

# Detection and characterization of trace element contamination on silicon wafers

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**Abstract.** Increasing the speed and complexity of semiconductor integrated circuits requires advanced processes that put extreme constraints on the level of metal contamination allowed on the surfaces of silicon wafers. Such contamination degrades the performance of the ultrathin SiO<sub>2</sub> gate dielectrics that form the heart of the individual transistors. Ultimately, reliability and yield are reduced to levels that must be improved before new processes can be put into production. It should be noted that much of this metal contamination occurs during the wet chemical etching and rinsing steps required for the manufacture of integrated circuits and industry is actively developing new processes that have already brought the metal contamination to levels beyond the measurement capabilities of conventional analytical techniques. The measurement of these extremely low contamination levels has required the use of synchrotron radiation total reflection x-ray fluorescence (SR-TXRF) where sensitivities 100 times better than conventional techniques have been achieved. This has resulted in minimum detection limits for transition metals of  $8 \times 10^7$  atoms/cm<sup>2</sup>. SR-TXRF studies of the amount of metal contamination deposited on a silicon surface as a function of pH and oxygen content of the etching solutions have provided insights into the mechanisms of metal deposition from solutions containing trace amounts of metals ranging from parts per trillion to parts per billion. Furthermore, by using XANES to understand the chemical state of the metal atoms after deposition, it has been possible to develop chemical models for the deposition processes. Examples will be provided for copper deposition from ultra pure water and acidic solutions.

## INTRODUCTION

Total reflection x-ray fluorescence in conjunction with synchrotron radiation (SR-TXRF) has demonstrated sensitivities for transition metals that are 50 times better when compared to conventional x-ray sources [1]. With the high flux, low divergence, and linear polarization of a synchrotron x-ray source, fluorescence signals are enhanced while background contributions from elastic and inelastic scattering are reduced. With the synchrotron TXRF facility at the Stanford Synchrotron Radiation Laboratory (SSRL), detection limits of  $8E7$  atoms/cm<sup>2</sup> for transition metals on silicon

surfaces have been achieved [1], allowing the semiconductor industry to conduct high sensitivity surface analysis for process development.

While TXRF can determine the amount of contamination on a silicon wafer surface, it is possible to exploit the broadband nature of synchrotron radiation to tune the excitation energy through an absorption edge of interest. From the x-ray absorption near edge structure (XANES), information on the unoccupied density of states can be acquired and the oxidation state of the contaminant of interest can be determined. By measuring the fluorescence yield using the grazing incidence SR-TXRF geometry, trace levels of impurities can be analyzed, allowing for trace contamination studies where knowledge of chemical information and impurity amount are needed.

One such relevant study involves trace copper metal deposition onto silicon wafer surfaces from ultra pure water (UPW) solutions that are commonly used by semiconductor manufacturers in post-clean rinse steps. Ever since the implementation of copper interconnect technology in chip processing, understanding how copper ions in solution interact with silicon surfaces has been of the utmost importance to the semiconductor industry, particularly since copper is a fast diffuser in silicon. For metal contamination in solution, there are two alternative reaction pathways that depend on the pH value of the solution. In lower pH solutions, it is expected that metal ions are electrochemically reduced and deposited on the surface as metallic particles [2]. For example, copper metal is reductively deposited on the silicon surface via the following chemical reaction:



