Heavy Ion Backscattering Spectrometry Analysis of TXRF Calibration Standards

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Abstract

Within a relatively short period of time Total Reflection X-ray Fluorescence (TXRF) has become one of the most widely used techniques in determining trace levels of surface metallic contamination introduced by a variety of semiconductor processing procedures and equipment. Unfortunately, TXRF is not a first principles technique, and the answers one obtains are only as good as the standards used to calibrate the instrument. One of the concerns has always been the accuracy of the primary standards, as large instrument-to-instrument variations have been noted when samples have been analyzed on different TXRF systems within Motorola. Round robins involving systems outside the company have noted similar discrepancies.

The most obvious approach to begin attacking this problem is to ensure that the calibration standards are accurate. Fortunately, a new non-destructive, sensitive, and precise technique—Heavy Ion Backscattering Spectrometry (HIBS)—recently became available, and it was used to provide single-element impurity concentration measurements on the TXRF calibration standards. HIBS makes use of the familiar principles of RBS and is capable of detecting surface impurities with concentrations down to $10^9$ atoms/cm$^2$. As with RBS, concentration measurements from HIBS are based upon first principles. This HIBS analysis represents the first industrial use of the Sematech HIBS instrument located at Sandia National Laboratories.

Using the results from the HIBS as well as TXRF intensities obtained from a single instrument, the certified values of the TXRF standards were adjusted so that all of them were self-consistent. The four TXRF instruments involved in the study were then recalibrated using the standards whose certified values had been adjusted to the HIBS results.

As a check of the effectiveness of this common calibration procedure, wafers which had been uniformly contaminated with multiple elements by spin coating and drying were analyzed by the TXRF instruments in four different labs. The round robin results showed excellent agreement between instruments.

HIBS has proven to be a valuable tool in checking with confidence the accuracy of vendor-supplied reference standards for TXRF, which has allowed for the consistent and accurate calibration of all instruments in the company.

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Introduction

Over the past five years total reflection X-ray fluorescence (TXRF) has become one of the most widely used techniques in determining trace levels of surface metallic contamination introduced by a variety of semiconductor processing procedures and equipment. Within each large semiconductor manufacturing company there are typically several TXRF instruments providing data for internal customers. The technique is very sensitive for surface metallic contamination, with detection limits down to \(10^{10}\) atoms/cm\(^2\) or below. The basic principles of TXRF have been well described in the literature,\(^1\) so there is no need to present them here.

Unfortunately, TXRF is not a first principles technique, and the answers one obtains are only as good as the standards used to calibrate the instrument. A number of fabrication procedures have been suggested for producing standards for TXRF,\(^4-6\) and the strength and weaknesses of each have been reviewed.\(^7\) Many TXRF users find themselves in circumstances in which they are not able to produce their own standards. In these cases, calibration standards must be acquired from an outside source, and in many instances the certified values provided by the supplier are accepted without question. Concerns have been raised about the accuracy of these primary standards, as significant instrument-to-instrument variations have been noted when samples have been analyzed on different TXRF systems within the same company, and external round robins have noted similar discrepancies.\(^8\)

The most obvious approach to begin attacking this problem would be to ensure that the calibration standards are accurate. Producing uniformly contaminated standard wafers and verifying the levels on those wafers are not trivial matters.\(^4\) The methods used in the past to certify TXRF standards have been either Rutherford Backscattering Spectrometry (RBS) or vapor phase decomposition (VPD) followed by either inductively-coupled plasma/mass spectrometry (ICP/MS) or graphite furnace atomic absorption (GFAA). These methods suffer from a number of drawbacks—the sensitivity of conventional RBS to low levels of impurities on a surface is limited to \(~1 \times 10^{13}\) atoms/cm\(^2\), and the VPD technique is destructive, non-spatially resolved, and has recovery problems. Fortunately, a new non-destructive, sensitive, and precise technique known as Heavy Ion Backscattering Spectrometry (HIBS) has recently become available, and this paper describes its use to verify TXRF calibration standards and to extend the resulting universal calibrations across TXRF systems located in different laboratories.

