X-ray Absorption spectroscopy on copper trace impurities on silicon wafers

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ABSTRACT

Trace metal contamination during wet cleaning processes on silicon wafer surfaces is a detrimental effect that impairs device performance and yield. Determining the chemical state of deposited impurities helps in understanding how silicon surfaces interact with chemical species in cleaning solutions. However, since impurity concentrations of interest to the semiconductor industry are so low, conventional techniques such as x-ray photoelectron spectroscopy cannot be applied. Nonetheless, chemical information on trace levels of contaminants can be determined with x-ray absorption near edge spectroscopy (XANES) in a grazing incidence geometry. In this study, silicon samples were dipped in ultra pure water (UPW) and 2% hydrofluoric (HF) solutions with copper concentrations of 5 and 1000 ppb, respectively. These samples were then analyzed using XANES in fluorescence yield mode to determine the oxidation state of deposited copper contaminants. It was found that copper impurities on the silicon surface from HF solution were metal in character while copper impurities deposited from the spiked UPW solution were deposited as an oxide. These results show that XANES can provide information on the chemical state of trace impurities even at surface concentrations below a few thousandths of a monolayer.

INTRODUCTION

For over 20 years, the device density of silicon chips has been increasing, leading to more stringent requirements for silicon surface cleanliness. Metallic impurities can cause device degradation such as diminished carrier lifetimes, threshold voltage shifts, and leakage currents, leading to poor device performance and low processing yields. Furthermore, the chemical state of trace metal contaminants can change how they affect device properties, such as the gate oxide integrity.

A key source of metal contamination often includes cleaning solutions. These solutions are aggressive acid solutions used either in combination or alone to remove metals and organics as well as ultra pure water (UPW) in rinse steps. Any metals in these solutions will be readily ionized and thus the solutions behave like an electrochemical bath in which the metals can be deposited on the silicon surface. The deposition is affected by a variety of factors including oxygen content in the solution, doping in the semiconductor, and pH value [1]. For metal contamination during the wet cleaning process, there are two alternative reaction pathways in accordance with 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:

$$Cu^{2+} + e_{Si}^- \Rightarrow Cu^{1+} + e_{Si}^- \Rightarrow Cu^0$$
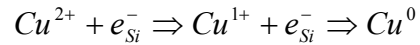
Conversely, in higher pH solutions, metal ions are precipitated and included into the oxide layer as a metal oxide/hydroxide [3].

Total reflection x-ray fluorescence spectroscopy (TXRF) can determine the concentration of transition metal impurities at levels above 5E9 atoms/cm^2, when used with a conventional x-ray source. However, when used in combination with high brightness synchrotron radiation, detection limits can be improved to 8E7 atoms/cm^2 for transition metals, as achieved at the Stanford Synchrotron Radiation Laboratory (SSRL) [4]. With this high detection sensitivity in the femtogram level, insights into mechanisms for metal deposition in trace quantities can be conducted.

In addition, the oxidation state of trace impurities can be determined by x-ray absorption near edge spectroscopy (XANES) in fluorescence yield, which is especially useful for the detection of dilute samples [5]. This technique exploits the broadband nature of synchrotron radiation by tuning the excitation energy through an absorption threshold of interest. XANES images the energy dependence of the number of unoccupied states reflecting the local electronic structure of the material. The local chemical environment at the site of the absorbing atom defines the shape and the energy position of XANES spectra, making this spectroscopy well suited for studying systems without long-range order. The spectra also yield information about the oxidation state and local symmetry of the absorbing atomic center. Additionally, by using XANES spectra of reference materials as fingerprints, specific details about the chemical environment can be derived. It will be demonstrated that the oxidation state of copper trace contamination on silicon surfaces can be determined with XANES even for contamination levels as low as 6E10 atoms/cm^2.

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. Following this, the samples were intentionally contaminated using solutions of ultra pure water or 2% HF with copper concentrations of 5 ppb and 1000 ppb, respectively.

In order to determine the surface concentration of Cu, these samples were first analyzed with SR-TXRF at beamline 6-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). The synchrotron radiation was monochromatized using a high flux, double multilayer monochromator set at an energy of 11.2 keV, giving a high excitation cross section for transition metals. The angle of incidence was 0.1°, 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.

The XANES measurements were carried out at the same beamline, this time 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.

