for $^{56}\text{Fe}$; $^{28}\text{Si}^{29}\text{SiH}$ or $^{29}\text{SiH}$ for $^{58}\text{Ni}$; $^{28}\text{SiO}_2$ or $^{30}\text{Si}_2$ for $^{60}\text{Ni}$; $(^{28}\text{Si})_2^{16}\text{O}$ for $^{72}\text{Ge}$; $^{74}\text{GeH}$ or $^{29}\text{Si}^{30}\text{Si}^{16}\text{O}$ for $^{75}\text{As}$; etc. Trace element accelerator mass spectrometry (TEAMS) is a complimentary technique to SIMS that allows the removal of molecular interferences by breaking up the molecules through electron stripping in the terminal of a tandem accelerator and therefore, in many cases, results in higher sensitivities [4,5].

2. Experimental methods

The TEAMS system, shown in Fig. 1, consists of three major components: an ultra-clean ion source, a tandem accelerator and a detector. The ultra-clean ion source reduces sample contamination from elements that are present in the ion source hardware and cross-contamination from other samples. The tandem accelerator allows molecular interferences to be removed by electron stripping of the atomic and molecular ions and acceleration of the ions to MeV energies. Almost all molecular ions that are stripped to a $3^+$ charge state or higher dissociate in the terminal [6]. The post acceleration beam line detection system provides momentum/charge ($mv/q$) and energy/charge ($E/q$) discrimination and total energy detection for elemental identification and quantification. Since the ions are at MeV energies, nuclear particle detectors or ionization chambers ensure 100% detection efficiency. The TEAMS system magnets and electrostatic analyzers are calibrated by running mass scans for elements of known concentration, e.g. the elements and molecules from the matrix. For Si, one could use $^{28}\text{Si}$, $^{29}\text{Si}$, $^{30}\text{Si}$, $^{28}\text{Si}_2$, $^{29}\text{Si}_3$, etc.

The TEAMS system is under computer control and may be operated in either a bulk-analysis mode or a depth-profiling mode. In the depth-profiling mode, the sensitivity is less than the bulk-analysis mode because there is only a limited amount of material available for analysis. In the bulk-analysis mode, one can count for longer times to measure low levels, but uniform impurity or dopant distribution throughout the sample is required. For both analysis modes, the count rate can be converted to concentration in atoms/cm$^3$ by running a standard and comparing the count rates. In the depth-profiling mode, the depth can be calibrated by measuring the crater depth with a profilometer and knowing the length of time of the run. Typical measurement parameters are shown in Table 1.

2.1. Quantifying TEAMS data using implant standards

For example, for a 200 keV, $2 \times 10^{14}$ atoms/cm$^2$ $^{60}\text{Ni}$-implant in Si, the normalization factor,
\[ N = \text{fluence} / (A \times S), \quad \text{where,} \quad A = \text{area under the counts per second (cps) vs. time curve (} 4.29 \times 10^6 \text{ counts in this example}) \text{ and} \quad S = \text{sputtering rate} \left(2.6 \times 10^{-8} \text{ cm/s}\right). \] Therefore, \[ N = 2 \times 10^{14} \text{ atoms/cm}^2 / (4.29 \times 10^6 \text{ counts} \times 2.6 \times 10^{-8} \text{ cm/s}) = 1.82 \times 10^{13} \text{ atoms/cm}^2/\text{cps}. \] The concentration, \( \text{conc} = \text{cps} \times N. \) The detection limit is \( N \times \text{least count in the depth profile}. \)

Allowances must be made for differences in negative ion formation probability, isotopic abundance and transmission which includes charge state fractionation in the stripping process in the tandem accelerator since only one charge state can be transmitted at a time. The biggest factor in determining the detection limit, is the negative ion formation probability. Some elements (N, Mn, etc.) do not form negative atomic ions at all, while for others, the production rate can be three orders of magnitude lower than the matrix ion. Usually, one can pick a molecular ion of the form \( \text{MX}^- \), where \( \text{M} \) is a matrix atom and \( \text{X} \) the impurity atom, and obtain a good yield of the required impurity ion. The relative sensitivity factors of SIMS \cite{3} provide a good guide for selecting the appropriate ion for analysis.

3. Results and discussion

The transition metals are some of the more troublesome impurities in Si. Ion implanters often implant low levels of transition metals during implantation due to inadequate mass resolution of the analyzing elements. The metals are believed to cause deep level traps. The Semiconductor Industry Association (SIA) roadmap predicts allowable surface impurity concentration levels for transition metals as low as \( 5 \times 10^8 \text{ atoms/cm}^2 \) \cite{7}.

Fig. 2 shows depth profiles of three common transition metals (constituents of stainless steel). Mixed metal implants like these are typically used to calibrate SIMS instruments. The tail of the distribution is usually about three orders of magnitude lower than the peak and is due to a combination of several factors including ion-beam mixing and sidewall contributions. The actual sensitivity of the instrument is determined from the least count of the ionization chamber, which is determined by the maximum time available for measuring each element, which in turn depends upon the desired depth resolution. There is always a tradeoff between depth resolution and sensitivity. The more time is spent measuring one metal, the more sensitivity can be achieved, particularly since the ionization chamber used for MeV energy charged particle counting is exceptionally sensitive with virtually no background current and 100% accuracy for low counting rates. Sensitivities for Cr, Fe and Ni are given in Table 2 along with sensitivities for a number of other elements. Thus, counting for 100 s implies that the lowest detectable count rate is 0.01 cps. Of course, this also means that the sample is being consumed for 100 s and the measured count-rate represents the average.