TXRF Experimental

The situation that we have observed with TXRF calibration standards is illustrated by the following example. When discrepancies were first noticed between TXRF instruments within the company, an attempt was made to determine where the problem lay. The calibration standards from three laboratories were taken to a fourth laboratory and analyzed on the instrument there which had been calibrated using its standards. All data was acquired on a Technos 610T operated using the following conditions: tungsten rotating anode target operated at 30 kV and 200 mA, W L\(_\beta\) incident beam selected by a crystal monochromator, 0.09 degree angle of incidence, 1000 sec. acquisition time, and the standard calibration which was in use at that time on the instrument. The standards were analyzed in the same time frame and on the same TXRF instrument to eliminate any drift or instrument-to-instrument considerations. The standards from the three other laboratories were all analyzed as though they were unknown samples. For each standard the analysis sites chosen were the same ones normally utilized by the home laboratory. All standards were single crystal silicon wafers which had been purchased from outside suppliers and which had been fabricated by the spin coat contamination method,\(^9\) the certification values had been obtained by either RBS or VPD-GFAA techniques. Standards from three different suppliers were included in the study, one of whom produced multielement standards.

The results of this interlaboratory standards analysis are presented in Figure 1 below.
FIGURE 1: TXRF Results vs. Certified Values. The TXRF results shown are the averages of between 4 and 6 sites on each standard. The numbers after the element symbols designate a particular laboratory’s wafer set, all of which were single element standards from Vendor 1, except for the standard marked with an asterisk which was obtained from Vendor 2. “Multi” refers to a multielement standard obtained from Vendor 3.

At the very least the results indicate a lack of agreement between Lab 4’s standards and the other three lab’s standards. Because of the design of the TXRF software, if an entry is made for more than one element in the calibration file, it is possible to obtain results which are self-inconsistent between elements. Since Lab 4’s instrument was calibrated using four different single element standards, part of the disagreement between standards may be attributable to this software idiosyncrasy. This cannot be the total explanation for the discrepancies, however, as serious differences are evident even when just considering the standards for a single element. The results are somewhat surprising when one considers that, except for the multielement standard and the Lab 3 nickel standard (marked with an asterisk in Fig. 1), all of the standards were produced by the same vendor using identical fabrication and certification methods.

HIBS Description & Experimental

Fortunately, the newly developed HIBS technique has recently become available and promises to allow for the sensitive and accurate determination of the concentration of surface contaminants heavier than silicon. HIBS makes use of the familiar principles of RBS, which is a well-known ion-beam analysis technique widely used for compositional profiling; however, its sensitivity to low levels of impurities on a surface is limited to $\sim 1 \times 10^{13}$ atoms/cm$^2$. Conventional RBS directs a monoenergetic beam of He$^{2+}$ ions (typically 1-3 MeV) at the sample. Some of the incident He$^{2+}$ kinematically scatters from atoms in the material back toward a solid state detector which allows counting of backscattered He$^{2+}$ and measurement of its energy. Because atom concentrations are determined on the basis of known scattering probabilities, no standards are necessary. HIBS distinguishes itself from RBS through the use of time-of-flight detection for improved mass sensitivity. To detect the surface contamination on wafers with greatly increased sensitivity relative to RBS, HIBS makes use of the fact that the differential scattering cross section (or probability of backscattering into a detector) is proportional to $Z^2/E^2$.

* An entry for an element into the calibration file defines a sensitivity curve which covers the entire Z-range. An entry for a second element will define a second sensitivity curve, and so on. The software makes no attempt to reconcile any discrepancies between these separate curves into a single sensitivity curve covering the entire Z-range, but rather uses different sensitivity curves to quantify different elements.
where \( Z \) is the atomic number of the incident beam and \( E \) is its energy. Therefore, by using a higher \( Z \) and lower energy incident beam than would normally be used for RBS, the cross section is greatly enhanced. In the Sandia HIBS system, \(^{10,13-16}\) shown in Fig. 2, 50 to 200 keV \( C^+ \) ions backscattered from the sample surface pass through a thin C foil which ranges out most of the ions backscattered from Si (and any lighter mass material) and simultaneously produce electrons which are detected by a multichannel plate (MCP) and give a timing start pulse. The C particle continues along its flight path until being stopped in a second MCP, giving a stop pulse. Three time-of-flight detectors are used in parallel to give a large solid angle, increasing the efficiency and sensitivity of the system. This time-of-flight detector technology allows higher mass resolution than surface barrier detectors. HIBS concentrations are calculated from first principles using integrated counts for the element of interest, just as in RBS. A 4-axis wafer goniometer accepts samples ranging from 1 cm\(^2\) up to 200 mm wafers, inserted via a Class 10 mini-environment for analysis. The theoretical interference-free detection limits for the HIBS system are calculated to be \(~5 \times 10^9\) atoms/cm\(^2\) for Fe, Ni, and Cu and \(~5 \times 10^8\) atoms/cm\(^2\) for Au. \(^{10,12}\) Figure 3 compares approximate sensitivities for TXRF to anticipated detection limits for HIBS on silicon substrates.