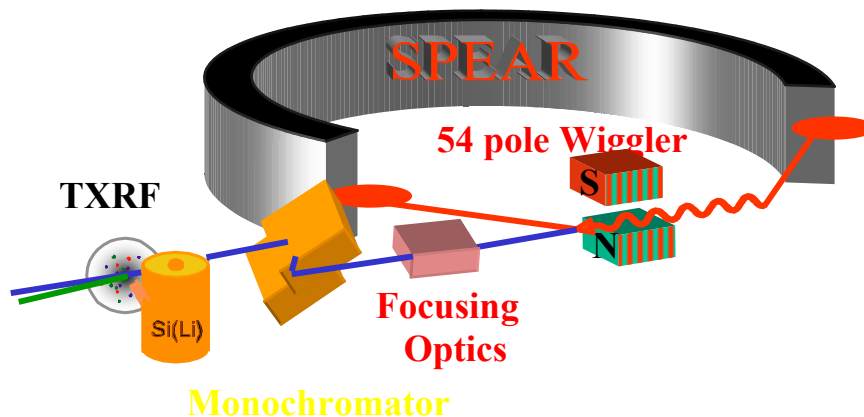
Conversely, in higher pH solutions, an oxide layer readily forms on the silicon surface, and metal ions are precipitated and included into the oxide layer as a metal oxide/hydroxide [3]. In ultra pure water solutions where the pH is neutral, it is proposed that both reaction pathways can occur simultaneously, and that the deposition mechanism is sensitive to other factors such as the dissolved oxygen content. By utilizing both SR-TXRF and XANES, it is possible to investigate copper deposition mechanisms in ultra pure water solutions.

## EXPERIMENTAL

Samples were prepared by cleaving silicon wafers into 20 cm x 10 cm pieces, which were subsequently cleaned using a 4:1 sulphuric acid/hydrogen peroxide mixture ( $H_2SO_4 = 96$  vol %;  $H_2O_2 = 30$  vol %) for 10 minutes followed by a rinsing in ultra pure water (UPW). These samples were then dipped into a solution of 0.5% HF for 1 minute to prepare a clean, hydrogen terminated surface. In order to study the influence of oxygen, de-oxygenated ultra-pure water solutions were prepared by Argon sparging, reducing the dissolved  $O_2$  content to 0.3 ppm, while air saturated ultra-pure water solutions contained 3.4 ppm of dissolved oxygen. Copper in a 2% nitric acid

matrix was then introduced at concentration levels of 10 and 100 ppb and surface contamination was then accomplished by immersing the hydrogen terminated silicon samples into these solutions.

To determine the surface concentration of copper, these samples were first analyzed with SR-TXRF at beamline 6-2 at the Stanford Synchrotron Radiation Laboratory (SSRL), using the setup shown in Fig. 1. The synchrotron radiation was monochromatized using a high flux, double multilayer monochromator set at an energy of 11.0 keV, giving a high excitation cross section for transition metals. The angle of incidence was  $0.1^\circ$ , which is below the critical angle for total external reflection resulting in a high surface sensitivity. A semiconductor (Si(Li)) detector was mounted so that the face of the detector was aligned perpendicular to the polarization vector of the linearly polarized synchrotron radiation. This geometry reduces the background contribution due to elastically scattered x-rays. Samples were measured for a standard counting time of 1000 seconds.



**Figure 1.** Schematic of the SSRL TXRF facility showing the SPEAR2 storage ring, BL6-2 54 pole wiggler, torroidal focusing mirror, double multilayer monochromator, Si(Li) detector oriented along the polarization vector of the incident radiation and the vertically mounted wafer.

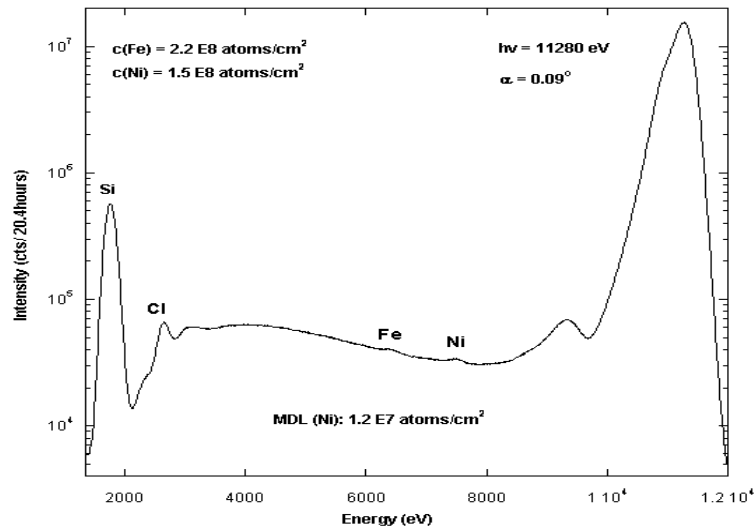
Before absorption edge measurements were conducted on the silicon samples, reference XANES spectra of CuO and Cu<sub>2</sub>O, that were prepared as thin powder samples in cells with Kapton tape windows, as well as a 5  $\mu\text{m}$  thick copper foil were measured in transmission. This gave representative spectra for copper in its 3 oxidation states. The silicon samples that were contaminated in de-oxygenated solutions were then analyzed with XANES. These measurements were carried out at the same beamline, using a high-resolution double-crystal (Si 111) monochromator

