Energetic Metals Characterization of Purion XEmax With and Without Boost Technology™ Using VPD ICP-MS

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Abstract

Trace metallic contamination is a critical concern for CIS devices, causing image quality and sensor performance issues [1]. To better characterize metal contamination in ion implanters, Axcelis has invested in a VPD ICP-MS (vapor phase decomposition, inductively coupled plasma mass spectrometry) for both surface and bulk detection. This system is the industry standard for surface detection of trace metals due to its lack of introduced contamination, high sensitivity, and low detection limits from 1E6 at/cm^2 to 1E9 at/cm^2, depending on the element. Bulk silicon etch (BSE) uses HF vapor and ozone gas to etch the implanted silicon wafer to a controlled depth allowing the detection of energetic contaminants [2]. This paper presents BSE verification using metal implanted calibration wafers and experiments performed with BSE ICP-MS to characterize the use of Boost Technology™ in the Purion XEmax high energy implanter, designed to meet the challenges of the evolving CIS market [3].

1. Introduction

Energetic metals pose a significant challenge in CIS fabrication due to their potential to increase dark current and degrade image quality [1,4]. Energetic metal contamination can occur

when aliasing exists with the implanted dopant specie and charge state meaning the contaminants have the same magnetic rigidity. Notable interferences exist with As^{3+} and As^{4+} implants [3].

To better characterize energetic metal contamination in ion implantation, Axcelis has invested in a fully automated vapor phase decomposition (VPD) sample preparation system (RORZE Expert VPD System) and a triple quadrupole inductively coupled plasma mass spectrometer (Perkin Elmer NexION 5000 ICP-MS) shown in Fig. 1a. Having this metrology capability in-house allows for customized testing, better quality control, and makes collecting large sample sizes practical leading to faster innovation.

The Purion XEmax ultra high energy implanter with Boost Technology™ was designed to meet the challenges of the evolving CIS market. Boost Technology™ employs the use of charge exchange reactions to convert lower charge state ions into higher charge state ions prior to additional LINAC acceleration (Fig. 1b). Between the two LINAC sections, the higher charge state ions pass through a charge selector magnet, separating them from the lower charge state ions. This technology has been applied for As^{3+} implants as isotopes of Ti, V, or Cr at 50 AMU could co-implant and for As^{4+} as $^{56}Fe^{3+}$ can be co-implanted as well. Use of this technique yields higher achievable beam currents, longer source life, increased energy range, better angle control, and dramatically reduces the risk of energetic metals contamination [3].

This paper reviews findings from the characterization process of VPD ICP-MS & BSE ICP-MS as well as initial findings validating the use of XEmax Boost Technology™ to prevent energetic metal contamination.

2. Materials and Methods

2.1 Experimental Details

All tests were performed on 300mm Siltronic N-type wafers. All implants were done on an Axcelis Purion XE-series high-energy implanters. A series of ^{75}As 8 MeV implants were done with and without Boost Technology: As^{2+} was converted to As^{3+} (with Boost) and implanted with a dose of 1E15 at/cm^2, As^{3+} (without Boost) with 1E15 at/cm^2, As^{3+} was transformed to As^{4+} (with Boost) with 5E14 at/cm^2 and finally As^{4+} (without Boost) with 5E14 at/cm^2.

The implanted wafers were processed using Bulk Silicon Etch (BSE) Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for trace level metals contamination analysis. Wafers were etched down to 8 μm to fully pass the implanted layer then dried for 5 min at 100°C. Unimplanted control wafers were also etched to 8 μm to provide accurate wafer background subtraction.

The NexION 5000 ICP-MS method were setup to run in standard and dynamic reaction cell (DRC) modes with each at a 1 second dwell time with 3 replicates. The DRC mode (O_2 or NH_3) used for each element was selected for the best signal to noise ratio. The ICP-MS method was calibrated for isotope quantification using a multi-element calibration standard (SPEX); all isotopes had a correlation coefficient of > 0.99. The ICP-MS was tuned daily to obtain maximum sensitivity using a setup solution (Perkin Elmer).

The surface VPD method uses 49% hydrofluoric acid vapor to etch the SiO_2 (native oxide) off the Si wafer surface, exposing the surface contaminants. The contaminants are then recovered with a 1000 μL of a scanning solution comprised of 3% HF and 4% H_2O_2 using a nozzle scanned across the wafer surface with a 2mm edge exclusion [2].

The BSE method is used to fully etch ion implanted silicon, with only implanted contaminants remaining on the etched silicon surface. A combination of ozone and HF vapor is used to iteratively

grow and etch the oxide allowing a wafer to be etched several microns in depth. Once etched, energetic contaminants are recovered with 1000 µL of a scanning solution comprised of 3% HF and 4% H_2O_2 using a nozzle scanned across the wafer surface with a 2mm edge exclusion [2].