**FIGURE 2: Schematic of Sandia Time-of-flight HIBS Detector.** Utilizes a large area stop detector and a relatively short 13 cm flight path to maximize solid angle while maintaining energy resolution within acceptable bounds. (Reference 17: used by permission)

**FIGURE 3: HIBS and TXRF Sensitivities.** Comparison of approximate sensitivities for TXRF using various x-ray sources to detection limits attainable for HIBS on silicon substrates using the Sandia system.
HIBS was used to provide single-element impurity concentration measurements on several of the TXRF calibration standards. The HIBS data was acquired during two separate sessions on the instrument, with a space of several months ensuing between the two sessions. The TXRF standards in this study contained impurities on the order of $10^{12} - 10^{13}$ atoms/cm$^2$, detectable well within the theoretical capabilities of HIBS. Therefore, they provided an excellent opportunity to evaluate the HIBS technique firsthand as a viable reference for TXRF. Only standards containing levels above $10^{12}$ atoms/cm$^2$ were chosen for this study in order to minimize any errors that inadvertent contamination might cause.

The HIBS work described here represents the first industrial use of the Sematech HIBS instrument located at Sandia National Laboratories. This user facility was developed by Sandia National Labs through a CRADA with Sematech.

**HIBS Results**

A typical HIBS spectrum obtained on one of the TXRF calibration standards which had been deliberately contaminated with chromium is presented in Figure 4.

![HIBS Spectrum](https://example.com/figure4.png)

**FIGURE 4: Typical HIBS Spectrum.** This spectrum was acquired on the Lab 2 chromium standard which had a vendor-certified concentration of $4.6 \times 10^{12}$ atoms/cm$^2$ on its surface.

It will be noted in Figure 4 that the chromium peak is rather wide; this points out one of the limitations of HIBS, namely that it cannot easily resolve peaks from elements which differ little in atomic number. Thus, while HIBS may be very useful in verifying single-element calibration standards for TXRF, it is unlikely to replace TXRF as a commonplace analysis tool, as it is not unusual to encounter real-world samples with multiple contaminants in the same Z-range. The group at Brookhaven is currently exploring a possible solution to this problem by using a high current nanosecond pulsed Si ion beam, which has an added advantage of improving sensitivity as well. The HIBS resolution situation is demonstrated in the spectrum acquired on one of the multielement TXRF calibration standards and presented in Figure 5.
FIGURE 5: HIBS Spectrum of Multielement TXRF Calibration Standard. The TXRF spectrum of this same sample can be viewed in Figure 6 for comparison.

The simplicity of interpreting the TXRF spectrum acquired on the same multielement standard (presented in Figure 6) and the ease of resolving element peaks stand in stark contrast to the HIBS spectrum.

FIGURE 6: TXRF Spectrum of Multielement Standard. This spectrum was acquired on the same standard on which the HIBS spectrum was obtained in Figure 5.
The HIBS results on the TXRF calibration standards, listed in Table 1 below and presented graphically in Figure 7, indicate that, except for the copper standards, the HIBS values were generally within ±10% of the certified values.