with an energy resolution of 0.89 eV at 8.9 keV. The excitation energy was tuned through the copper 1s absorption threshold (8.979 keV) in the same grazing incidence TXRF geometry, monitoring the fluorescence yield originating from the decay of the excited core state vacancy. The spectra were obtained between 8.940 keV and 9.2 keV at increments of 0.5 eV between 8.97 keV and 8.99 keV near the copper K edge, 1 eV above the edge between 8.99 to 9.060 keV, and 5 eV between 9.06 and 9.2 keV. The signal was integrated for 10 seconds per point for each scan and up to 30 scans were accumulated on the low concentration samples to achieve a high signal to noise ratio. Finally, a control sample with copper metal on silicon that was prepared by immersing a pre-cleaned silicon sample in 2% hydrofluoric acid spiked with a 1000 ppb of copper was measured in order to evaluate possible systematic errors in the sample preparation as well as the effectiveness of using XANES for trace metal contamination on silicon surfaces. This sample was also used to determine the oxidation, if any, of the metallic copper during the deposition in the solution and subsequent transfer to the measurement chamber.

## RESULTS

### Synchrotron Radiation Total Reflection x-ray Fluorescence

A synchrotron radiation TXRF spectrum of a silicon wafer with very low levels of iron and nickel contamination is shown in Fig. 2. In this spectrum, a high-energy peak at 11.0 keV, which corresponds to the elastic scattering of the primary synchrotron radiation, can be seen. The asymmetric tail on the low energy side of this peak corresponds to the Compton scattering of the incident synchrotron radiation, forming the background in the high-energy region. In the low energy region, the background is dominated by the emission of bremsstrahlung radiation, created by photoelectrons in the wafer. The spectrum shows the iron, nickel, and chlorine  $K_{\alpha}$  fluorescence lines. The chlorine comes from the cleaning solutions used on this wafer, while the iron and nickel are trace contaminants deposited at levels  $2.2E8$  and  $1.5E8$  atoms/cm<sup>2</sup>, as quantified by measuring peak intensities relative to that of a standard wafer with a known concentration. A minimum detection limit (MDL) of  $1.2E7$  atoms/cm<sup>2</sup> was achieved for a counting time of 20.4 hours, which corresponds to a MDL of  $8.9E7$  atoms/cm<sup>2</sup> if a standard counting time of 1000 seconds were to be used.

