## Total Reflection X-ray Fluorescence Spectroscopy Using Synchrotron Radiation for Wafer Surface Trace Impurity Analysis\*

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#### ABSTRACT

Trace impurity analysis is essential for the development of competitive silicon Current best methods for chemically identifying and circuit technologies. quantifying surface and near-surface impurities include grazing incidence x-ray fluorescence techniques using rotating anode x-ray sources. To date. this method falls short of what is needed for future process generations. However, the work described here demonstrates that with the use of synchrotron radiation, total reflection x-ray fluorescence methods can be extended to meet projected needs of the silicon circuit industry until at least the year 2000. The present results represent over an order of magnitude improvement in detection limit over what has been reported previously. А double multilayer monochromator on a high-flux wiggler beam line resulted in a detection limit for Ni of 2.5 x  $10^8$  atoms/cm<sup>2</sup>. This is to be compared with a detection limit of 5 x  $10^9$  atoms/cm<sup>2</sup> obtained with a rotating anode system. This is due to the greatly improved signal to background in the case of the synchrotron. Furthermore, there is a path to improving the synchrotron case to reach a detection limit of 5 x  $10^7$  atoms/cm<sup>2</sup>.

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#### 1. INTRODUCTION

In order to remain competitive, the semiconductor industry is being constantly forced to increase the performance and reduce the cost of integrated circuits by shrinking device dimensions and increasing the number of devices per unit area on integrated circuit chips. At the present state of the art, a single integrated circuit requires hundreds of process steps, such as oxidation, etching, metallization and wet chemical cleaning. The optimization of each of these process steps in order to obtain high-performance circuits at high yields requires an understanding of a variety of physical processes. In many of these steps, strong correlations have been found between the presence of metal contamination on the wafer surfaces and process yields. Even very low levels of atomically dispersed metals present on a silicon wafer may aggregate during high-temperature processing steps and create atomic scale defects which lead to leakage currents, gate insulator breakdown or poor threshold voltage control; all of which can cause actual failure in the integrated circuits and/or device reliability problems. In addition, it is possible for metals to be deposited on the silicon wafer surface during a wet cleaning step and directly aggregate on the atomic scale defects. Examples of metals which can cause degradation include Fe, Co, Ni, Cu, Zn and Al-the actual list is much longer.

As a result of this, the cleanliness of silicon wafer surfaces has long been a quantity of interest to the process community. In 1993, the Semiconductor Industry Association, which represents the interests of the US semiconductor industry, published a "Contamination Road Map" in the proceedings on a workshop to define the goals of the industry for the next decade.(1) This road map indicated that the current generation of integrated circuits required the number of metal defects on a silicon wafer to be on the order of  $10^{10}$ atoms/cm<sup>2</sup> which is only  $10^{-5}$  of a monolayer. The road map further states that continuous improvement to lower levels is required for future device generations. Furthermore, in order to achieve any level of cleanliness, it is necessary to have measurement tools with detection limits ten times below the required levels for the simple reason that wafer cleaning procedures must be tested at each step to insure they meet specifications. In fact, according to this "rule of thumb", the current detection limits for metal contaminants of approximately 5 x  $10^9$  atoms/cm<sup>2</sup> are barely adequate for today's Although, the exact numerical requirements for future needs. detection limits are presently under discussion, it is clear from the industry road maps that detection limits on the order of  $10^8$  atoms/cm<sup>2</sup> or better will probably be required by the year 2000.

One of the methods which has reached a high level of industry acceptance for chemically identifying and quantifying surface and near-surface impurities is the Total Reflection X-ray Fluorescence technique (TRXRF or TXRF). There are approximately 100 TXRF instruments used in industry worldwide, and a number of industry groups that deal with wafer contamination have listed TXRF as an approved analytical test method. No other analytical technology for measurement has received comparable focus this by the semiconductor industry.(2) In TXRF, an x-ray beam is incident on the silicon wafer surface at a glancing angle (below the critical angle for total external reflection) and excites x-ray fluorescence from the silicon wafer surface, including any contaminants that may be on it. Quantification is done by the use of standards. By using the phenomenon of total external reflection, the excitation is limited to within approximately 30 Angstroms from the wafer surface, thus insuring a high sensitivity for impurities that are located on the The best conventional TXRF instruments use a rotating surface. anode x-ray source and have achieved sensitivities of 5 x  $10^9$  $atoms/cm^2$  for a limited number of elements which seems to be at the limit of what the conventional instrumentation will be able to do even in the future.

