# Characterization of Copper Deposition on Silicon Surfaces by Synchrotron Radiation

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Trace metal contamination during wet cleaning processes on silicon wafer surfaces is a detrimental effect that impairs device performance and yield. Currently, total reflection x-ray fluorescence spectroscopy (TXRF) using synchrotron radiation is one of the most powerful techniques for trace impurity analysis on silicon wafer surfaces and has been employed to better understand the deposition mechanism of copper trace impurities on silicon wafers. Our recent studies focus on silicon surfaces immersed in copper contaminated ultra pure water solutions ranging from 10 ppt to 500 ppb. We will focus on the correlation between the deposited copper concentration and the amount of dissolved oxygen present in the ultra pure water. Fig. 1 shows the TXRF spectra of two Si wafers after immersion into ultra pure water containing a small copper amount of 0.1 ppb. The black line shows the fluorescence spectrum obtained from the deoxygenated solution while the grey line shows the result of the air saturated solution. We find for copper concentrations below 20 ppb in the solution that a deoxygenated solution results in a smaller deposited amount of copper on the silicon wafer surface by more than an order of magnitude as compared to an air saturated solution. However, we will show that the opposite behavior is observed for higher copper concentrations above 20 ppb in the ultra pure water solution as shown in Fig. 3.

We will also demonstrate, that by measuring the TXRF copper fluorescence signal as a function of the angle of incidence, we can determine that, for deoxygenated solutions above 20 ppb, the copper deposits are particle-like in nature. In addition, the particle size can be derived by modeling this angular distribution. Furthermore, it will be shown that the particle size increases with increasing copper concentration in the solution. However, no particle formation can be observed for small copper concentrations below 20 ppb for both deoxygenated and air saturated ultra pure water solutions. In this case, we conclude that the copper is embedded within the silicon oxide layer, which is in line with AFM measurements on these surfaces.

The oxidation state of deposited copper trace impurities can be verified by combining TXRF with x-ray absorption near edge spectroscopy (XANES) exploiting the tunability of the broadband synchrotron radiation. This technique is very sensitive to the chemical environment of the absorbing atom and provides high detection sensitivity when used in a fluorescence detection mode for an angle of incidence below the critical angle of total external reflection. We will demonstrate that the oxidation state of deposited copper depends on the amount of dissolved oxygen in the ultra pure water as well as on the concentration of copper in the solution, which is connected to the size of the deposited copper particles. Our measurements further show that the copper impurities on the silicon wafer surface from deoxygenated ultra pure water solutions with copper concentrations above 20 ppb are predominantly metal in character, while copper impurities deposited from air saturated solutions show a stronger oxide character for the same concentrations. For small concentrations below 20 ppb our results verify, that copper mainly deposits as copper oxide on the silicon surface.

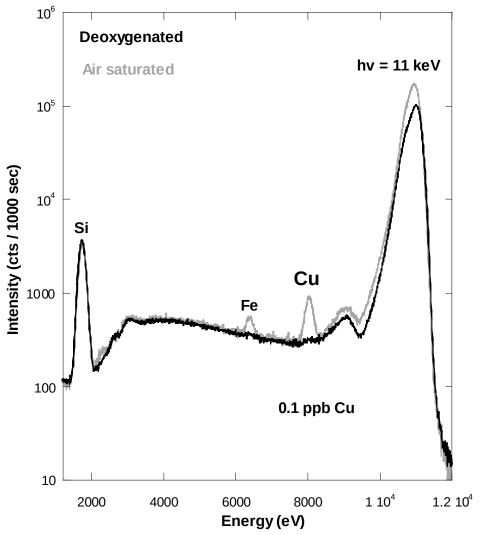

Fig. 1.TXRF spectrum of a silicon wafer after immersion into ultra pure water containing 0.1 ppb copper. The air saturated solution results in a higher amount of deposited copper concentration as compared to the deoxygenated solution.

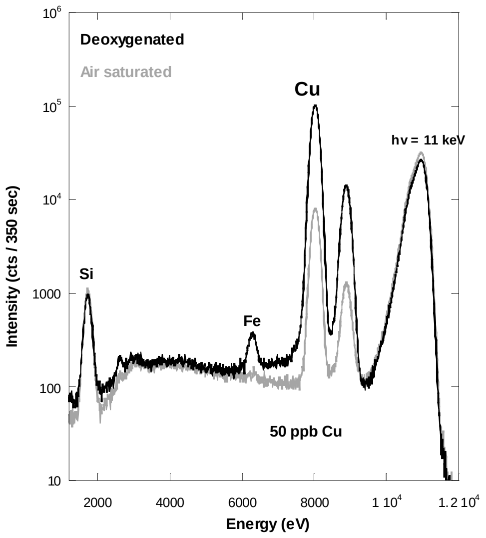

Fig. 2. TXRF spectrum of a silicon wafer after immersion into ultra pure water containing 50 ppb copper. The air saturated solution results in a smaller amount of deposited copper concentration as compared to the deoxygenated solution.