

FEASIBILITY OF *IN SITU* TXRF

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Abstract

Synchrotron radiation based total external reflection x-ray fluorescence spectroscopy (TXRF) is now being routinely used at the Stanford Synchrotron Radiation Laboratory (SSRL) to carry out industrially relevant measurements. For transition elements on Si wafer surfaces, detection limits of 8×10^7 atoms/cm² that correspond to 1 impurity atom among 30 million substrate atoms have proven more than adequate for the studies undertaken to date. New studies, which aim to develop a better understanding of the kinetics of metal deposition during Si wafer cleaning processes, are being pursued. By using a sample cell with a water delivery system that has been custom designed, silicon samples can be analyzed directly beneath a water layer (*in situ* TXRF). Initial results measuring silicon samples with known Cu concentrations are presented. Due to the increased scatter and background from the water layer along with the attenuation of fluorescence signals, minimum detection limits for the *in situ* TXRF setup increased to 8×10^{10} atoms/cm², in close agreement to predicted values extracted from modeling calculations.

Introduction

For over 20 years, the device density of silicon chips has been increasing, leading to more stringent requirements for surface cleanliness. According to National Semiconductor Technology Roadmap developed by SEMATECH, transition metal impurities and light metallic elements ($Z < 14$) must now be reduced to concentrations lower than 3×10^8 atoms/cm² and 5×10^9 atoms/cm² respectively, in order to achieve acceptable yields with current processing technologies [1]. At beamline 6-2 at the Stanford Synchrotron Radiation Laboratory (SSRL), these requirements have been met by applying synchrotron radiation based total reflection x-ray

fluorescence (SR-TXRF) to detect trace impurities on silicon wafer surfaces in a nondestructive manner [2]. Minimum detection limits (MDL) of 8×10^7 atoms/cm² (with a 1000 second spectrum) have been routinely achieved for transition metals, while an MDL of 8×10^9 atoms/cm² has been reached for aluminum using a bending magnet source [2,3].

Having exceeded the needs of the semiconductor industry for the minimum detection limit of transition metals, new experiments of studying silicon samples directly beneath a liquid layer have begun (*in situ* TXRF). Currently, the semiconductor industry uses a variety of cleaning procedures, but relatively little research has been done to understand the kinetics of these reactions. Some work has been done with *ex situ* techniques [6], but these studies often suffer from environmental interference and cannot resolve the kinetics that a real-time experiment can give. By observing samples directly beneath a liquid layer, it is believed that these cleaning mechanisms may be elucidated without environmental interference. With this in mind, a sample cell was designed with extreme cleanliness in mind and preliminary studies were conducted at beamline 6-2.

Extending TXRF to samples beneath a water layer poses numerous challenges. First, the applied water layer attenuates fluorescence signals that are emitted from the surface of the sample. Moreover, it increases the dominant sources of background in TXRF: photoelectron bremsstrahlung and inelastic scattering. To minimize these effects it is imperative that the water layer above the sample be kept as thin as possible. Finally, since the metal contamination on silicon surfaces during silicon wafer processing usually happens on the timescales of minutes, the measuring time needs to be shorter than what is used in *ex situ* TXRF (usually 1000 seconds). Theoretical models simulating a 20 μm thick water layer and a 10-second measuring time predict a detection limit of 8×10^{11} atoms/cm² (8×10^{11} atoms/cm² for a 1000 second spectrum).

Experimental Setup

The current setup for the *ex situ* TXRF station uses an x-ray beam produced by a 54 pole wiggler on beamline 6-2. The beam is focused with a quartz mirror and tuned to an energy of 11.2 keV by using a double multilayer monochromator and the size of the beam is defined with slits to be

.25 mm x 3 mm (h x v). The sample is placed vertically with the incident beam at a glancing angle less than the critical angle for total external reflection (~ 0.16 deg). In an effort to reduce the observed elastic scatter, the detector is positioned along the polarization vector of the x-ray beam. The TXRF setup is shown in Figure 1.

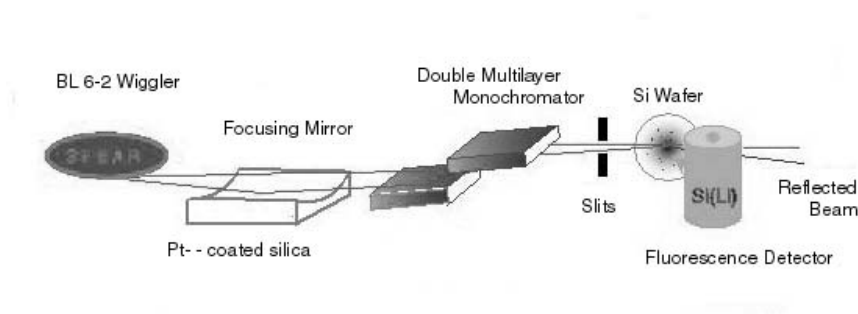


Figure 1 – Schematic representation of the experimental station used at SSRL. The beam is focused onto the Si wafer using the focusing mirror and monochromatized by the multilayers. The detector is aligned along the polarization vector of the synchrotron radiation to minimize scatter.