The minimum detection limits, MDLs, are calculated using:

$$MDL = 3 C (I_B)^{1/2} / I_P,$$
 (1)

where C is the concentration of a standard,  $I_P$  is the integrated intensity of the background-subtracted peak of interest and  $I_B$  is the integrated background intensity under that peak. The background is calculated by fitting a straight line through the average background on either side of the peak and then integrating over the width of the peak.(3)

This equation implies that by simply increasing the overall counting rate, it is possible to obtain a better detection limit. However, for trace surface impurity analysis, the total x-ray counting rate is dominated by the fluorescence and Compton scattering from the silicon atoms. Furthermore, both signals are increased due to the imperfect collimation of conventional sources which results in greater contributions from the bulk. Therefore, simply increasing the flux does not necessarily improve the detection limit since the detector saturation sets a practical limit on the overall counting rate. The well-known characteristics of synchrotron will lead to significant improvement in the detection limits. Since synchrotron radiation is over 95% linearly polarized in the horizontal plane, the Comptonscattered photons will be reduced by approximately an order of magnitude with respect to an unpolarized source when the detector is placed along the polarization vector of the radiation. In addition, the high degree of collimation of the synchrotron source insures that all of the photons are incident on the sample at a well-defined angle, resulting in greatly improved control of the penetration of the x-rays into the substrate and leading to a greatly reduced substrate fluorescence signal. These two effects make it possible to effectively use the high fluxes available from synchrotron radiation. The initial work exploiting the collimation and polarization properties of synchrotron radiation for these applications had demonstrated MDLs on the order of  $10^{10}$  atoms/cm<sup>2</sup> using a silicon monochromator.(4, 5, Subsequent work obtained an order of magnitude improvement 6) giving for Ni an MDL of 1 x  $10^9$  atoms/cm<sup>2</sup>. This work employed a wide bandwidth single multilayer monochromator on an 8-pole wiggler to further increase the photon flux.(7, 8) The factor of 100 increase in photon flux resulted in the factor of 10 improvement in the MDL as predicted by Equation (1). Since the detector was not yet in the saturation regime, further improvements would be possible with additional increases in flux.

The work described in this paper built on our earlier work in several ways. First, since the counting rate limitations of the detector had not yet been reached, a higher power wiggler beam line was used to further increase the flux. Second, the sources of background were analyzed in an effort to determine if they could be eliminated. One potential source of background was found to come from the finite multilayer reflectivity in the region below the Bragg peak for the single multilayer monochromator. This was effectively eliminated by using a double multilayer monochromator. These enhancements combined to give an MDL of 3 x  $10^8$  atoms/cm<sup>2</sup> for Ni. This is currently the best result obtained to date with TXRF and is 20 times better than what can be achieved by the best conventional system. Given some enhancements, which will be described below, this MDL represents a level which the semiconductor industry can practically use.

#### 2. EXPERIMENTAL

The experimental configuration used in this work is shown in Figure 1. The source of the radiation is the Beam Line 10-2 wiggler (15 period, 1.4 T) at the Stanford Synchrotron Radiation Laboratory (SSRL). The beam is focused by a torroidal mirror in a 1:1 geometry and monochromated by a double multilayer monochromator mounted in a standard SSRL two-crystal monochromator. A Bragg angle of  $1.2^{\circ}$  gave a scanning range of approximately 6 to 12 keV.

The multilayer was formed by magnetron sputtering from elemental targets in an Ar plasma (2.5 mTorr). The Mo target (DC powered) and C target (RF powered) were positioned on a circle of diameter 36 cm, and the substrate was oriented with its long dimension tangent to a similar circle with its surface 10 cm above the target plane. The sputtering rates were adjusted so that the Mo layer thickness was roughly 0.4 of the total period of the multilayer. The substrate rotated over targets with constant velocity to build up 100 periods. The resulting multilayer had a period of roughly 29.7Å, and the uniformity of the period over the surface is estimated to be better than  $\pm 1\%$ . For fluorescence excitation applications with a smooth spectrum incident on the multilayer, uniformity is not crucial since deviations from perfect uniformity do not decrease the flux incident on the sample but only spread out the energy bandpass of that flux. The multilayer was deposited on a 3.8 cm x 15.2 cm silicon substrate 3.2 cm deep which had been polished to 5Å rms roughness.