Furthermore, CuO and Cu_2O reference samples, prepared as thin powder samples in a cell with Kapton windows, as well as a 5 μm thick Cu foil, were measured in transmission geometry using two ion chambers placed in front and behind the sample. The absorption coefficient is then obtained according to the Lambert-Beer law [7]:

$$I(d) = I_o \exp(-\mu\rho d)$$

where Io is the incident x-ray intensity, I(d) the intensity after penetration to depth d, ρ is the density of the material, and μ is the mass-absorption coefficient which depends on the energy of the incoming x-rays.

DISCUSSION

Figure 1 shows the Cu 1s absorption spectra of the copper reference samples (Cu, Cu_2O and CuO) having the oxidation state 0, I, and II, respectively. Since it is well known that the copper absorption edge as determined by the first inflection point corresponds to 8.979 keV [8], each spectrum was energy calibrated with respect to a Cu 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.

As seen in figure 1, the Cu K absorption edge shifts to higher binding energies with increasing oxidation state of the copper sample. This chemical shift is quite noticeable for the fully oxidized form of Cu II (CuO) as the K edge energy shift is nearly 5 eV. In the pre-edge region below the ionization potential, a shoulder is clearly visible for all three spectra. This corresponds to a core electron transition into an unoccupied bound state above the Fermi level [6]. Figure 1 shows that its intensity strongly depends on the oxidation state of copper. Above the ionization potential, the spectra also show characteristic shape resonances, which are based on multiple scattering events [5]. Together, all of these characteristics provide a "fingerprint" for each reference sample that can be used in identifying the oxidation state of trace copper contaminants on a silicon sample.
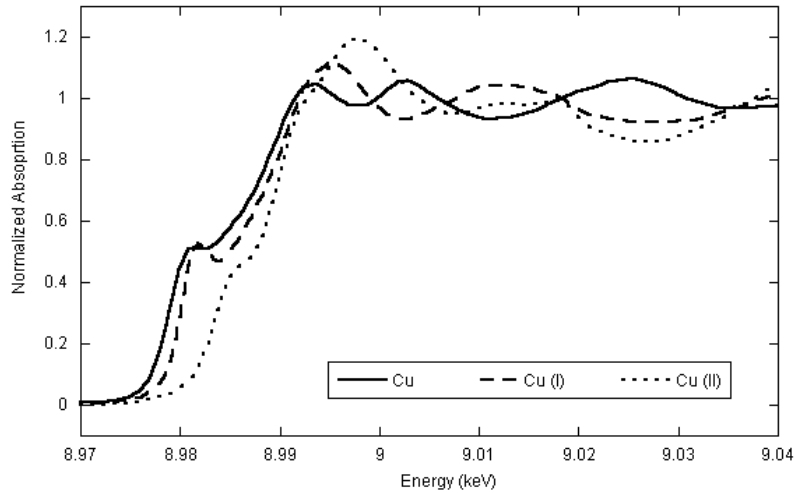
Figure 1. Copper K XANES spectra taken in transmission for Cu, Cu_2O, and CuO. Each of these reference samples represent copper in various oxidation states. As can be seen, the K edge shifts to higher energies with increasing oxidation state.

For the sample dipped in copper contaminated HF, the SR-TXRF measurement resulted in a copper surface concentration of 6E13 atom/cm^2, which corresponds to 6 hundredths of a Si monolayer. Figure 2 shows the XANES spectrum of this sample. Using XANES as a fingerprint of different chemical compounds, it is seen that the energy position of the absorption edge is slightly shifted by 0.35 eV towards higher binding energies as compared to the one of Copper metal. However, the spectrum corresponds well in fine structure below as well as above the ionization potential to the copper metal reference spectrum. This qualitative comparison verifies that the deposited copper exists as clusters that are metallic in character. This is also expected, since the reaction pathway for metal deposition in a low pH solution such as HF will be reductive [10].
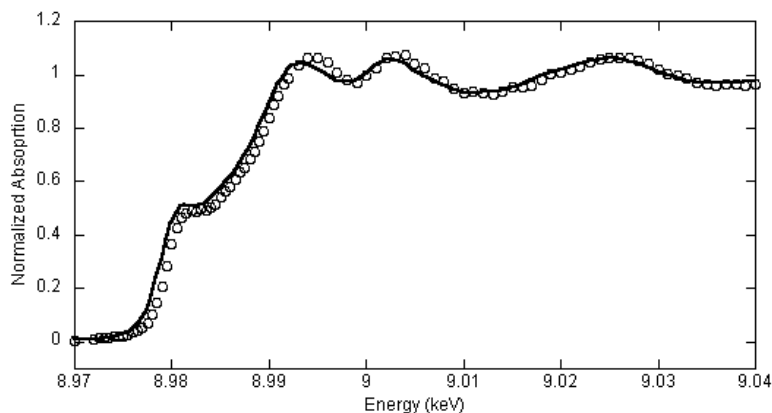

Figure 2. XANES spectrum of a silicon sample dipped in 2% HF with 1000 ppb copper concentration (circles), superimposed on a Cu metal foil reference sample (line).

