Analytical Techniques for Trace Elemental Analyses on Wafer Surfaces for Monitoring and Controlling Contamination

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Abstract

Direct measurement of trace elements on wafer surfaces by TXRF is quick and non-destructive. SR-TXRF has similar features to TXRF, but much better detection limits mainly due to the high flux. VPD-TXRF and VPD-SR-TXRF improve the detection capability to various degrees. However, some elements (e.g. Cu) may have recovery problems at certain concentrations. VPD-ICP-MS is a destructive technique because of dissolving native oxide, but it can analyze most of elements in the periodic table and especially well for low Z elements. By using NIST standards for calibration, quantification can be verified relatively easily. All of these techniques can be complementary to each other and provide comprehensive analyses for the semiconductor industry.

Introduction

Ultra-clean Si wafer surfaces are one of the most critical factors to the ULSI manufacturing because the uncontrolled contamination during the wafer processing can change the electrical characteristics, resulting in yield loss [1]. Metallic impurities at certain concentrations on wafer surfaces can cause serious device degradation such as diminished carrier lifetimes, dielectric breakdown of gate oxides, threshold voltage shift and leakage current of P-N junction. Sources of trace metal contamination include processing chemicals used during cleaning, stripping, photolithography, and deposition; processing equipment (furnaces, reactors, implanters); and wafer handling. Current methods for metal analyses on wafer surfaces include total reflection x-ray fluorescence (TXRF) [2-7], vapor phase decomposition total reflection x-ray fluorescence (VPD-TXRF) [8-11], vapor phase decomposition inductively coupled plasma mass spectrometry (VPD-ICP-MS) [12,13] and synchrotron radiation total reflection x-ray fluorescence (SR-TXRF) [14,15].

In TXRF analysis, x-rays at an incidence angle below the critical angle strike on the highly polished silicon surface and are reflected in a manner similar to the total reflection of visible light from a mirror surface. Under this condition, the penetration

depth can be restricted to a few nano-meters, leading to a substantially reduced background signal compared to conventional XRF. The excited fluorescence signals of the contaminants are emitted from the wafer surface and detected by an energy dispersive, Si(Li) solid state detector.

Using synchrotron radiation (SR) as a primary excitation source can increase the overall sensitivity of TXRF. Compared to regular x-ray sources produced by electron bombarding on metal targets, synchrotron radiation is produced as a natural byproduct of circulating or oscillating electrons in a storage ring. It contains all the wavelengths of the electromagnetic spectrum and is 100 or more times powerful than a x-ray generator of the standard instrument. Primary excitation source of synchrotron radiation has several advantages over a conventional x-ray tube: The high incidental flux combined with low divergence results in higher fluorescence intensities and so lower detection limits. Due to its linear polarization, the elastic scattering of the incoming beam can be reduced. The spectral background, which is already reduced by total reflection, is lowered further. The tunability of synchrotron radiation allows improving the sensitivity for special elements by increasing the photon absorption cross-section.

In the methods of VPD-ICP-MS or VPD-TXRF, 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. The droplet is transferred either automatically (by an instrument) or manually into a sample vial for elemental analysis by ICP-MS. In ICP-MS analysis, solutions are nebulized into an argon plasma. The contaminants dissolved in the solutions are vaporized, atomized, ionized and extracted into a mass spectrometer for analysis. During the past 17 years, ICP-MS has been developed to a mature technique for many applications. 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. The disadvantage of the VPD preparation is the tedious procedure of collecting the reaction products on the wafer surface.

If the VPD droplet dries on the wafer surface, the resulting residue can be measured by TXRF. The sensitivity enhancement of VPD-TXRF over TXRF direct measurement can be estimated from the ratio of the total wafer surface area (except edge exclusion) to the instrumental sampling area (corresponding to the solid angle of instrument detector). For example, a 200-mm wafer with 5-mm edge exclusion has a total surface area of 283.5 cm^2. The sampling area is 0.5 cm^2 for an Atomika TXRF 8030W, and is 0.126 cm^2 for the SR-TXRF at SSRL. The ratio of sensitivity enhancement by this pre-concentration process will be 1:567 and 1:2250, respectively. Although the VPD process loses the spatial contamination information because contamination from the entire wafer surface are collected, it may be advantageous since it integrates all contaminants into one residual droplet, thereby reducing the numbers of TXRF analysis spots on the wafer surface. Figure 1 shows a summary of detection limits of TXRF, VPD-TXRF, VPD-ICP-MS and SR-TXRF. Table 1 lists their advantages and disadvantages.

Copper (Cu) has been well known for its high diffusivity and solubility in silicon bulk. Copper contamination could cause gate oxide integrity degradation, premature breakdown and P-N junction leakage. Trace amounts of copper could be introduced into silicon wafers during the thermal processing, wet cleaning or other steps of silicon fabrication [16]. In addition, new copper interconnection processes introduce greater potential for copper contamination by diffusion, migration from the backside of the wafer and by cross contamination (airborne or wafer handling) to copper sensitive processes. This paper will give a comparison of TXRF, SR-TXRF and VPD by applying these techniques on the analysis of a Cu droplet residue on a Si wafer surface. In addition, issues associated with the quantification of Cu will be discussed.