Figure 2 shows the results of a calculation of the reflectivity for a single as well as double multilayer arrangement versus photon energy for a Bragg angle of 1.2°. Below 2 keV is the total external reflection from the surface. Between 2 keV and the 10 keV primary Bragg reflection, there is the small but finite reflectivity in the one multilayer case. Even though the reflectivity at 8 keV is 0.001 of the primary reflection, the flux from the wiggler is potentially high enough and the background signal low enough that this could represent a significant background in our experiment. This situation is greatly improved by the addition of the second multilayer which is also shown in Figure 2. In any case, the flux below 4 keV is effectively eliminated by carbon absorbers and Be windows in the beam line. In addition to the primary reflection at 10 keV, there is a second harmonic at 20 keV. For our experiment this was not suppressed by the focusing mirror, which has a cutoff energy of 22

keV. The calculated width in energy of the multilayer optic is roughly 200 eV.

Figure 3 shows the total flux transmitted by the single and double multilayer monochromators versus energy on two different beam lines for a range of energies between 6 and 11.5 keV. In all cases, these measurements were with a focused beam. In the range used for these experiments, around 11 keV, the flux from the double multilayer monochromator on Beam Line 10-2 is over an order of magnitude larger than that with the single multilayer monochromator on Beam Line 4-2. At 11 keV, the flux from Beam Line 10-2 is approximately 1.2 x  $10^{13}$  photons/sec/100 mA. Figure 3 also shows that the flux from the single and double multilayer monochromator on Beam Line 4-2 is identical. Different collimation conditions during the two measurements were responsible for the higher than expected flux from the double multilayer case.

The detector used for these experiments is a Si(Li) solid-state detector with a Quantum<sup>TM</sup> window and an intrinsic resolution of 140 eV at Mn K-alpha. A tungsten collimator was mounted on the end of the detector to control the solid angle subtended by the detector as well as the regions of the detector that were struck by the fluorescent x-rays. An ultrapure beryllium foil was incorporated into the collimator to further shield the detector. Finally, a 25 µm Teflon film was mounted on the collimator to reduce the silicon fluorescence reaching the detector by a factor of 0.003 while the radiation above 6 keV is practically unattenuated.(8) This helps reduce the substrate fluorescence to a level where the detector does not saturate with the additional flux in the new configuration. The detector was mounted on a retractable post passing through a vacuum bellows into a stainless steel vacuum chamber that has been described previously.(5, 7) The chamber was large enough to hold 150 mm diameter silicon wafers that were mounted on a wafer chuck that minimized warping of the wafer. The chamber was mounted on a Huber goniometer to permit precise adjustment of the incident x-ray angle. A horizontal translation stage inside the chamber permitted centering of the wafer surface on the rotation axis.

Wafers were obtained from a Hewlett-Packard/Toshiba collaboration and from Intel. Standard wafers were intentionally contaminated with 1 x  $10^{11}$  atoms/cm<sup>2</sup> of Fe, Ni and Zn. In addition, "clean" control wafers were prepared by industry standard cleaning processes. Since levels of 1 x  $10^{11}$  atoms/cm<sup>2</sup> are well within the detection limits of conventional TXRF systems, it was straightforward to insure that the test wafers had the desired levels of contaminants. In addition, we were able to cross calibrate our system with the conventional TXRF instruments at H-P, Intel and Charles Evans and Associates by means of a round-robin calibration exercise.

#### 3. RESULTS AND DISCUSSION

Figure 4 shows a typical fluorescence spectrum from a sample intentionally contaminated with 1 x  $10^{11}$  atoms/cm<sup>2</sup> Fe, Ni and Zn. In addition to the signals from these elements, which are clearly seen in the spectrum, signals from the Si substrate, Ca, Cl, Cu and the scatter from the incident beam are also present. A broad background, starting at approximately 3 keV and seemingly extending all the way to 10 keV, should also be noted. This figure should be compared to Figure 5 which shows our previous results from a similar wafer on Beam Line 4-2 using the single multilayer monochromator. The relative features in the two spectra are similar. The primary difference is the vertical scale. In the case of the Beam Line 10-2 data (Figure 4), there are approximately ten times more counts for the same amount of analysis time (1000 seconds) than in Figure 5. As mentioned above, this is primarily due to the higher power source of Beam Line 10-2. The detection limits calculated using Equation (1) are found to be  $4.3 \times 10^8$  atoms/cm<sup>2</sup> for Fe, 2.5 x  $10^8$  atoms/cm<sup>2</sup> for Ni and 3.3 x  $10^8$  atoms/cm<sup>2</sup> for Zn. In the case of Ni, these results are approximately a factor of four better than was obtained in our earlier work (Figure 5). Inspection of Equation (1) clearly shows that most of this improvement can be attributed to the ten times higher total counts in the spectrum. In the case of Fe, the detection limit is approximately five times better than in our earlier Again, most of this improvement is attributable to the higher work. counting rate of the experiment. In both cases, we assume that the background is proportional to the signal allowing a simple ratioing based on the square root of the total number of counts in the peak of However, if the use of the double interest. multilaver monochromator had the desired affect of reducing the contribution of the finite reflectivity of the multilayers to the scattered photons in this region of the spectrum, an additional improvement in detection limit would be expected. In fact, since the simple arguments based on Equation (1) would lead to only a factor of approximately 3.5 improvement for both the Fe and Ni rather than the observed factor