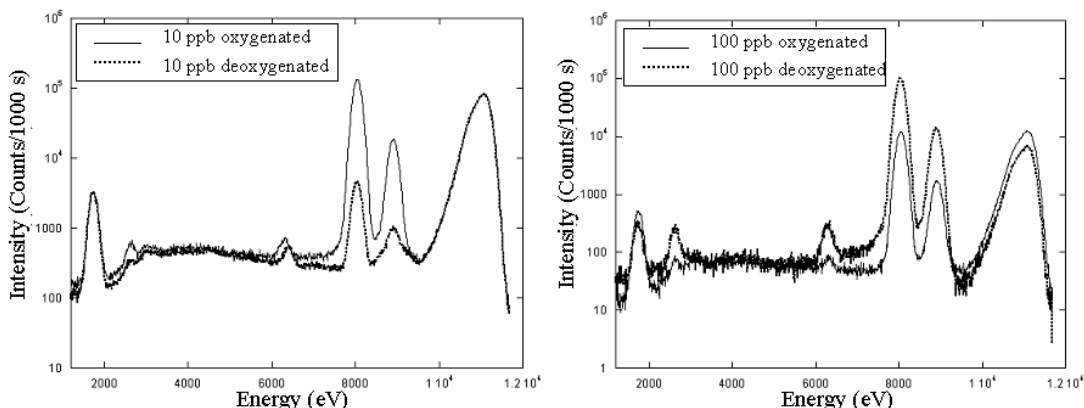


**Figure 2.** TXRF spectrum of an unintentionally contaminated wafer taken for 20.4 hours of counting time at an excitation energy of 11.28 keV. The MDL for this spectrum is  $1.2 \times 10^7$  atoms/cm<sup>2</sup>.

Synchrotron radiation TXRF measurements on the silicon samples that had been submerged in 10 and 100 ppb copper contaminated ultra pure water solutions are shown below in Fig. 3. The spectrum shows the copper  $K_{\alpha}$  and  $K_{\beta}$  fluorescence lines from the intentional contamination as well as the Fe  $K_{\alpha}$  fluorescence line due to unintentional iron contamination at levels below  $1 \text{E}9$  atoms/cm<sup>2</sup>. It was determined that the copper concentration for the 10 ppb deoxygenated and oxygenated samples shown on the left of Fig. 3 were  $4 \text{E}10$  atoms/cm<sup>2</sup> and  $9.3 \text{E}11$  atoms/cm<sup>2</sup>, respectively. For the 100 ppb deoxygenated and oxygenated samples shown on the right of Fig. 3, the copper concentration was found to be  $8.4 \text{E}11$  atoms/cm<sup>2</sup> and  $6.3 \text{E}12$  atoms/cm<sup>2</sup>, respectively.

From the SR-TXRF measurements, it can be seen that there is a two order of magnitude increase in the amount of copper deposited on silicon in deoxygenated solutions when the copper concentration in the ultra pure water solution is increased from 10 to 100 ppb. Conversely, with the same increase of copper in the UPW solution, the amount of copper deposited from oxygenated solutions remains nearly the same. This drastic increase in the amount of deposited copper in deoxygenated solution can be attributed to the deposition mechanisms occurring at the silicon surface. In deoxygenated solutions, it would be expected that the primary mode of copper deposition would be a reductive one, resulting in copper metal cluster formation while in oxygenated solutions, copper precipitates into the growing oxide as copper oxide/hydroxide. At low concentrations, such as 10 ppb, the concentration in the UPW is not high enough for metal cluster growth in deoxygenated solutions, and any deposited copper is re-dissolved by the UPW solution. Therefore, the only copper that is deposited at 10 ppb occurs by precipitation into the oxide. This results in higher copper deposition amounts for the air saturated solution, since an oxide grows more

readily when compared to the deoxygenated solutions. Alternatively, at higher concentrations, such as 100 ppb, copper cluster growth via the reductive mechanism can occur and therefore the amount of copper deposited is higher for the deoxygenated solutions since copper is deposited both reductively and incorporated into the oxide.



