Investigation of Trace Metals Analyses of Dry Residue on Silicon Wafer Surfaces by TXRF and ICP-MS

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Abstract. TXRF, ICP-MS and SR-TXRF have been used for the quantification of trace metallic contaminants such as copper (Cu) and nickel (Ni) in dry spots of a NIST solution on a silicon wafer. It is found that the element combination influences the TXRF results in a dry residue. The results of Ni in a dry spot by TXRF can be well-quantified regardless of the surface concentration if the dry spot contains Ni, Cu, Ti and Ca. However, the Ni results can be suppressed by 50% if the dry spot contains 27 elements with 1 ng each. On the other hand, the Cu results can be suppressed by 15% to >50% depending on the elemental combination and concentration of the dry spots. Noticeably however, at lower concentration, e.g.0.05 ng Cu, the "lower-than-expected" phenomenon no longer exists. A further investigation of the analysis of dry spot by SR-TXRF has shown that the Cu result at level of E9 atoms/cm^2 can be well quantified.

Introduction

The method of VPD (vapor phase decomposition) has been widely used to collect contaminants on the wafer surface for later analysis by TXRF (total reflection x-ray fluorescence) or ICP-MS (inductively coupled plasma mass spectrometry). In the methods of VPD, a wafer is exposed to saturated HF vapor, which reacts with the surface native or thermal oxide. The silicon oxide is dissolved and the contaminants are collected by scanning the wafer surface with a droplet of solution (ultrapure water, diluted HF, HF/H_2O_2 or others). The droplet is either dried on the wafer surface for VPD-TXRF analysis or transferred into a sample vial for VPD-ICP-MS. Some quantification issues on VPD-TXRF have been discussed in previous reports, e.g. mass absorption effects [1,2], Calibration issues [3-5] and shadow effects [6]. This paper extended the discussion [7] of some issues concerning quantification of Cu and Ni using NIST standard solution dried on wafer surface.

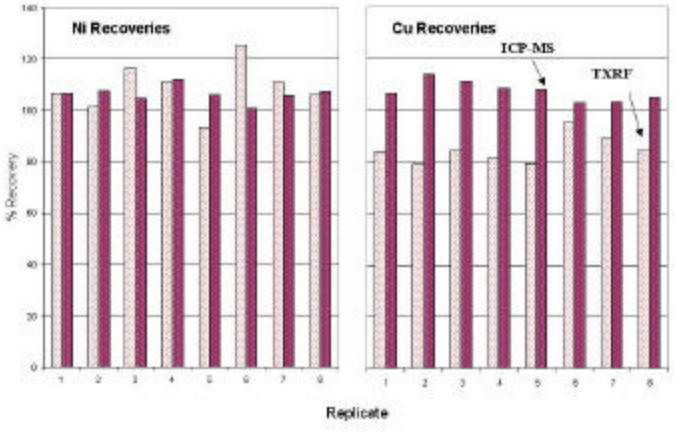

Figure 1. Recoveries of 1 ng Ni/Cu Solution studied with TXRF and ICP-MS

1. Recoveries of Ni and Cu in Dry Spots on wafer Surface by TXRF and ICP-MS

Solutions of Ni and Cu diluted from NIST standard solution with

1%HNO_3/1%HF were deposited and dried on a wafer surface under nitrogen purge. The dry spots were analyzed by TXRF (Atomika 8030W). After that, the dry spots were extracted twice with 0.5 mL solution of H_2O_2/HF. The extracted solutions were then analyzed by ICP-MS (PE 6000). Figure 1 shows recoveries of Ni and Cu by TXRF and ICP-MS. The recoveries are defined as the following: Ni TXRF recoveries = (TXRF results/2040E10)*100%; where 2040E10 atoms/cm^2 is the surface concentration of 1 ng Ni in a dry spot on a sampling area of 0.503 cm^2, *i.e.* 2040E10 = (1*10^{-9}*6.022E23)/(58.71*0.503). Cu TXRF recoveries = (TXRF results/1890E10)*100%. Ni/Cu recoveries for ICP-MS = (measurement of extracted solution from the dry spot/1 ng of Ni/Cu)*100%. As can be seen, the Ni results for TXRF as well as for ICP-MS show consistent recoveries of 100 ±10%. These results are similar to a current report [8]. In contrast, the Cu recoveries show ~ 80% by TXRF, ~100% by ICP-MS. By taking into account that both TXRF and ICP-MS have Ni recoveries near 100%, the possibility of missed location during TXRF measurement can be excluded. It was found that our finding from this work differs from a recent report, in which the results of Cr, Fe, Ni, Cu, and Zn by TXRF are all lower than that by ICP-MS [6]. One of the possibilities for the discrepancy may attribute to different drying conditions. For this work, the mixed Cu/Ni droplet was dried in a chamber at room temperature with nitrogen purge; while for that report, the mixed elements solution was dried by using an IR heat lamp. Nevertheless, the lower recovery of Cu by TXRF could be due to some unknown factors during the drying process.

