

## Application of synchrotron radiation to TXRF analysis of metal contamination on silicon wafer surfaces

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Synchrotron Radiation based Total Reflection X-ray Fluorescence (TXRF) has been shown to meet the critical needs of the semiconductor industry for the analysis of transition metal impurities on silicon wafer surfaces. The current best detection limit achieved at the Stanford Synchrotron Radiation Laboratory (SSRL) for Ni is  $8 \times 10^7$  atoms/cm<sup>2</sup> which is a factor of 50 better than what can be achieved using laboratory based sources. SSRL has established a TXRF facility which meets the cleanliness and stability requirements of the semiconductor industry. This has enabled both industrial and academic researchers to address industrially relevant problems. In addition research is being carried out for the analysis of light elements such as Al and Na.

### 1. Introduction.

As the dimensions of integrated circuits become smaller and smaller, the thickness of the gate oxide is being reduced to a level where it has become necessary to control the process to virtually atomic levels. With oxide thicknesses less than 100 Angstroms, surface metal impurities can have deleterious affects on the oxide properties. Metals, such as Ti, Fe, Ni, and Cu can be deposited on the surface at any number of the processing steps ranging from wet chemical etching to ion implantation.

Much of the processing steps involved in fabricating an integrated circuit are actually cleaning steps designed to remove metal contamination. The levels of allowable metal contamination are being driven down along with the feature sizes by improved processes, which in turn are made possible by improved measurement techniques. Therefore, trace impurity analysis has become essential for the development of competitive silicon circuit technologies.[1]

Currently, the best methods for chemically identifying and 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 (SR), Total Reflection X-ray Fluorescence (TXRF) methods can be extended to meet projected needs of the silicon circuit industry into the next century.

To date, SR-TXRF has achieved a sensitivity for transition metals of  $8 \times 10^7$  atoms/cm<sup>2</sup>, as determined from Fe, Ni and Zn standards. This represents a detection limit of 1 femtogram over the detected area on the wafer surface

of 8 mm<sup>2</sup> as compared to 500 femtograms over a 100 mm<sup>2</sup> area in the conventional TXRF systems. These sensitivities are achieved by exploiting the high photon flux using a high-power wiggler x-ray source at the Stanford Synchrotron Radiation Laboratory (SSRL) and efficiently coupling the radiation to the silicon wafer using a high throughput multilayer monochromator.[2,3] To make this technique useful for industrial applications, it has also been necessary to add cleanroom facilities and a wafer mapping capabilities to the system.[4]

Another area into which TXRF is beginning to make inroads is the detection of light elements such as Al and Na. However, due to the presence of the large Si substrate peak, it has not been possible to observe Al in conventional TXRF systems. However, it is possible to selectively excite the Al atoms on the surface of the wafer without exciting the substrate Si atoms by using radiation with an energy below the Si edge.

Detection limits on the order of  $1 \times 10^{10}$  atoms/cm<sup>2</sup> have been demonstrated in early SR based experiments.[5,6] However, the full potential of SR for light elements has not yet been realized. This paper will describe current work aimed at understanding the limitations of light element analysis with TXRF.

### 2. Experimental details.

The basic experimental configuration used for both the transition metal and light element experiments is shown in Fig. 1. The source of the radiation for the transition metal experiments is a high flux, 54 pole wiggler on the SPEAR storage ring at SSRL. The beam is focused in a 1:1 geometry onto the sample by a platinum coated bent cylindrical mirror with a critical energy of 21 keV.

The beam is then monochromated by a double multilayer monochromator mounted on a standard, water-cooled two crystal SSRL monochromator. The multilayers

were purchased commercially and consist of alternating layers of Mo and B<sub>4</sub>C with a d-spacing of 29 Angstroms.[7] The tuning range of the monochromator is typically set to be from 6 to 14 keV with 11.2 keV being the standard energy for transition metal analysis. This photon energy was chosen because it gives a high cross section for the transition elements while preventing overlap of the detector escape peak with the signals of interest. Higher photon energies are sometimes used to excite heavier elements such as As whereas lower photon energies are used to eliminate the fluorescence from thin films such as Cu when they are present on a wafer.