**TABLE 1: HIBS Results vs. Vendor Certified Values**

<table>
<thead>
<tr>
<th>Element</th>
<th>Vendor / Lab</th>
<th>Analysis Location</th>
<th>Certified Value (e10)</th>
<th>HIBS Results (e10)</th>
<th>Certified – HIBS (Rel %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>V 1 / L 2</td>
<td>4-pt Avg</td>
<td>460</td>
<td>492</td>
<td>-6.1</td>
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<tr>
<td>Fe</td>
<td>V 1 / L 2</td>
<td>4-pt Avg</td>
<td>510</td>
<td>557</td>
<td>-8.4</td>
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<tr>
<td>Ni</td>
<td>V 1 / L 1</td>
<td>4-pt Avg</td>
<td>5760</td>
<td>5423</td>
<td>6.4</td>
</tr>
<tr>
<td>Ni</td>
<td>V 2 / L 3</td>
<td>6-pt Avg</td>
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<td>355</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu</td>
<td>V 1 / L 1</td>
<td>4-pt Avg</td>
<td>450</td>
<td>591</td>
<td>-23.6</td>
</tr>
<tr>
<td>Cu</td>
<td>V 1 / L 2</td>
<td>4-pt Avg</td>
<td>450</td>
<td>499</td>
<td>-9.3</td>
</tr>
</tbody>
</table>

**FIGURE 7: HIBS Results vs. Certified Values.** An asterisk indicates that the standard was analyzed during the second session at the HIBS facility, while the lack of one indicates results from the first session.

Since the data in Table 1 indicate that the HIBS results and the vendors' certified values are in essential agreement and since the TXRF and certified values disagreed significantly, the conclusion must be drawn that there are serious discrepancies between the TXRF results and the HIBS values. One of the possible explanations for the HIBS/TXRF discrepancies may be related to the location of the contaminating species relative to the wafer surface. For polished samples TXRF generally detects contaminants no deeper than about 50 Å below the surface, whereas the HIBS analysis depth can be as deep as 1000 Å. Thus, any portion of the contaminants which migrate to greater than 50 Å but less than 1000 Å below the surface will no longer be detectable.
by TXRF, but will still be accounted for in the HIBS analysis. This may be the explanation for some of the low TXRF readings reported in Table 1. Another possible contribution to the discrepancies may be related to the calibration scheme utilized by the manufacturer of the TXRF instruments, which allows discontinuities in the calibrations curves to occur.

Using the HIBS result for each single element standard wafer as well as the observed TXRF intensity (from the comprehensive standards analysis performed in Lab 4 and described earlier), a TXRF sensitivity factor for that element can be calculated. From that one point, the sensitivity factors for all the other elements can be calculated as well to give rise to a sensitivity curve. [The results on the copper standards were disregarded, as copper has proven to be very unstable as a TXRF standard. Whether this is due to diffusion of the copper below the TXRF analysis depth as described previously or to some other problem is not known.] In Figure 8 the resulting sensitivity curves obtained for the standards analyzed by HIBS in the first analysis session are shown, as well as another point of interest—the curve used by a well-known outside laboratory which is based on a V standard. [Shortly before this study the Lab 4 instrument had been used by the outside lab while their instrument was being repaired, and their calibration file remained behind on the instrument.]

*FIGURE 8: TXRF Sensitivity Curves Based on HIBS Results.* The units for the sensitivity factors are as TXRF counts per second divided by HIBS-determined concentrations in $10^{10}$ atoms/cm$^2$. The V curve is not based on HIBS results and was not included in the average; it is only included as an interesting point of reference.

It will be noted in Figure 8 that there is quite a bit of variability in the HIBS derived sensitivity curves from the different element standards. In fact, there appears to be a Z-related dependence on the sensitivity curves; e.g., the curve derived from the Ni standard has higher sensitivity factors than those produced by the Fe-derived curve, which in turn has higher factors than the Cr-derived curve. This effect may be an indication that the TXRF instrument manufacturer’s software does not do a good job in calculating the sensitivity curves. It may also be a combination of the analysis depth problem mentioned previously (where each element has diffused down to a different depth) and pure chance that the results lined up in order of atomic number. Other explanations include the possibility that some portion of the contaminating element for some standards are present as residues rather than in plated form or the possibility that native oxide thicknesses may be different between standards (possibly due to enhanced growth after the contaminant is introduced) and that the locations of the contaminating elements relative to the native oxide may be different.

In the absence of any other information, the average of the HIBS-derived sensitivity curves was chosen as the “universal” standard, as this minimized the differences between the TXRF and
HIBS results. The TXRF data for all of the calibration standards were then reprocessed using the calibration generated by the HIBS universal standard, and the resulting values, which were then all self-consistent, were reassigned to the respective standards from all laboratories as the new "certified values". This necessitated assigning values to some standards which were different than both the HIBS and certified values, but this was the only way to achieve uniformity among the TXRF standards, and ultimately, TXRF instruments.