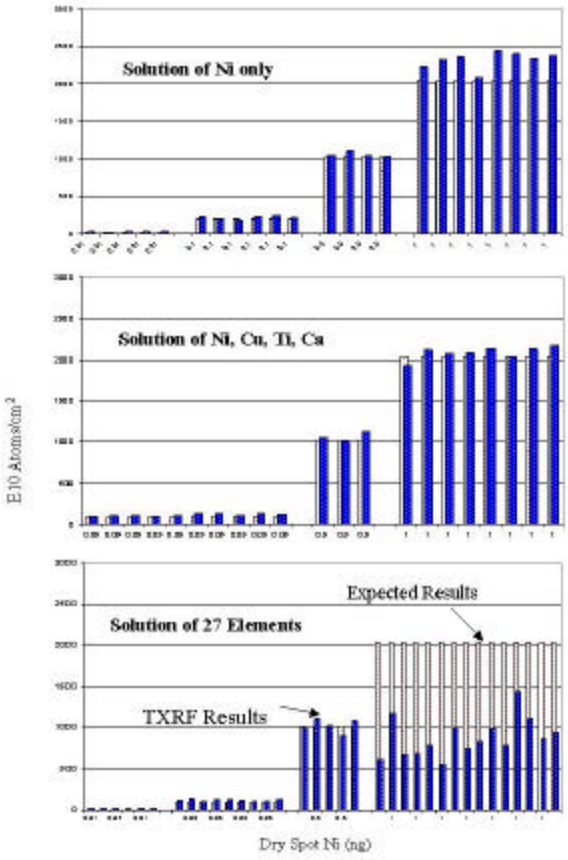

Figure 2. Ni TXRF Results of Dry Spots from Different Solutions

2. TXRF results in dry spots of Ni solution on the wafer surface

Figure 2 shows the Ni results in dry spots from different solutions. If a droplet of solution containing 1 ng Ni dried on a wafer surface, the expected results from the TXRF measurement should have a surface concentration of 2040E10 atoms/cm^2 (theoretical value) under a sampling area of 0.503 cm^2 of the detector. For solutions of Ni only and of Ni, Cu, Ti and Ca, the Ni results are close to what we expected regardless of the solution concentration and components. However, if the solution contains 27 elements (which cover a wide range of elements in the periodic table), the Ni results can be suppressed by 50% if the dry spot contains 1 ng each. The Ni results are found to be close to the expected value if the dry spot contains equal or less than 0.5 ng/each regardless of the solution components. It must be emphasized that in reality, a VPD droplet may not contain as many as 27 elements at all. The purpose of the example presented here is to raise an interesting question: what causes the signal suppression?

3. Dry spots of Cu solution on a wafer surface studied by TXRF:

It is found that in the TXRF analysis of Cu dry residue, the Cu results are usually lower than expected when the surface concentration of Cu was above a certain level. For example, a droplet containing 1 ng Cu dried on a wafer should have a surface concentration of 1890 E10 atoms/cm^2 (theoretical value) under a sampling area of 0.503 cm^2. However, an average of 1612 E10 atoms/cm^2 from five replicates was found from a Cu-only solution, indicating 15% lower than the theoretical result. For a solution of 27 elements, the Cu results can be suppressed by more than 50%. It is worth mentioning that at lower surface concentrations, e.g. for a dry spot of 0.05 ng Cu, this phenomenon no longer exists. It needs to be clarified that the analysis of a known amount of Cu (e.g. 1 ng Cu) in a single droplet on the wafer surface is similar to the one resulting from a VPD process. If