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of 5 and 4, respectively, the results are consistent, with some of the improvement being due to the reduction of the background. Furthermore, since the improvement is actually better at lower photon energy (i.e., the improvement in the Fe MDL was better than that of the Ni MDL), this is also consistent with a reduction of the scattered radiation by use of the double multilayer monochromator since the reflectivity of the multilayers increases with decreasing photon energy. If this argument is found to be ultimately correct, it still does not explain the fact that the reduction in the scattered radiation in this region only improved the MDL by an average of This is much less impressive than the comparison shown in 40%. Figure 3 which shows that in going from a single to a double multilayer, the scattered radiation in the 6 to 8 keV range should be reduced by 1000. So if this were the only source of background, an improvement in the MDL by a factor of 30 would be expected just from the background reduction alone. The fact that this is clearly not the case led us to investigate other sources of background. It should also be mentioned that the 25 µm of Teflon used in front of the detector has the effect of reducing the intensity of the Si, Ca and Cl peaks in the spectrum as well as causing a rolloff in the background in going from 4 to 2 keV. This was twice as much Teflon as was used in our earlier work shown in Figure 5. This was the primary reason we were able to use the higher flux beam line without saturating the detector.

When the incident x-rays interact with the silicon wafer, high-energy photoelectrons are created with energies as high as the primary photon beam. Those that do not escape from the wafer are stopped by the silicon atoms and emit bremsstrahlung with its characteristic shape up to the maximum energy of the incident photoelectron. In addition, those electrons which escape from the sample can potentially strike the Teflon filter in front of the detector and emit bremsstrahlung as well. Although this has been considered before and determined to be negligible for standard x-ray fluorescence work using an x-ray tube, the extremely high fluxes used in these experiments and the extremely low inherent background levels may, in fact, bring it into a regime where the bremsstrahlung becomes significant. In an effort to test this possibility, we performed an experiment in which spectra were taken with a magnetic electron trap in front of the detector to prevent electrons from striking the Teflon filter. These traps are routinely used to suppress stray electron backgrounds in the detector when Si(Li) detectors are used in scanning electron microscopes. First, we took spectra in a

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configuration in which the filter was placed in front of the trap. The results showed that in this case, where the filter was shielded, the background was 20% less than in the case where the photoelectrons were allowed to strike the filter. Although these results are not yet conclusive, they are certainly qualitatively consistent with a model in which bremsstrahlung can be a significant source of background in TXRF. This may then be a physical limit on the background in TXRF and is currently being analyzed in detail.

In examining a number of nominally clean wafers, low-level signals from Fe, Ni and Cu were consistently observed. To determine their origin, a filter was inserted between the sample and detector. Signals originating from the sample were attenuated according to the absorption coefficient of the detector. Those originating from the detector were proportional to the intensity of the scatter peak because it is by many orders of magnitude the largest high-energy In this case, the signals were clearly peak of the spectrum. proportional to the scatter peak indicating that they originated from the detector. We have verified that the detector does contain Fe, Ni and Cu either in components which can be replaced with other noninterfering materials or in areas which can be shielded more effectively. Therefore, we believe that the problem with parasitic signals is soluble with appropriate engineering and is currently being addressed by the upgrading of our detector to a different version.