The flux transmitted through this optical system is approximately  $3 \times 10^{15}$  photons/sec cm<sup>2</sup>. After monochromatization, the beam is shaped by a 0.2 mm x 2 mm entrance slit and enters the chamber through a Be window and strikes the wafer. The wafer is held vertically on an electrostatic chuck mounted on a computer controlled XY stage that allows 150 and 200 mm wafers to be mapped in the beam. In addition, software is available to allow localized contamination to be carefully mapped.

The wafer is mounted vertically with its surface normal perpendicular to the polarization vector of the radiation. This allows the detector to be mounted both close to the wafer (to increase the solid angle) and with its axis along the polarization vector (to minimize the scattered radiation into the detector). The detector used for these experiments is an energy dispersive Si(Li) solid state detector with an 8 μm thick Be window, a 50 mm<sup>2</sup> active area and an intrinsic resolution of 150 eV for Mn Kα. In addition, the counting rate load on the detector from the Si substrate signal is reduced by a factor of 0.003 by a 25 μm Teflon film that is mounted on the detector. It should also be mentioned that the detector has undergone extensive modifications to eliminate all spurious transition element peaks.[8,9]

The stainless steel vacuum chamber is operated at a pressure of less than  $1 \times 10^{-4}$  Torr in order to eliminate both air scatter and Ar fluorescence. Extreme care has been taken in the design and construction of the chamber as well as the wafer loading, pumping and venting procedures, which are all under computer control, to minimize the possibility of contamination of the sample wafers. In addition, an ULPA filtered mini-environment surrounds the chamber and a robot is used to load and unload the wafers. With these arrangements, it is possible to perform routine wafer analyses with the assurance that no metals will be added to the wafer surface as a result of the measurement.

The orientation of the chamber, wafer and detector are rigidly fixed with respect to each other. In order to vary the angle of incidence of the wafer to the beam, the entire chamber is rotated on a large precision turntable driven by a motorized micrometer.

The angle of incidence is determined automatically by fitting the measured reflectivity of the wafer as a function of angle to a standard theory. Since the quality of

the quantification is dependent on accurately controlling the angle of incidence, this measurement is critical. This approach has proven to be extremely reliable and allows for automated mapping of the wafer with reliable quantification. Quantification is achieved by comparing the samples of interest with calibration standards.

In the transition metal experiments, the standards used were wafers intentionally contaminated with  $1 \times 10^{11}$  atoms/cm<sup>2</sup> of Fe, Ni and Zn. In addition, wafers prepared with state of the art cleaning processes showing no detectable contamination are used to ensure the absence of parasitic signals as well as measurement induced contamination problems.[9]

As mentioned above, the detection of light elements with TXRF at high sensitivity is difficult because of the much stronger silicon substrate signal which tends to dominate the spectrum. Only by tuning the photon energy below the Si K absorption edge can good detection limits be achieved [5]. Therefore, the measurements on light elements were carried out at a soft x-ray bending magnet beamline at SSRL.

The experimental configuration is very similar to the one sketched in Fig. 1. The incoming beam is focused by a platinum-coated fused quartz cylindrical mirror with a critical energy of 3 keV that accepts up to 10 mrad of synchrotron radiation from a bending magnet. The beam is monochromated by a double multilayer monochromator using alternating layers of Mo and B<sub>4</sub>C with a periodicity of 30 Å especially designed for high reflectivity (about 70 %) between the Si-K- and Al-K edges at 1839 eV and 1559 eV, respectively. The monochromator was tuned to 1750 eV.

The detector used for this experiment is an energy dispersive Si(Li) solid state detector with a 5 μm beryllium entrance window and an active area of 10 mm<sup>2</sup> having an energy resolution of 130 eV for Mn Kα.

As with the transition metal measurements, in order to achieve the best detection limits for light elements, the standard TXRF experimental setup was used with the silicon wafer placed vertically in front of the detector mounted perpendicular to the E vector of the linearly polarized synchrotron radiation. The wafer position is adjustable in XYZ and can be rotated along an axis perpendicular to the incoming beam to adjust the angle of incidence for the total external reflection condition.