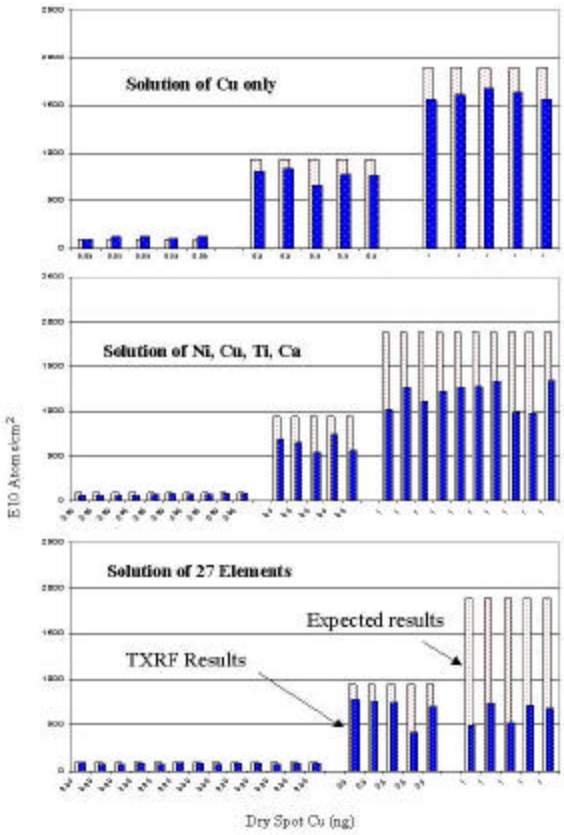

Figure 3. Cu TXRF Results of Dry Spots from Different Solutions

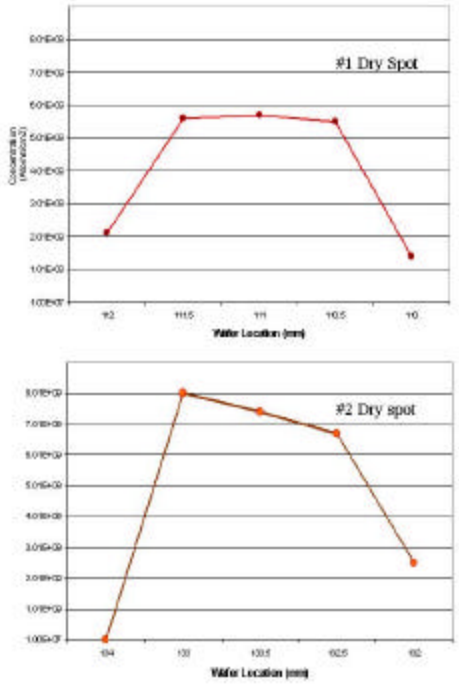

Figure 4. Cu surface concentration vs. SR-TXRF beam position scanned across the wafer in steps of 0.5mm

the spot of 1 ng Cu is originally from the entire 200-mm wafer surface as a result of the VPD process (with 5-mm edge exclusion), the resulting surface concentration would be 3.3E10 atoms/cm^2. This amount has been found to be a common range of Cu contamination on wafers. There are still some open questions on how Cu diffuses into Si substrate and how the drying process is influenced by the concentration of Cu. In addition, the assumption of formation of various micro-crystals or particulates, different compounds or islands of materials [1, 5, 6] during the drying process remains debatable.