#### 4. SUMMARY

On the technical side, it is clear from this work that, given some of the improvements discussed above, MDLs of 2.5 x  $10^8$  atoms/cm<sup>2</sup> free of parasitics are achievable. This detection limit is a factor of 20 better than what is available with conventional technology and, with a modest investment in air purifying equipment, would permit the execution of a number of commercially important experiments. In addition, this work indicates that the background seems to be well behaved, i.e., the current experience has shown that by increasing the total counts in the spectrum, the MDL is improved approximately according to Equation (1). Therefore, increasing the total number of counts by a factor of 36 would bring the detection limit to 5 x  $10^7$ atoms/cm<sup>2</sup>. A brighter source or improved coupling of the present source to the sample would clearly be of help. In either case, however, a higher speed detector is required. Conversely, since the beam is incident on the sample at a very small angle, it will typically

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illuminate a long stripe on the wafer surface of which the detector only sees approximately 5-10 mm. The addition of multiple detectors along this stripe will effectively increase the total number of counts at the cost of a decrease in the spatial resolution. In TXRF, spatial resolutions on the order of 1 cm<sup>2</sup> are adequate since a knowledge of the characteristic rather than the local properties of the silicon wafer is of primary importance. Given such a system, the multiple detectors would also allow faster multipoint analysis at the single-detector detection limit.

In order to make the current detection limits truly useful to the semiconductor industry, it will be necessary to provide a clean environment and wafer-handling capabilities that will not add contamination to the wafer. Even the present detection limits are just beyond the current state of the art for contamination control, so that in order to achieve a *system* capable of  $5 \times 10^7$  atoms/cm<sup>2</sup>, development work will be required. With these developments, the semiconductor industry could use these tools as an integral element of their programs to develop advance wafer cleaning technology.

Finally, for synchrotron radiation TXRF to become more than an R&D tool, the interaction between industry and the synchrotron-based facility will need to become similar to that with a commercial analytical service. In the latter case, industry requires a service that is reliable, timely and easily accessible. Although this will ultimately translate into dedicated facilities and staff, the optimum path that needs to be taken to reach this goal is not yet clear and is the subject of intense discussion.

## 5. ACKNOWLEDGEMENTS

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#### REFERENCES

- S. J. Semiconductor Industry Association, San Jose, CA, USA, Semiconductor Technology Workshop Working Group Reports (1993).
- 2. R. S. Hockett (Personal Communication).

- 3. P. Bertin, Principles and Practice of X-ray Spectrometric Analysis (Plenum, New York, 1975).
- 4. A. Iida, Advances in X-ray Analysis, C. S. Barrett, Ed. (Plenum Press, New York, 1992), vol. 35, p. 795.
- 5. M. Madden, D. C. Wherry, P. Pianetta and S. Brennan, Proceedings of the Materials Research Society **307**, 125 (1993).
- 6. S. S. Laderman and P. Pianetta, Proceedings of the Workshop on Applications of Synchrotron Radiation to Trace Impurity Analysis for Advanced Silicon Processing, Stanford Linear Accelerator Center Technical Report (1992),
- S. Brennan, W. Tompkins, N. Takaura, P. Pianetta, S. S. Laderman, A. Fischer-Colbrie, J. B. Kortright, M. C. Madden and D. C. Wherry, Nucl. Instrum. Meth. (1994).
- 8. S. S. Laderman, Bull. Am. Phys. Soc. 39, 514 (1994).

# **Beam Line Optical Components**



Figure 1. Configuration of the experimental system installed on Beam Line 10-2. The source is a 15 period, 1.4 T wiggler. The double multilayer monochromator was installed into the standard SSRL monochromator.



Figure 2. Theoretical reflectivity versus energy from a Mo/C multilayer with a d-spacing of 29.7 Å at an angle of incidence of  $1.2^{\circ}$ . The theoretical reflectivity for a double reflection from the same multilayer is also shown.



Figure 3. Measured flux from the single and double multilayer for both Beam Lines 4-2 and 10-2 as a function of photon energy.



Figure 4. Fluorescent spectrum from a silicon wafer intentionally contaminated with Fe, Ni and Zn atoms excited by the flux transmitted by the double multilayer monochromator on Beam Line 10-2 giving detection limits of 4.3 x  $10^8$ , 2.5 x  $10^8$  and 3.3 x  $10^8$  atoms/cm<sup>2</sup> for Fe, Ni and Zn, respectively.



Figure 5. Fluorescent spectrum from a silicon wafer intentionally contaminated with Fe, Ni and Zn atoms excited by the flux transmitted by the single multilayer monochromator on Beam Line 4-2 giving detection limits of 2 x  $10^9$  and 1 x  $10^9$  atoms/cm<sup>2</sup> for Fe and Ni, respectively.