This angle is determined by observing the beam downstream from the wafer on a glass window coated with a phosphorescent material. The zero of the angle was determined by minimizing the width of the wafer shadow on the screen. Increasing the angle of incidence results in an additional spot on the screen that is reflected from the wafer surface.[5]

For determination of aluminum detection limits standard wafers from Hewlett-Packard Co. with an intentional aluminum contamination of  $8 \times 10^{12}$  atoms/cm<sup>2</sup> and  $3 \times 10^{11}$  atoms/cm<sup>2</sup> were used.

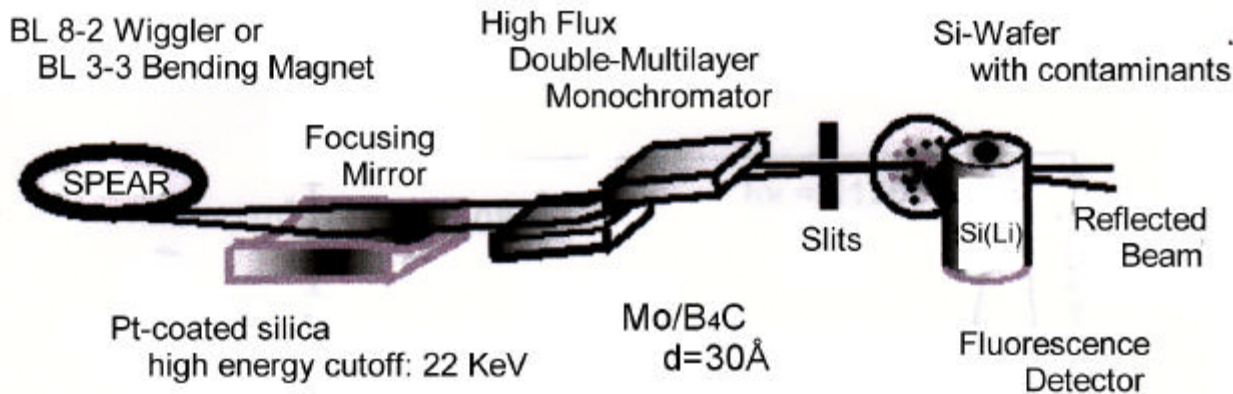


Fig. 1. Schematic representation of the experimental system used for synchrotron radiation TXRF experiments.

### 3. Results and discussion.

Figure 2 shows the fluorescence spectrum of silicon wafer cleaned using a state of the art process. The Fe and Cu concentrations on this wafer are not detectable with conventional techniques and would show the wafer to be clean. This single fact demonstrates the importance of SR TXRF to the semiconductor industry.

An extended counting time of 5000 sec was used to obtain this spectrum in order to demonstrate that detection limits in the low  $10^7$  atoms/cm<sup>2</sup> are achievable with the SSRL system. Using the standard counting time of 1000 seconds, minimum detection limit (MDL) is still  $7.6 \times 10^7$  atoms/cm<sup>2</sup> which is still more than adequate to measure the contamination present on this wafer. The MDL is proportional to the signal divided by the square root of the background.[10] Therefore, simply increasing the count time will improve the MDL by the square root of the relative count times. Even at the MDL of  $3.4 \times 10^7$

atoms/cm<sup>2</sup> no instrumental limitation due to parasitic fluorescence or other artifacts has yet been found. This was verified by measuring a wafer with no detectable contamination under the same conditions. Therefore, we believe the system design is capable of a detection limit below  $1 \times 10^7$  atoms/cm<sup>2</sup>. [6]

The feature which dominates the spectrum is the peak from the scattering of the incident synchrotron radiation at 11.2 keV and is accompanied by its escape peak at 9.46 keV. The Si K $\alpha$  peak at 1740 eV would dominate the spectrum except for the Teflon filter discussed above. The Cl K $\alpha$  peak comes from the particular cleaning chemistry that was used and is not considered to be a problem from the device perspective since this element is easily removed in subsequent processing steps.

The Ag peak is an experimental artifact from an Ag collimator in front of the detector. This peak has not been a problem since it is not near any of the peaks of interest and is easily changed to another material if the need were to arise. Finally, the high plateau-like background is due to emission of bremsstrahlung in the wafer by the Si 1s photoelectrons which are excited by the primary photon beam.[8] It is this background which provides the physical limit to the detection limit achievable with SR TXRF.