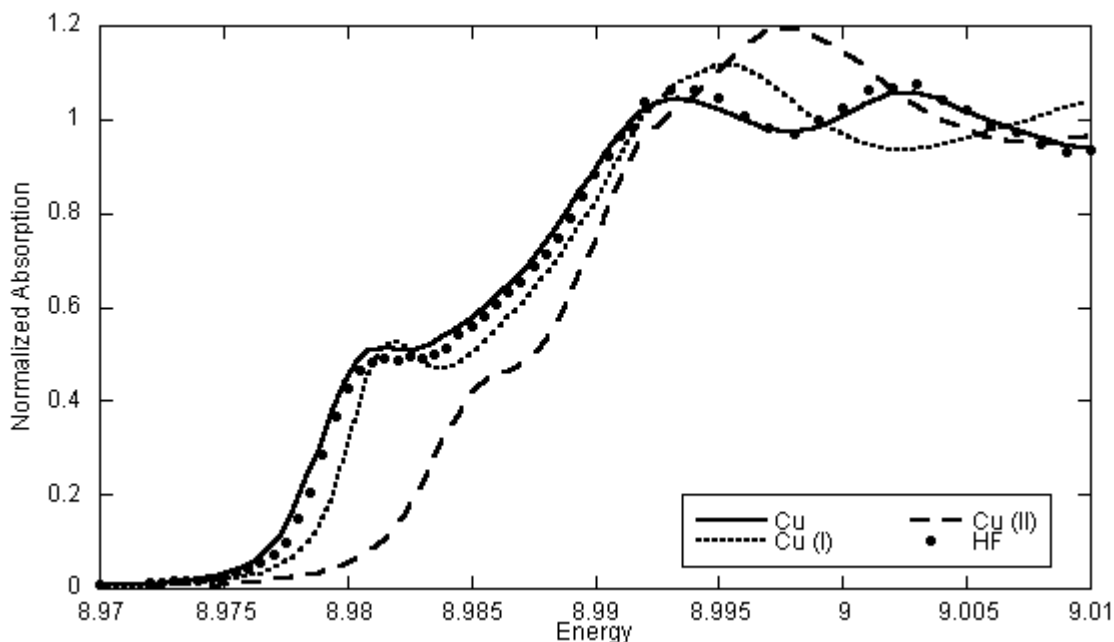
**Figure 3.** TXRF spectra of silicon samples dipped in oxygenated and deoxygenated UPW spiked with 10 and 100 ppb copper.

### X-Ray Near Edge Absorption Spectroscopy

Fig. 4 shows the copper 1s absorption spectra of the copper reference samples (Cu, Cu<sub>2</sub>O and CuO) having the oxidation state 0, I, and II, respectively. The copper 1s absorption edge was determined by the first inflection point, corresponding to 8.979 keV [8], and each spectrum was energy calibrated with respect to a copper reference metal spectrum that was measured periodically. A linear background fit to the pre-edge region was subtracted, and each spectrum was normalized with a spline fit done from the post-edge region starting at 9 keV up to 9.2 keV. It can be seen that the copper K absorption edge shifts to higher binding energies with increasing oxidation state of the copper sample. In addition to this energy shift, the detailed shape of the structure in the near edge region is strongly dependent on the atomic structure around the absorbing atoms.

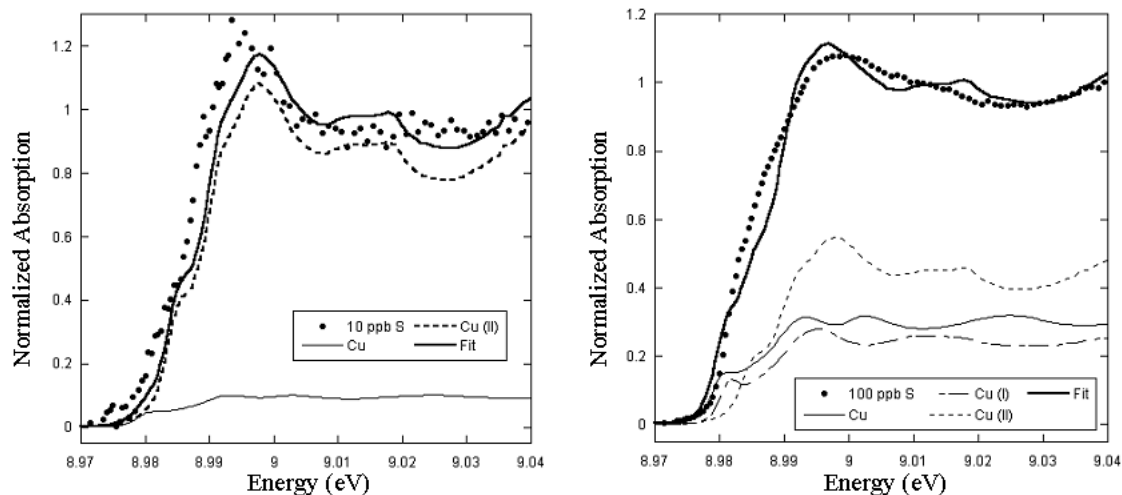
Also plotted in Fig. 4 is the copper metal on silicon sample that was created by contaminating a clean silicon sample in 2% HF spiked with copper at a concentration of 1000 ppb. Since reductive deposition dominates in low pH solutions, it would be expected that any copper deposited in 2% HF would be metallic in nature [5]. This is confirmed by the XANES spectrum which clearly shows that the metal on silicon sample resembles the copper metal foil spectrum. However, the energy position of the absorption edge is slightly shifted by 0.35 eV towards higher binding energies as compared to the copper metal foil reference. Except for this shift, the spectrum