4. Dry spots of Cu solution studied by SR-TXRF:

To quantify Cu at a very low concentration by SR-TXRF (Synchrotron Radiation TXRF), a droplet of 0.1 pg Cu in 0.1% HNO_3 (diluted from NIST standard solution) was deposited and dried on the wafer surface. The wafers were transferred to the Stanford Synchrotron Radiation Laboratory (SSRL) for SR-TXRF analysis within a wafer box sealed with cleanroom tapes. The surface concentration was

calculated based on a sampling area of 0.126 cm^2 of the detector. Thus the theoretical value of 0.1 pg Cu is 7.5 x 10^9 atoms/cm^2. Figure 4 shows the Cu surface concentration as a function of position as an area on the wafer is scanned through the SR-TXRF beam in steps of 0.5 mm. When the detector sampling area covers the entire dry spot, a maximum Cu intensity can be seen. When the detector sampling area covers only part of the dry spot, the Cu intensity decreases. Given the potential sources of error when working at these low concentrations, the theoretical value (7.5 x 10^9 atoms/cm^2) corresponds well to the measured value of 5.8 x 10^9 atoms/cm^2 in Figure 4. Another spot shows a result of 8.0 x 10^9 atoms/cm^2. It confirms that the quantification problem is no longer an issue if the surface concentration is at a low level.

5. Residue analysis after Cu removal studied by SR-TXRF:

A single droplet of 1 ng Cu was deposited and dried on the wafer surface. The surface concentration of this Cu dry spot was measured by TXRF. Similar to what was mentioned earlier, the result was found to be lower than the theoretical value. The surface of the wafer was then extracted with H_2O_2/HF by scanning the wafer surface using a Padscan instrument (Programmable Automatic Droplet Scanner) to remove Cu residue. The wafer surface was then rinsed with ultra pure water (UPW). It was found to be necessary that two marks by a marker pen be put on both sides (10 mm apart) of the residue in order to locate the spot. The mark ink contains high levels of Fe and Co, which can be used as an indicator for estimating the location of the drop on the wafer when the synchrotron x-ray beam is striking on the wafer. Figure 5 shows the concentrations of Cu, Fe and Co as a function of the wafer position in steps of 0.5 mm. The signals of Fe and Co increase as the x-ray beam moves towards the marker and excites the ink components. The maximum surface concentration of Cu was found to be 4E9 atoms/cm^2 after the Cu dry spot removal. It seems that although copper tends to diffuse into the Si substrate during the drying process, the copper residue can be completely removed after the H_2O_2/HF extraction because 4E9 is insignificant compared to a theoretical value of 7E13 atoms/cm^2 (*i.e.* 1 ng Cu on an area of 0.126 cm^2). The carryover is only 0.006% in this droplet study.

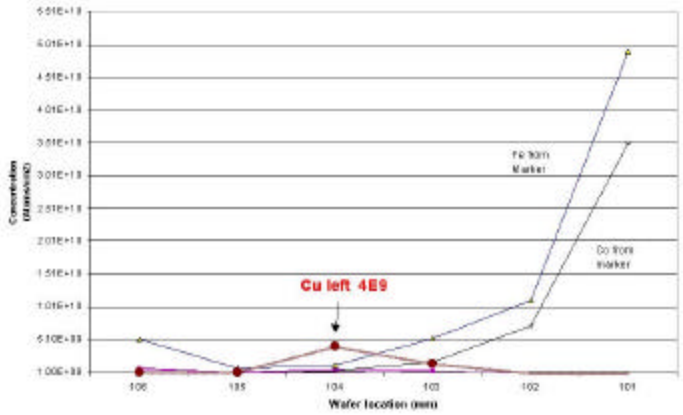

Figure 5. Cu surface concentrations vs. the SR-TXRF beam scanned across the wafer in steps of 0.5 mm.

Summary

We have studied the TXRF results of Ni and Cu when a droplet is dried on a wafer surface. We found that some elements (e.g. Ni, Cu) may have recovery problems above a certain concentration and under certain circumstances. Lower-than-expected results of Cu may contribute to diffusing to the Si substrate. It seems that although copper tends to diffuse into the Si substrate during the drying process, copper residue can be completely removed after H_2O_2/HF extraction. A further investigation is on the way to reveal the cause of lower-than-expected results of Ni and others. For example, TXRF measurement in a solution of 1 ng Ni + 100ng Al dried on the wafer surface show the Ni results are

close to the theoretical values. Similarly, TXRF measurement of a solution of 1 ng Ni + 100 ng Si does not show Ni signal suppression. It indicates that mass absorption or shadow effects may not be able to explain the signal suppression phenomena. More theories (e.g. catalytic behaviors, diffusion, etc.) and more experiments are needed to completely understand the effects of VPD-TXRF.

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