Using an *in situ* sample cell in place of the wafer chamber, it is possible to measure various samples beneath a water layer using a similar setup shown in Figure 1. The *in situ* cell used in these experiments is comprised of a machined Teflon chuck, upon which a clean PFA Teflon petri dish is placed. The sample is placed on the backside of the petri dish and an aluminized Mylar film covers it. A seal is created by using an o-ring in conjunction with a clamp. Teflon tubing is fed through the chuck and holes in the petri dish in order to provide a supply of water. A syringe pump is used with the inlet tubing, while the outlet tubing drains the water to a reservoir. By varying the flow rate of the syringe pump the thickness of the water layer can be controlled. A detailed figure of the cell design is shown in Figure 2.

Results

Solutions spiked with 20 to 200 ppb Cu were used to intentionally contaminate silicon samples that were initially measured in vacuum using *ex situ* TXRF for comparison. With the Cu surface concentrations established, these samples were then measured using the *in situ* setup without Mylar or water. Shown below in figure 3 is a representative spectrum comparing the *ex situ* vacuum setup to the *in situ* air setup normalized such that the integrated and non-attenuated Cu K α fluorescence signature is the same for both spectra. As can be seen, the addition of an air volume results in additional elastic and inelastic scatter in the high energy part of spectrum as well as an additional Ar peak at 2958 eV. The silicon fluorescence signal from the substrate is also attenuated heavily due to the presence of the air and an additional Teflon filter that was used with the *in situ* setup. Finally, it should be noted that there was slight unintentional contamination when measuring the sample with the *in situ* setup resulting in a small but noticeable Fe peak.

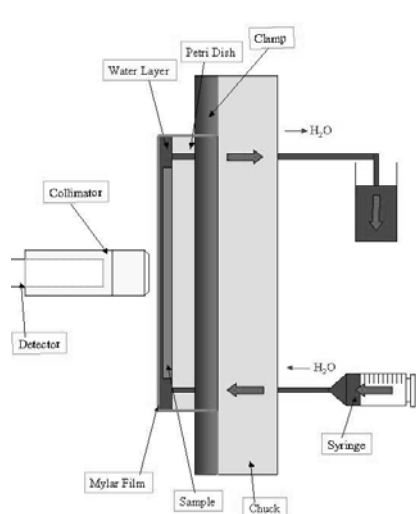


Figure 2 – *In situ* cell design. The liquid is filled using a syringe pump, which delivers a constant flow rate of water.

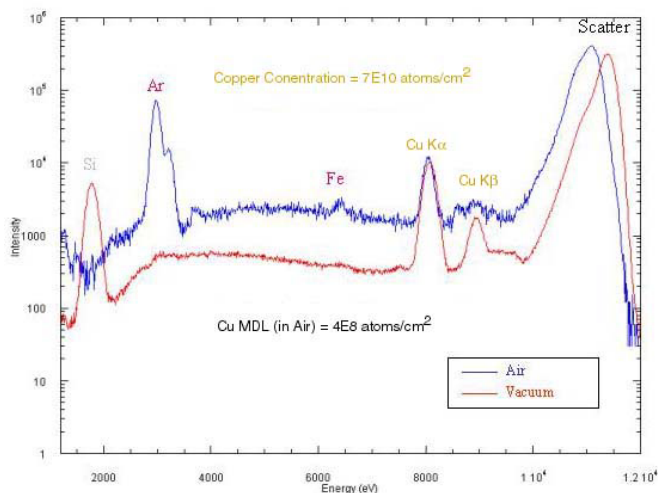


Figure 3 – Two spectra comparing a sample in vacuum (*ex situ* setup) to a sample in air (*in situ* setup). Both spectra were normalized to the integrated Cu K α signal since this concentration was assumed to remain constant. The presence of air increases the scatter and background, attenuates the Si signal, and gives rise to an argon peak.

Next, the Mylar and water were applied to the sample with the *in situ* setup and the resulting spectrum overlaid with the *ex situ* vacuum measurement, shown in figure 4, was measured. As can be seen, the addition of Mylar and water resulted in Fe and Zn contamination and attenuation of the Cu signal. Moreover, the elastic and inelastic scatter contribution continued to increase, all of which degrade our detection limits. Lastly, it should be noted that while this spectrum shows complete attenuation of the Cu signal, other samples had a sufficiently high Cu concentration to be visible beneath the water layer thereby allowing for quantification.

Quantification

Using the Lambert-Beer law as shown below, it is possible to calculate the water layer thickness by measuring the attenuation of the Cu signal due to the presence of the water layer.

$$I = I_o * \exp[-\mu * x]$$

where I_o is the incident flux, μ is the linear absorption coefficient, and x is the thickness of the sample. For a flow rate of 2 ml/min, a water layer thickness of 10 μm is calculated.