corresponds well in fine structure below as well as above the ionization potential, demonstrating the utility of using reference samples to identify the oxidation state of copper contamination on silicon samples. Moreover, the data from this sample shows that the sample preparation is effective and that copper metal on silicon can be measured with minimal environmental interference using the cleanroom setup at SSRL.



**Figure 4.** Copper K XANES spectra taken in transmission for Cu, Cu<sub>2</sub>O, and CuO are shown. Each of these reference samples represents copper in different oxidation states. Also shown in dots is the XANES fluorescence yield data for the silicon sample dipped in 2% HF, spiked with 100 ppb copper.

Fig. 5 shows the copper 1s absorption spectra of silicon samples that were contaminated in deoxygenated UPW solutions with copper concentration of 10 and 100 ppb. A linear background subtraction and normalization using a spline fit to the post edge region was again conducted. Linear combination fits using the Cu, Cu<sub>2</sub>O and CuO reference samples are also plotted in Fig. 5, with the percent contribution of each component plotted as well. These fits were conducted from 8.975 keV to 9.040 keV by performing a chi-squared minimization procedure with the WinXAS program (Ressler, 1998) between the XANES data and a linear combination of the reference samples.



**Figure 5.** Copper K XANES spectra are shown for silicon samples dipped in 10 and 100 ppb copper contaminated UPW that was deoxygenated. A linear combination fit showing the percent contribution from the three copper reference spectra are also displayed with the overall fit depicted as the bold solid line.

From these linear combination fits of the x-ray absorption spectra it can be seen that the copper deposited for deoxygenated solutions with 10 ppb of copper are almost completely oxide in character (90% CuO and 10 % Cu metal), while the sample contaminated in 100 ppb deoxygenated ultra pure water is mixed between the copper metal, Cu(I) and Cu(II) oxidation states with a contribution of 30 %, 24%, and 46 %, respectively. This supports the TXRF data in that copper is primarily deposited as an oxide from deoxygenated UPW solutions at 10 ppb, since the amount of copper in the UPW is not enough for copper metal cluster growth. However, at higher concentrations, if cluster growth is energetically favorable, both oxidative and reductive mechanisms occur simultaneously giving rise to mixed oxidation character, which is seen for the sample contaminated in 100 ppb deoxygenated UPW solution.

## CONCLUSION

It has been demonstrated that the amount and chemical state of copper deposited from ultra pure water solutions depend strongly on the dissolved oxygen content and copper concentration in the solution. With SR-TXRF, it was found that the amount of copper deposited on silicon from deoxygenated UPW solutions greatly increased when the amount of copper in solution was augmented from 10 to 100 ppb. With XANES spectroscopy in a grazing incidence geometry, it was possible to distinguish the chemical state of trace contaminants deposited onto silicon surfaces from solution by using the chemical shifts of the absorption edges along with other



spectral features. For the deoxygenated solutions, it was found that copper deposited from a 10 ppb copper contaminated solution was 90% oxide in character while the copper deposited from a 100 ppb copper contaminated solution had copper in all three oxidation states.

Future studies will analyze air-saturated solutions in order to develop a complete representation of the surface deposition chemistries occurring in UPW solutions. Moreover, other systems involving trace metal deposition from solution could be examined as well. For example, co-deposition mechanisms, where other contaminants in solution have affected copper deposition, have been studied [6]. With XANES, the chemical state of trace contaminants deposited from such solutions can be directly determined, providing more insights into trace metal deposition phenomena.

## ACKNOWLEDGEMENTS

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