![Fig. 2. Mixed metal implant of Cr, Fe and Ni in silicon.](image)

| Table 2 | TEAMS detection limits in Si and GeSi in depth profiling mode at the UNT |
|-----------------|-----------------|-----------------|
| Element | Matrix | Depth profiling detection limits (atoms/cm²) |
| B | Si | \( 4 \times 10^{14} \) |
| F | Si | \( 2 \times 10^{13} \) |
| P | Si | \( 3 \times 10^{13} \) |
| Cr | Si | \( 3 \times 10^{14} \) |
| Fe | Si | \( 1 \times 10^{15} \) |
| Ni | Si | \( 1 \times 10^{14} \) |
| Cu | Si | \( 2 \times 10^{14} \) |
| Zn | Si | \( 1 \times 10^{15} \) |
| As | Si | \( 2 \times 10^{14} \) |
| Mo | Si | \( 1 \times 10^{13} \) |
| Sb | Si | \( 1 \times 10^{15} \) |
| Se | Si | \( 1 \times 10^{12} \) |
| As | Ge,Si$_{1-x}$ | \( 1 \times 10^{12} \) |

The depth window is \( \sim 50 \text{ A} \).
concentration over a depth of 100 times the sputtering rate. For a sputtering rate of 2.5 Å/s, this limits the depth resolution to 250 Å. Usually the depth resolution is important near the peak of the implant, where the required counting time is quite low. For example, in the case of Ni in the figure, the maximum detected count rate was 5000 cps, implying an actual detector count rate of ~50,000 cps, since 90% of counts are rejected to achieve side-wall suppression. Of course, when bulk low-level atomic ratio measurements are desired, irrespective of depth, then the counting time can be increased to much higher values, as is the case in radioisotope AMS. Fig. 3 is a TEAMS depth profile for a 150 keV, $1 \times 10^{14}$ atoms/cm$^2$ $^{64}$Zn implant in Si. Here, one can obtain improved sensitivity by measuring only one element.

A number of electronic and optoelectronic devices can be made on strained GeSi/Si substrates by doping the substrate with impurities, such as As. The GeSi layered matrix provides an opportunity to exploit the advantages of heterojunctions in Si-based technology. However, the devices may be affected by impurity and dopant concentrations in the ppb range, especially as device size decreases. It is important to be able to measure the distribution of As in the GeSi layers in the presence of $^{74}$GeH and $^{29}$Si$^{30}$Si$^{16}$O. More common impurity analysis techniques, such as SIMS, are hampered by molecular interferences as discussed earlier. Fig. 4 shows the depth profile of 100 keV, $1 \times 10^{14}$ atoms/cm$^2$ As implant in a Si$_{75}$Ge$_{25}$ film on a Si substrate. Arsenic is measured in the GeSi matrix, free of any molecular interferences, with a detection limit of $1 \times 10^{15}$ atoms/cm$^3$.

The detection of Cu impurities has become increasingly more important with the recent development of Cu interconnects in place of Al in integrated circuits. Cu is an unwanted impurity because it is fast diffusing and causes junction leakage current problems [8]. Fig. 5 shows a TEAMS measurement of impurity copper in 10 keV, $1 \times 10^{16}$ atoms/cm$^2$ As-implanted Si. SIMS data are shown for comparison and the agreement is quite good to a depth of ~0.4 µm, where the
TEAMS data shows improved sensitivity of about a factor of six. Teams measurements were made for both isotopes of Cu and showed identical depth distributions and the count rate scaled with natural abundance. Therefore, the Cu isotopes were probably not introduced into the wafer along with the As implant, since they differ by two mass units.

4. Conclusions

TEAMS is a relatively new impurity analysis technique for semiconductor materials that is complimentary to SIMS. In many cases, TEAMS can be used to determine impurity concentrations with better sensitivities than SIMS, due to the removal of molecular interferences. Measurement standards provide quantification of results. TEAMS can measure impurities and dopants in bulk or depth profiling modes. Table 2 lists sensitivities for a number of elements in Si and SiGe determined in the depth-profiling mode. For uniform distributions, the bulk mode can provide even higher sensitivities because of almost unlimited material for analysis.

The transition metals are a contaminant problem for semiconductor fabrication that is produced by the implantation and processing equipment. With the scaling of device speeds and operating voltages, electronic devices are especially sensitive to the presence of these impurities. Impurities in compound semiconductor materials (e.g. GeSi, GaAs, HgCdTe, SiC, etc.) are particularly troublesome because of the increased number of molecular combinations possible. Here, TEAMS can be utilized very effectively, because molecular interferences can be completely eliminated, producing improved sensitivities for detection.

Acknowledgements

Work supported in part by NSF, ONR and the Robert A. Welch Foundation.

References