For the silicon sample dipped in 5 ppb copper contaminated UPW, the SR-TXRF measurement resulted in a copper surface concentration of 6E10 atoms/cm^2. Such low concentrations are well below the detection limits of conventional techniques that determine the chemical state of the surface contaminants, such as x-ray photoelectron spectroscopy. Figure 3 shows the corresponding XANES spectrum. In contrast to figure 2, it can be seen that the deposited copper is consistent with the absorption spectrum of CuO (II). Moreover, the K edge has shifted to 8983.5 eV and the shape of the pre-edge shoulder is consistent with the one of the CuO reference sample, further validating that the deposited copper is in a highly oxidized state. In UPW, copper impurities can precipitate from solution into the native surface oxide layer that grows readily on the silicon surface in the presence of water. These copper impurities would be incorporated throughout the oxide as copper oxide contaminants, resulting in an absorption spectrum as seen in Figure.3.
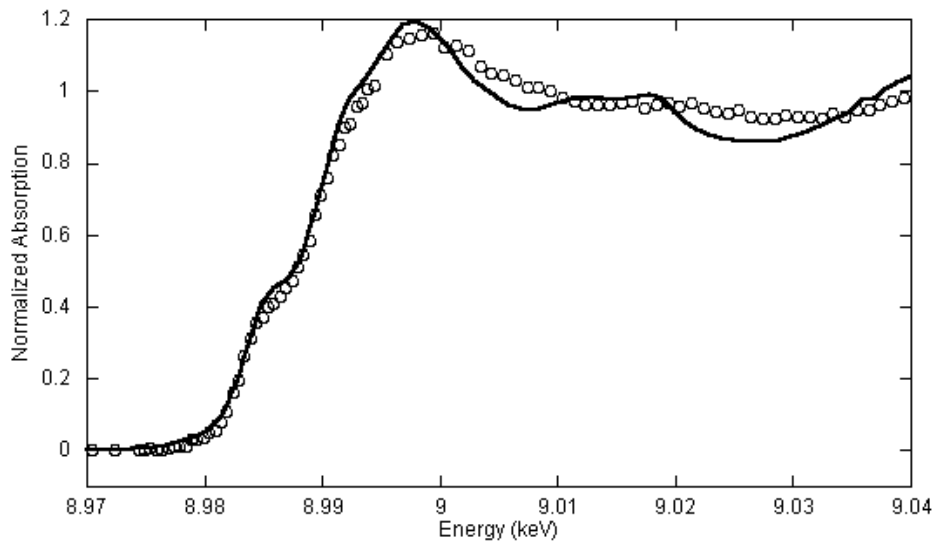

Figure 3. XANES spectrum of a silicon sample dipped in UPW containing 5 ppb copper (circles) as well as of a CuO reference sample (line). The Cu contaminated sample shows good agreement with respect to the energy shift of the CuO film (8.984 keV) and the energy position of the pre-edge shoulder at 8.987 keV.

CONCLUSION

This work demonstrates that XANES spectroscopy in a grazing incidence geometry is capable of distinguishing 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, the oxidation state of Cu contaminants present on the surface could be determined. It was found that copper deposited reductively from 2% HF exhibited metal character, while copper precipitated into a surface oxide layer formed from UPW displayed copper oxide character, giving insights into the chemistry that occurs during the deposition process in various solutions.

Future studies could apply the same principles developed in this study to examine other systems involving trace metal deposition from solution. For example, the deposition mechanisms of copper have been found to vary with the amount of dissolved oxygen in solution, with high oxygen content resulting in copper oxide deposition and low oxygen content resulting in copper metal deposition [9]. Using XANES, the chemical state of trace contaminants deposited from solutions with varying amounts of dissolved oxygen can be directly determined, providing more insights into trace metal deposition phenomena.

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