**TXRF Round Robin**

Each of the four TXRF instruments involved in the study were then recalibrated using one of the standards from each lab whose certified value had been adjusted to the HIBS universal calibration. Choosing a single point calibration eliminates the discontinuity problem in the software, which is another potential source of discrepancies between instruments.

As a check of the effectiveness of this common calibration procedure, two wafers which had been uniformly contaminated with multiple elements by spin coating and drying were analyzed by the TXRF instruments in the four different labs. The results of this round robin are shown graphically in Figure 9 and in Table 2. The average of the absolute values of the differences between instruments was 6.5% relative, with only one element on one sample exceeding 10% relative (indicated by the shaded cell in Table 2). This demonstrates that the effort to place the four TXRF instruments in common calibration was quite successful. Any other instrument can easily be calibrated to the same common reference point at any time in the future.

**FIGURE 9: Round Robin TXRF Results.** The results shown are the averages obtained from the same five analysis sites on each wafer.

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TABLE 2: Results of TXRF Round Robin
(all values as $10^{10}$ atoms/cm$^2$)

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<tr>
<th></th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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<tbody>
<tr>
<td>Lab 1</td>
<td>456</td>
<td>352</td>
<td>339</td>
<td>192</td>
<td>395</td>
<td>1194</td>
<td>1094</td>
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<td>Lab 2</td>
<td>453</td>
<td>368</td>
<td>324</td>
<td>178</td>
<td>402</td>
<td>1333</td>
<td>1427</td>
<td>2406</td>
<td>1667</td>
<td>2490</td>
</tr>
<tr>
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<td>455</td>
<td>328</td>
<td>322</td>
<td>184</td>
<td>380</td>
<td>1328</td>
<td>1142</td>
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<td>1655</td>
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<td>Lab 4</td>
<td>422</td>
<td>315</td>
<td>303</td>
<td>166</td>
<td>353</td>
<td>1247</td>
<td>1128</td>
<td>2344</td>
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<tr>
<td>Average</td>
<td>447</td>
<td>341</td>
<td>322</td>
<td>180</td>
<td>382</td>
<td>1275</td>
<td>1198</td>
<td>2433</td>
<td>1664</td>
<td>2410</td>
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<tr>
<td>% RSD</td>
<td>4.2</td>
<td>7.5</td>
<td>4.7</td>
<td>6.4</td>
<td>5.8</td>
<td>7.8</td>
<td>15.3</td>
<td>4.3</td>
<td>2.9</td>
<td>4.7</td>
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</tbody>
</table>

Conclusion

Very good correlation was obtained between the HIBS results and the vendor-certified values for the large majority of the TXRF calibration standards, with agreement generally within 10 % relative. The only major disagreements occurred on the copper standards, but even then the worst discrepancy was only about 30 % relative. The correlation of TXRF results vs. either the HIBS or the vendor-certified values is not nearly as good. If one were to calibrate a TXRF instrument on a given single element standard using either the HIBS or certified values, at least some of the other standards in the group would not agree with that calibration. This is true even if the unreliable copper standards are disregarded and if the group of standards contains only those which have been fabricated and certified by the same vendor using the same processes. Clearly, further work is needed in this area to understand these discrepancies.

HIBS has proven to be a valuable tool in checking with confidence the accuracy of vendor-supplied reference standards for TXRF and has allowed for the consistent and accurate calibration of all instruments in the sector. The four TXRF instruments participating in this study are now calibrated to a common reference point which is based on a first principles technique—HIBS—in which there is very high confidence. This has resulted in an improvement in correlation results between those different instruments from greater than 100 % to less than 10 % relative discrepancies, and has created a situation in which seamless and transparent backup utilizing alternate instruments is possible whenever any one of the TXRF instruments goes down. The ultimate result is that customers will now receive highly accurate and consistent results from the participating TXRF instruments.

The HIBS portion of this project demonstrated a workable approach for analytical methods development by cooperation between Sematech (and its member companies), universities, and government laboratories. In addition, it represented the successful conclusion of a Sematech project. HIBS is a new, accessible analytical tool for both manufacturing and technology which provides a first-principles alternative to TXRF for the surface analysis of contaminants.
REFERENCES