Since the water thickness is known, it is possible to calculate the Cu concentration by normalizing the Cu signal to a known fluorescence signal present on the sample. The known signal used is the silicon peak, as its surface concentration is well known to be 3×10^{15} atoms/cm². The fluorescence signal from an impurity Z is given by [5]:

$$S_z = N_{ph} * X_z * \sigma_z(E) * \omega_z * \kappa_z * T(E_z) * d\Omega$$

where N_{ph} is the incident photon flux (photons/s), σ_z is the photo-ionization cross-section, ω_z is the fluorescence yield, κ_z is the relative transition probability of $K\alpha$ to $K\beta$, T is the transmission factor, E_z is the fluorescence x-ray energy, and $d\Omega$ is solid angle subtended by detector. Normalizing the Cu signal to the silicon signal removes the dependence of constant terms such as incident flux and solid angle subtended and gives:

$$\frac{S_{Cu}}{S_{Si}} = \frac{X_{Cu} * \sigma_{Cu}(E) * \omega_{Cu} * \kappa_{Cu} * T(E_{Cu})}{X_{Si} * \sigma_{Si}(E) * \omega_{Si} * \kappa_{Si} * T(E_{Si})}$$

From this equation, Cu concentrations for several spectra can be calculated and are in close agreement to values measured with the *ex situ* SR-TXRF station with no water layer present.

From these calculations, the MDL for the *in situ* TXRF setup with a 10 μm thick water layer is 7×10^{10} atoms/ cm^2 (for a thousand second spectrum), well within the range for kinetic studies.

To insure that Cu impurities from the ultra pure water (UPW) are negligible compared to the samples being studied, clean Si samples were measured with the *ex situ* TXRF setup before and after dipping into a bath of UPW. The results are shown in figure 5, and as can be seen, trace impurities of Cu, Fe, and Zn were present in concentrations of 5.4×10^8 , 1.4×10^9 , and 4.7×10^8 atoms/ cm^2 , corresponding to a 10 ppt level concentration in the water itself [4]. Since the solutions used to contaminate samples measured with the *in situ* experiments were all above 20 ppb, it can safely concluded that Cu contamination from the water to the sample is insignificant.

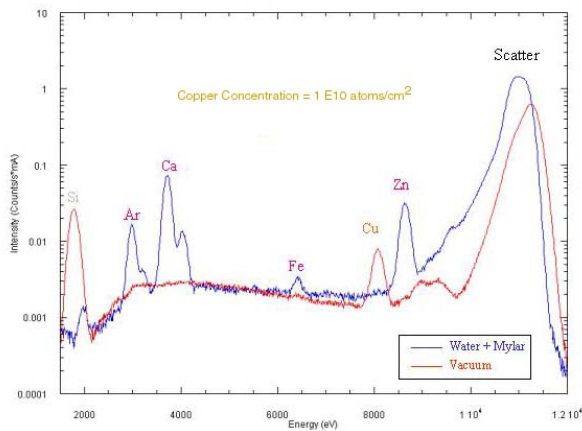


Figure 4 – Two spectra comparing *in situ* versus *ex situ* TXRF. Due to unintentional contamination from the mylar layer, Ca, Fe, and Zn peaks are present. Moreover, the Cu peak is completely attenuated due to the presence of the water layer.

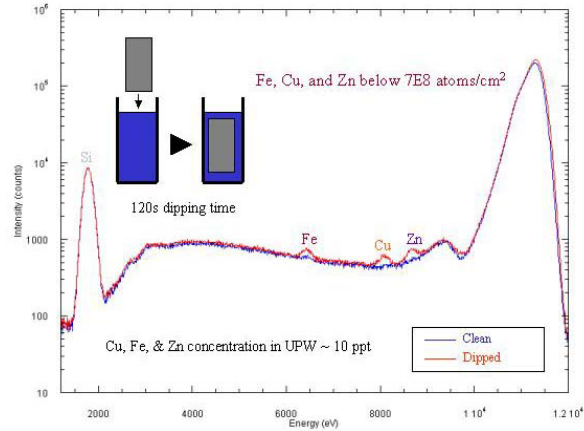


Figure 5 – The cleanliness of the ultra pure water was tested by measuring silicon samples before and after dipping them into a bath of ultra pure water. As can be seen, trace amounts of Fe, Cu, and Zn were deposited onto the silicon surface after dipping.

Conclusion

From these early experiments it is apparent that further cleanliness is required as Zn and Fe contamination from the environment interferes with the *in situ* spectra. Especially detrimental is the Zn signal due to its proximity to the Cu signal being measured. The development of a cleanroom environment for sample preparation along with clean chemicals will aid in this endeavor.

After developing a clean environment, it will also be possible to use spiked solutions to observe the deposition of other transition metals as a function of time. Models showing the enhanced deposition of Cu in the presence of Fe ions have been proposed by Homma et al [6] and *in situ* studies could confirm this result. Finally, by extending this technique, it will be possible to conduct *in situ* x-ray absorption near edge spectroscopy (XANES) to determine the chemical state of the Cu deposited on the silicon. Homma et al [4] have proposed that the presence of dissolved oxygen disturbs the reductive deposition of Cu while enhancing hydroxide formation. Since the chemical shifts of the various Cu oxides are well characterized, measuring silicon samples with spiked solutions using XANES will provide useful results.

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