Quantification Issues for the Measurement of Copper on Silicon Wafer Surfaces

Jason Wang[1], Marjorie Balazs[1], Brian Tansy[2], Piero Pianetta[3], Katharina Baur[3] and Sean Brennan[3]
[1]Air Liquide Balazs Analytical Services, Fremont, CA
[2]SEH America, Vancouver, WA
[3]Stanford Synchrotron Radiation Laboratory (SSRL), Stanford University, Stanford, CA
jwang@Balazs.com

Abstract

With the increasing popularity of copper metallization for ultralarge scale integrated circuits (ULSI), copper (Cu) contamination on the silicon wafer has become a greater concern. Total Reflection X-ray Fluorescence (TXRF) and Vapor Phase Decomposition Inductively Coupled Plasma Mass Spectrometry (VPD-ICP-MS) have been widely used for measuring surface metal contamination. However, there are some issues on the quantification of Cu on the wafer surface.

It has been found that the TXRF results from the dry spots of NIST standard Cu solutions were lower than expected when Cu > 0.5ng (equivalent to ~1.8E10 atoms/cm^2 on a 200mm wafer). Multiple element solutions affect Cu results even more, ranging from 15% to 50%. By contrast, the quantification is no longer an issue if the surface concentration is at a low level, *e.g.* at or below 0.05ng [(1)].

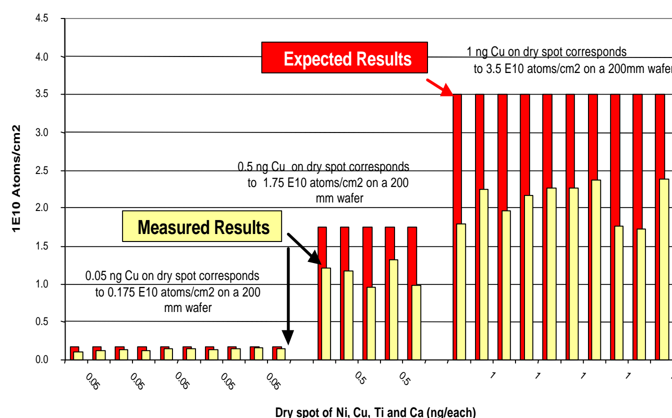
Our findings on spincoated wafers are similar to that on wafers dipped in a bath [(2)]. For the scanning solution after the VPD process, sufficiently high oxidizing power (e.g. high concentration of H_2O_2) is necessary to force the equilibrium of Cu/Cu^{2+} from the Si substrate to the solution so that the Cu on the wafer surface can be fully collected for analysis.

Copper Quantification by VPD-TXRF

In the VPD-TXRF method, a wafer is exposed to saturated HF vapor, which reacts with the surface native or thermal oxide (vapor phase decomposition). The matrix of silicon dioxide is removed by formation of SiF_4 (gas form). A liquid droplet is then pipetted onto the wafer surface and moved over the entire surface area of the wafer for VPD residue collection. If the VPD droplet is dried on the wafer surface, the resulting residue can be measured by TXRF. The sensitivity enhancement of VPD-TXRF over a TXRF direct measurement can be estimated from the ratio of the total wafer surface area (except edge exclusion) to the TXRF instrumental sampling area (corresponding to the solid angle of the detector). For a 200-mm wafer with 5-mm edge exclusion, the ratio of sensitivity enhancement by the VPD pre-concentration process will be 1:567. That is a dramatic increase in analytical capability.

In an earlier investigation, we found that the TXRF results from the dry spots of NIST standard Cu solutions were lower than expected when Cu ≥ 0.5 ng (equivalent to ~1.8E10 atoms/cm^2 on the entire surface of a 200mm wafer). Multiple element solutions affect Cu results more, ranging from 15% to 50% lower. The phenomenon of lower-than-expected results raises a quantification issue that the Cu contamination level may be underestimated if a VPD-TXRF method is used. There are still some open questions on how the drying process is influenced by the concentration of Cu and how Cu diffuses into the Si substrate. In addition, the assumption that various micro-crystals or particulates, different compounds or islands of materials form during the drying process remains debatable.

Cu TXRF Results on Dry Spots from Solutions of Ni, Cu, Ti & Ca on 200mm Wafer

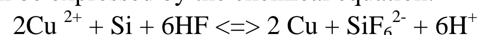


By contrast, the dry spots of NIST standard Cu solutions at and below 0.05 ng can be well quantified by TXRF. This can be further confirmed by measuring a dry spot of 0.0001 ng Cu (*i.e.* 0.1 pg) by SRTXRF (synchrotron radiation TXRF). The theoretical value is 7.5 x 10^9 atoms/cm^2 using the 0.126cm^2 sampling area of the SRTXRF instrument. The results from two measurements turn out to be 5.8 x 10^9 and 8.0 x 10^9 atoms/cm^2, respectively. Given the potential sources of error when working at these low concentrations, the SRTXRF results are well matched to the theoretical value. It confirms that the quantification is no longer an issue if the surface concentration is at a low level.

Copper Quantification by VPD-ICP-MS

In the VPD-ICP-MS method, the wafer is exposed to saturated HF vapor. A droplet of solution scans the wafer surface and then is transferred into a sample vial for elemental analysis by ICP-MS. One of the advantages of VPD-ICP-MS is that a wide range of elements in the periodic table from Li to U can be analyzed at one time.