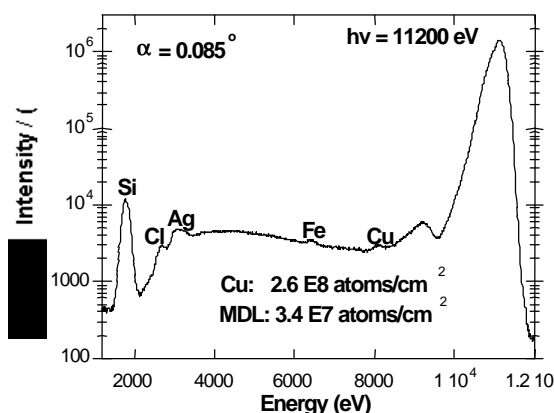


Fig. 2. TXRF spectrum (5,000 second count time) of a wafer cleaned using a state of the art process. The spectrum shows the Si substrate peak, Cl from the wafer surface, Ag from the collimator of the detector, as well as Fe and Cu contamination at very low levels. The spectrum also shows the scattered peak at 11.2 keV. The Cu concentration and minimum detection limit (MDL) for Cu are also shown.

In addition to its excellent detection limits, TXRF can also be used to map the concentration of contaminants on wafers. This is illustrated in Figure 3 where the strength of the Cu signal is plotted as a function of position as an area of localized contamination on the wafer is scanned vertically through the beam in 0.5 mm steps.

The contaminated area was prepared by placing a droplet of known volume from a solution of known Cu concentration onto the wafer. In this particular case the mass of Cu atoms in the spot is 0.1 pg. At these concentrations, the droplet, once dried, becomes very small (approximately 0.2 mm). Figure 3 then implies that the vertical FWHM of the photon beam is approximately 1.8 mm.

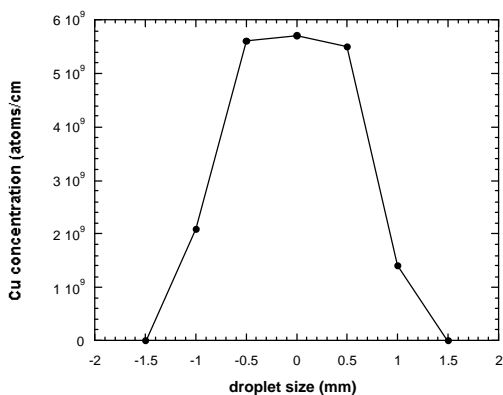


Fig. 3. Cu concentration in a spot on a Si wafer versus position. The spot was made by drying a droplet of a known volume from a solution containing Cu at a known concentration on a Si wafer. The mass of Cu in the droplet is 0.1 pg.

A similar experiment shows that the horizontal FWHM of the photon beam which is seen by the detector is approximately 7 mm.[8]

Therefore, 1 pg of Cu in a 1.8 mm x 7 mm area gives a density of approximately 7.5 x 10<sup>9</sup> atoms/cm<sup>2</sup>. Given the potential sources of error when working at these low concentrations, the calculated value corresponds rather well to the measured value of 5.8 x 10<sup>9</sup> atoms/cm<sup>2</sup> and provides an independent verification of the system calibration.

Figure 4 shows typical fluorescence spectra from a wafer intentionally contaminated with 8 x 10<sup>12</sup> atoms/cm<sup>2</sup> of Al obtained using the light element setup described above for an excitation energy below the Si-K edge and for three different angles of incidence, namely 0.2°, 0.7° and 1.0°. The Al Kα fluorescence signal at 1487 eV is seen on the low energy side of all the spectra. On the high energy side at 1750 eV one finds the signal from the scattered primary photons. Between these two peaks, the spectra show a third peak whose intensity increases with increasing angle and becomes dominant at the larger angles.

This extra peak is due to resonant x-ray Raman scattering.[11,12] The cross section is generally low compared to the elastic Rayleigh or inelastic Compton scattering, but it can become significant if the incident photon energy is close to a major absorption edge of the sample matrix due to resonant enhancement. The actual profile of the x-ray Raman scattering is obtained by convoluting the cross-section with the detector broadening, which is represented by a Gaussian distribution with its standard deviation equal to the detector resolution.