3. Results and Discussion

3.1 Spiked Wafer Recovery

During system qualification, a spiked wafer recovery test was performed by depositing 400ppt of calibration standard onto 3 unimplanted wafers. The solution was immediately dried at the VPD drying station at 75°C for 8 minutes. A time study was then conducted with each spiked wafer processed for surface recovery with VPD ICP-MS. The first wafer was measured after several hours, the second after 24 hours and the third after 48 hours. Wafers were kept in a clean FOSB and in a class 10 cleanroom. After 24 hours the quantity of some recovered elements shifted. Fig. 2a shows the normalized plot of the spike wafer testing. On the second day K, Cu, and Bi signal degraded to 50%, 15%, and 15% respectively. Na and Ca signals increased 50% and 110%, respectively, with Ca continuing to increase on the third day by an additional 35%. This finding highlights the importance of having in-house metals metrology to fully understand surface contamination after ion implantation. Other elements that were tested and did not vary by more than 10% were: Al, Ba, Be, Cd, Cs, Cr, Co, Ga, Hf, Pb, Li, Mg, Mn, Mo, Ni, Nb, Rd, Sr, Ta, Tl, Sn, Ti, W, V, Zn, & Zr.

3.2 BSE Characterization

To validate the BSE method for recovering and quantifying energetic contamination, aluminum was implanted into Si wafers at levels selected to mimic a trace energetic contaminant. An Axcelis

Purion XE high energy implanter was used to implant Al+ 350keV at doses of 5E10, 7E10, and 9E10 at/cm^2. SRIM was used to determine the energy necessary to implant so that the aluminum range did not penetrate deeper than 1_µm [5]. Prior to BSE, surface contaminants are removed using VPD ICP-MS. Results from the dose split in Fig. 2b and c show that an implanted contaminant can be recovered within 20% accuracy.

Stability of instrument detection limits was also analyzed for several months. Fig. 3 and 3b show the detection limits over time of a selection of highly critical metallic elements. Detection limits can be characterized as stable with no significant outliers seen.

3.3 XEmax Boost Technology^{TM}

Energetic cross contamination can be problematic with high charge state ion implantation. The Purion XEmax high energy ion implanter has the option to use Boost Technology^{TM} which utilizes charge exchange reactions to convert lower charge state ions into higher charge state ions, prior to the second stage of LINAC post acceleration (see Figure 1 b). This technique eliminates energetic contamination, potentially originating from the source, with a similar mass-to-charge ratio as the dopant ions from co-implanting into the substrate. Since different beam currents and doses were used for this testing, BSE etch time had to be determined for each implant using implanted setup wafers for each dose and dose rate to ensure that each etch depth was consistent among each set of implants. Wafer background subtraction was used to deconvolve the implant signal from wafer background signal. Wafers for background subtraction (N=5) were used from the same lot as implanted wafers and etch depth was matched to the implanted wafer. Results from BSE ICP-MS analysis (Fig. 4a and 4b) showed that when Boost Technology^{TM} is used for arsenic implants, problematic contaminants such as elements with 50 AMU and ^{56}Fe are undetectable with BSE ICP-MS.

These results were compared to previous SIMS results from XEmax performed on Si wafers in the same energy range and dose levels shown in Fig. 4c. From this we can determine that for elements with 50 AMU and ^{56}Fe BSE and SIMS are in perfect agreement, indicating that for trace energetic contaminant analysis both techniques are equivalent and that the Boost Technology^{TM} is successful in preventing metals contamination for CIS devices.

4. Conclusions

The BSE ICP-MS method for evaluating energetic metals has been validated for the in-house system at Axcelis Technologies. This method has been proven to be a sensitive and effective technique for measuring trace levels of contamination and is comparable to quantification with SIMS. In addition, it was shown that XEmax Boost Technology^{TM} is effective in removing energetic contamination. We also showed that in-house metrology is preferable to transporting externally as measured concentrations for various elements can vary if wafers are held for long periods of time.

References

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Data Availability Statement

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Author Contributions

All authors contributed to the study, conception and design. Material preparation, data collection and analysis were performed by Olivia Campbell. The first draft of the manuscript was written by Olivia Campbell and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Figure Captions

Fig. 1.　　　(a) Fully automated vapor phase decomposition (VPD) sample preparation system (RORZE) and triple quadrupole inductively coupled plasma mass spectrometer (Perkin Elmer NexION 5000 ICP-MS). (b) Layout of XEMax and booster with charge selector magnets [3].