It has been well known that Cu ions present in aqueous HF solutions intend to adsorb on a Si wafer surface in the form of a metallic particles [(3)]. This electrochemical process can be expressed by the chemical equation:



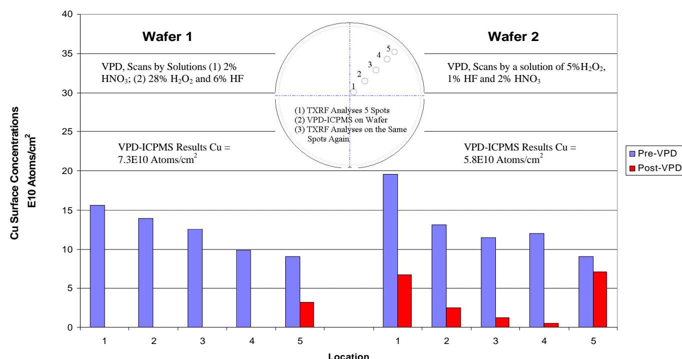
$$2Cu^{2+} + Si + 6HF \Leftrightarrow 2\,Cu + SiF_6^{2-} + 6H^+$$

This is because Cu^{2+} ion has a higher redox potential than Si does. The Cu^{2+} ion can take electrons from Si and be reduced to metallic Cu. Si releases electrons and is oxidized to become SiO_2 although this mechanism may not explain exactly how the chemical reaction of Si oxidation takes place.

A recent publication has also revealed that during wafer rinsing with UPW (ultra pure water), 10-20nm diameter Cu particles were formed by reductive deposition of ionic species to the metallic form, which was enhanced under deoxygenated conditions. On the other hand, dissolved oxygen favors the formation of an oxide layer at the Si surface and includes metal contamination into the oxide layer [(4)]. In other words, Cu may be included in the silicon oxide layer, or may be deposited on the silicon substrate, depending upon the chemical processes.

As shown in the figure below, two spin-coated wafers were measured from the center to near the edge at 5 locations by TXRF. Each bar represents the Cu surface concentration at each location. After the VPD process, the wafer on the right (*i.e.* wafer 2) was scanned by a solution of 5% H_2O_2+1%HF+2%HNO_3 to collect Cu. The wafer on the left (*i.e.* wafer 1) was scanned by a solution of 28%H_2O_2+6%HF. Then, these two wafers were measured at the same 5 locations again by TXRF. The darker bars clearly show some Cu left on the wafer surface after scanning by the solution of 5% H_2O_2+ 1%HF +2%HNO_3. However, very little Cu was left on the wafer (*i.e.* wafer 1) after scanning by the solution of 28%H_2O_2+6%HF.

Cu Results of Spincoated Wafers by TXRF



The Cu collection efficiencies are based on the ratio of the remaining Cu fractions after VPD droplet scanning versus the initial contamination level. The Cu collection process can be considered as an equilibrium between adsorbing and collecting of Cu. It has been reported [(2)] that sufficiently high oxidation power (e.g. high concentration of H_2O_2) is necessary to force the equilibrium of Cu/Cu^{2+} from the Si substrate to solution for a wafer dipped in a diluted HF bath contaminated with Cu. Thus, the collection efficiencies are influenced to a great degree if different scanning droplets with different compositions are used. For example, a variety of collecting solutions have been used for collecting metallic contaminants including Cu in an international round robin test in 1998. The collecting solutions include 2%HF + 2%H_2O_2, 5%HF + 6%H_2O_2, 20%HF+ 2%H_2O_2, 15%HF+ 25%HNO_3, 15%HCl+3%H_2O_2, 5%HCl + 5%H_2O_2, 2%HF + 5%HNO_3 + 5%HCl, 6%HF + 28%H_2O_2 and so on. The Cu results by VPD-TXRF and VPD-ICP-MS were found to be considerably different in the samples tested from 28 participants. The reason for that may, in part, be due to the different collecting solutions, as discussed above.

Conclusions

We found that (1) the TXRF results from the dry spots of NIST standard Cu solutions were lower than expected when Cu ≥ 0.5ng (equivalent to ~1.8E10 atoms/cm^2 on a 200mm wafer). (2) Multiple element solutions affect Cu results more. (3) Cu can be well quantified at level of 0.05 ng (equivalent to 2E9 atoms/cm^2 on 200mm wafer) or lower by TXRF or SRTXRF. The reason for the phenomenon remains debatable.

Our findings on a spincoated wafer are similar to that on a wafer dipped in a bath. In order to fully collect Cu from wafer surface, the scanning solution after the VPD process must have a sufficiently high oxidation power (e.g. high concentration of H_2O_2) to force the equilibrium of Cu/Cu^{2+} from the Si substrate to the solution.

References

(1) J. Wang, M. Balazs, P. Pianetta, K. Baur and S. Brennan, Ultra Clean Processing of Silicon Surfaces (UCPSS 2000), Ostend, Belgium.

(2) S. De Grndt, A. Huber, B. Onsia, S. Arnauts, K. Kenis, D.M. Knotter, P.W. Mertens and M.M. Heyns, Ultra Clean Processing of Silicon Surfaces (UCPSS 1998), p93-96.

(3) H. Morinaga, M. Suyama and T. Ohmi, J. Eletrochem. Soc. Vol 141, 2834, 1994.

(4) T. Homma, J. Tsukano, T. Osaka, M. Watantsu and K. Nagai, Procedings of 6th symposium on high purity Si, Electrochem. Soc Proceeding, Vol 00-17, 670, 2000.