Therefore the energy range for TXRF excitation is restricted: the photon energy must be sufficiently below the Si K edge to avoid exciting Si fluorescence yet it must be sufficiently high such that the Raman peak does not overlap with the Al signal. Photon energies between 1730 and 1750 eV seem to satisfy both criteria. In a more general sense, for sample systems in which the substrate atomic number is just one greater than that of the element

of interest, the Raman scattering becomes a major limitation to the achievable sensitivity since it dominates the background.[13] Similar behavior is observed for heavier substrates such as GaAs when the photon energy is tuned below the Ga and As 1s binding energies in order to measure trace amounts of transition elements.[6]

Since Raman scattering is directly proportional to the amount of silicon with which the photon beam interacts, it is reasonable to expect that the magnitude of the effect will increase with increasing angle of incidence. That is, the larger the angle of incidence, the larger the penetration depth and thus the larger the Raman signal. Therefore, the Raman scattering becomes low for angles significantly below the critical angle (0.9° at 1730 eV) where total external reflection dominates. The effect of small angles is seen in Fig. 5 which shows the fluorescence spectrum of a second standard wafer intentionally contaminated with 3 x 10<sup>11</sup> atoms/cm<sup>2</sup> of Al measured for 10,000 seconds with an excitation energy of 1730 eV at 0.1°. This spectrum clearly shows a pronounced valley between the Al and scatter signals confirming that the Raman signal is very small.

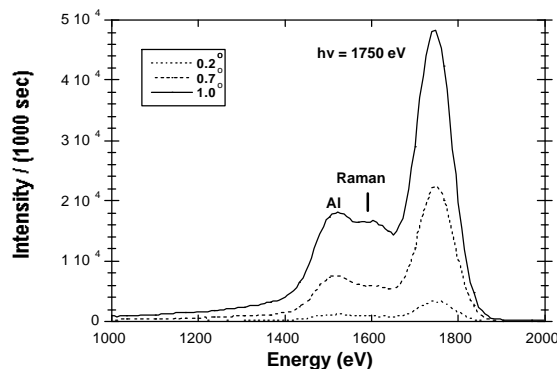


Fig. 4. Fluorescence spectra from a wafer intentionally contaminated with Al at a concentration of 8 x 10<sup>12</sup> atoms/cm<sup>2</sup>.

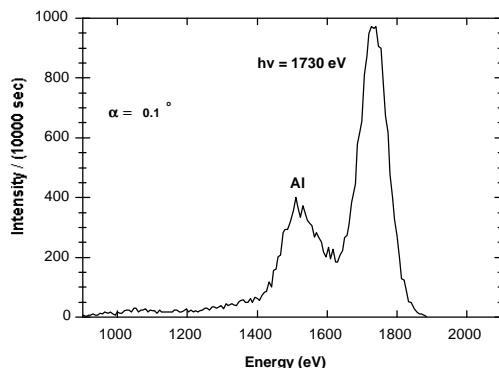


Fig. 5. Fluorescence spectra from a wafer intentionally contaminated with Al at a concentration of 3.4 x 10<sup>9</sup> atoms/cm<sup>2</sup>.

The minimum detection limit calculated for Al using these experimental conditions is thus 3.4 x 10<sup>9</sup> atoms/cm<sup>2</sup>, which is much lower than what may be achieved by conventional TXRF using a rotating anode.

It should be pointed out that the overall count rate for this spectrum is only 50 counts per second and that the detector could easily handle a factor of 250 more. Such an increase could be achieved by using an undulator source. With such an increase in counting rate, it would be possible to bring the measurement time down to the standard 1000 sec and still obtain a factor of 5 better detection limit, i.e., the MDL would be approximately  $7 \times 10^8$  atoms/cm<sup>2</sup>. This would be well beyond what would be achievable using other methods.

#### 4. Conclusions.

The SSRL Synchrotron Radiation TXRF facility is being routinely used by the semiconductor industry for a variety of real world problems. The minimum detection limits for transition elements can easily handle the most demanding industrial applications. The application of TXRF to light elements is still in the R&D phase but the initial results are quite promising.

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