Fig. 2.　　　(a) Recovery levels of K, Cu, Bi, Na, Fe, and Ca over time from spiked wafer testing. (b) Table of implanted aluminum 350 keV 5E10, 7E10 and 9E10 at/cm^2 doses and recoverd doses with BSE ICP-MS. (c) Aluminum BSE verification: implanted vs recovered doses of Al.

Fig. 3.　　　(a) Table of detection limits and standard deviations for elements of interest. (b) Stability of detection limits over several days.

Fig. 4.　　　(a) Normalized Fe concentration for multy charged arsenic implants (dose 5E14 at/cm^2 at 8000 keV) vs contol wafer and limit of detection. (b) Normalized AMU 50 concentration for multiply charged arsenic implants (dose 1E15 at/cm^2 at 8000 keV) vs contol wafer and limit of detection. (c) Comparison of BSE vs SIMS for energetic contaminants.
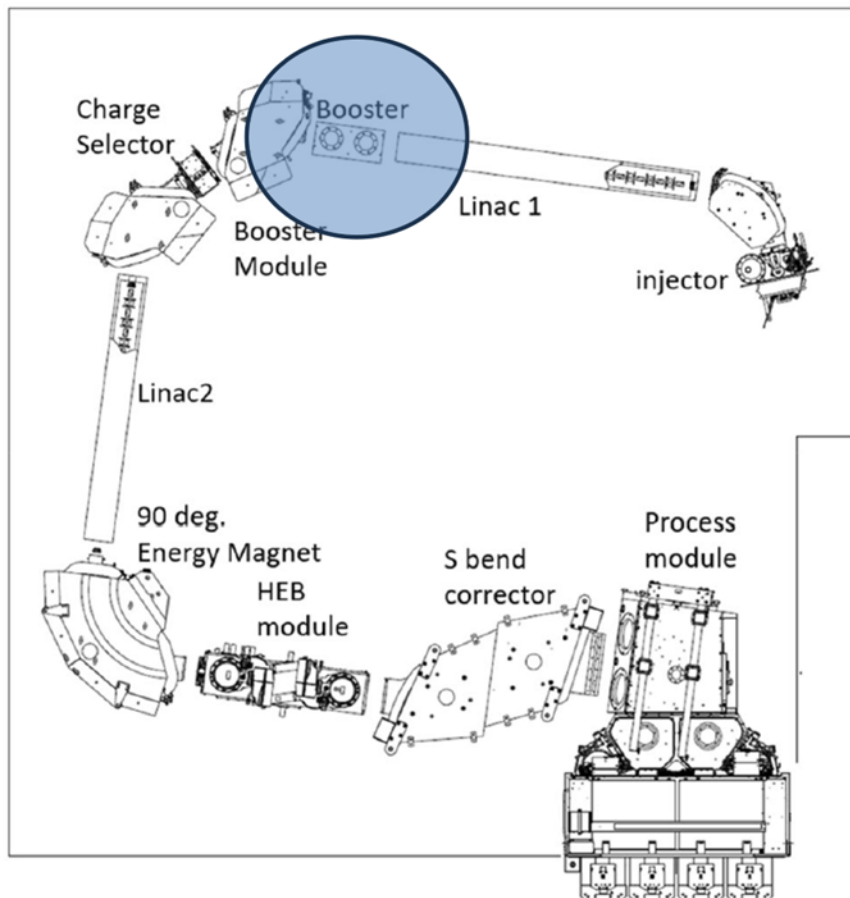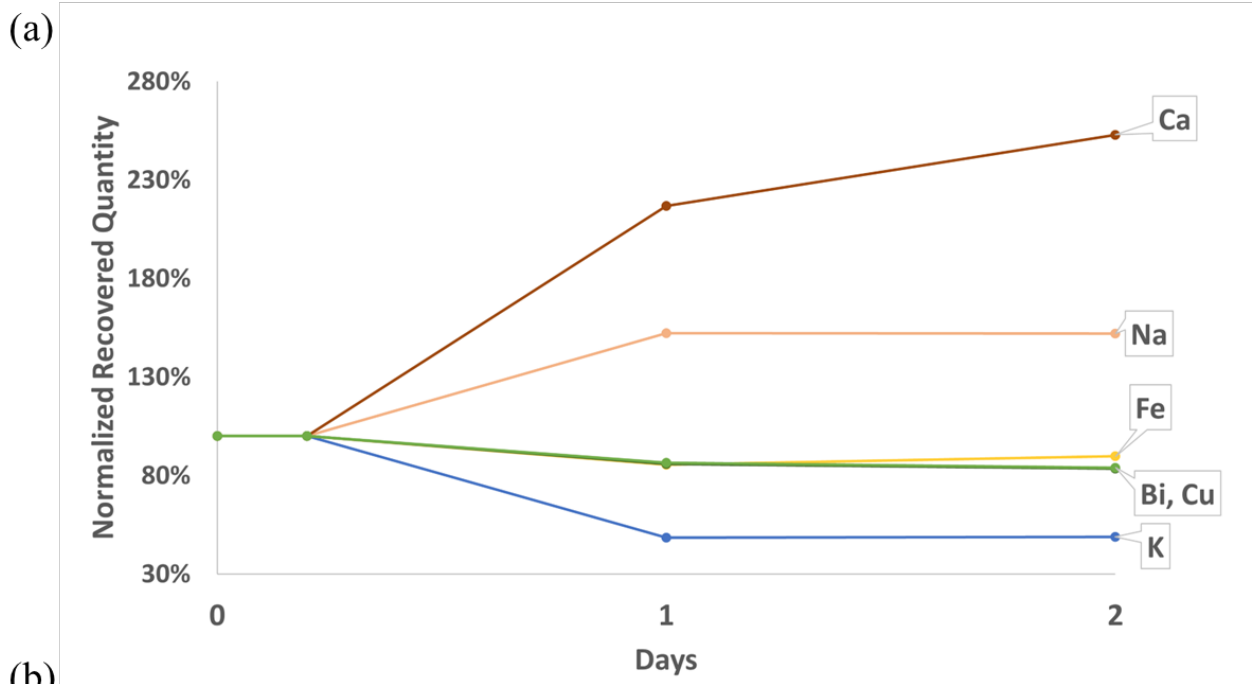
Fig.1

(a)

(b)

Fig.2

(a)

(b)

Implanted Al Dose (at/cm^2)	Recovered Al Concentration (at/cm^2)	Recovered Dose
5.00E+10	4.45E+10	89%
7.00E+10	8.21E+10	117%
9.00E+10	1.01E+11	113%

(c)
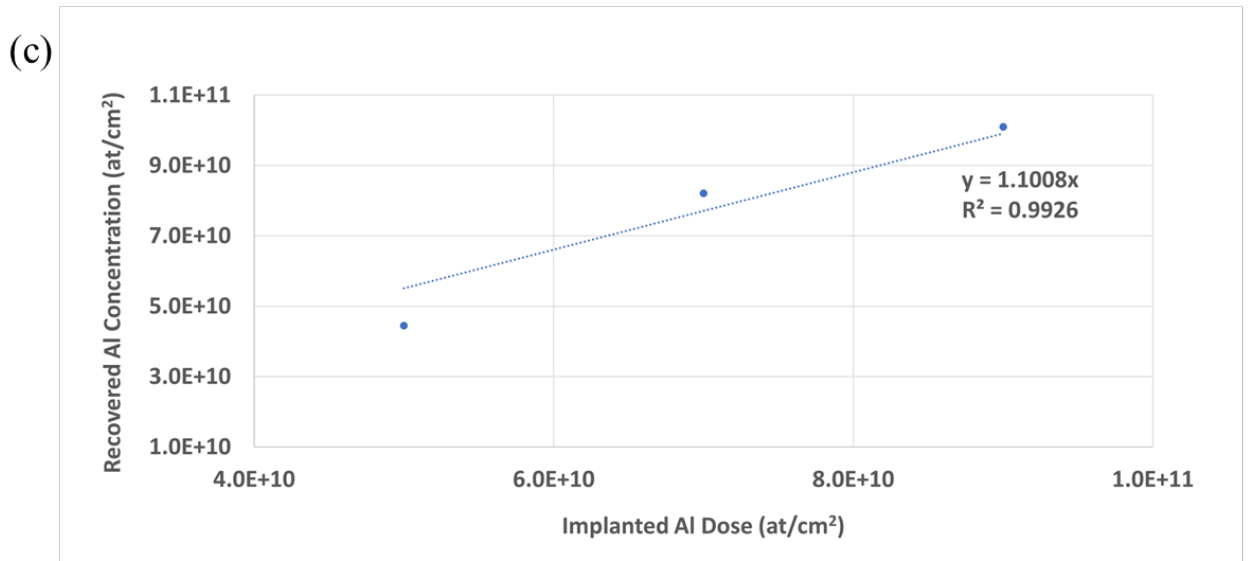
Fig.3

(a)

Element	Al	Ti	Cr	Fe	Ni	Co	Cu	Zn	Mo	W
Avg Detection Limit (at/cm^2)	5.9E+07	7.8E+07	2.6E+07	5.3E+07	2.4E+07	4.2E+06	6.8E+06	1.1E+08	2.4E+06	1.3E+06
Standard Deviation (at/cm^2)	2.7E+07	4.5E+07	7.3E+06	2.4E+07	1.6E+07	2.3E+06	2.9E+06	4.9E+07	7.5E+05	5.4E+05

(b)

Fig.4

(a)

(b)

(c)