	Advantage		Disadvantage	
TXRF	Capable of Mapping Minimum matrix effect	Non-destructive	Low Z Elements Na, Mg, Al difficult, Li, Be, B not available	
	DL = ~10^{10} atoms/cm^2			
VPD-TXRF	Some DL's are lower than VPD-ICP-MS	Cl, Br, S can be measured	Low Z Elements Na, Mg, Al difficult, Li, Be, B not available Lose local contamination information	Des-tructive
	DL = ~10^8 - 10^{10}atoms/cm^2		Tedious procedure; Drying conditions critical and some problems with quantification	
VPD-ICP-MS	A wide range of elements from Li to U can be analyzed. Very sensitive for Na, Mg, Al, Li, Be, also B, P.	Cl, Br, S not available	Tedious procedure; Lose local contamination information; must consider matrix effects	Des-tructive
	DL = ~10^8 -10^{10}atoms/cm^2			
SR-TXRF	Lowest DL for direct measurement Capable of Mapping; Minimum matrix effect; Energy tunable for special applications	Non-destructive	Instrumentation cost very high and not easily available	
	DL = ~10^8 atoms/cm^2	Cl, Br, S can be measured		

Table 1. Comparison of TXRF, VPD-ICP-MS, VPD-TXRF and SR-TXRF. DL's for VPD-ICP-MS and VPD-TXRF are based on 200-mm wafers

Experimental

Wafer preparation and analyses by VPD-TXRF and VPD-ICP-MS were performed in an ultra clean environment in a cleanroom. After depositing a known amount of Cu solution (e.g. 50 µL) on a bare Si wafer surface, the size of the droplet was found to be 4-5 mm in diameter. After drying at room temperature within a clean box with nitrogen purge, the size of the dry spot decreased to less than 1 mm in diameter. The dry spot on the wafer was then analyzed by a TXRF instrument (Atomika 8030W). The surface concentration was calculated based on a sampling area of 0.5 cm^2. A standard wafer with a Ni dry spot on the wafer surface provided by the TXRF manufacturer was used to calibrate the instrument. Standard procedures were used to ensure the

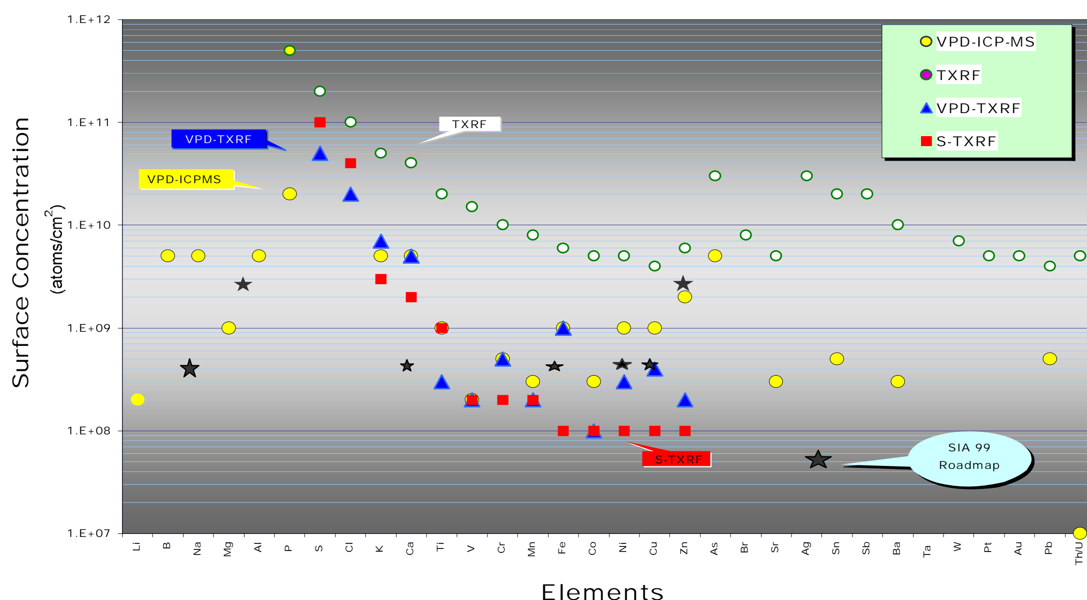

Figure 1. Detection limits of TXRF, VPD-ICP-MS, VPD-TXRF and SR-TXRF on 200 mm Si wafer. (DL's for TXRF are based on the instrument detection limits from Atomika; DL's for VPD-ICP-MS are based on the routinely reporting detection limits from Balazs Analytical Lab; DL's for VPD-TXRF are based on the measurements of 13 dry spots of diluted HF on a clean wafer and their standard deviation multiplied by 3 at Balazs Analytical Lab; DL's of SR-TXRF are estimated based on the findings from SSRL)

reproducibility for all analyses.

Synchrotron radiation SR-TXRF experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) at a horizontally focussed wiggler beamline (6-2) using a double multilayer monochromator. The surface concentration was calculated based on a sampling area of 0.126 cm^2. Experimental conditions can be found in reference 14.

Discussion

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

A single droplet of copper (Cu) solution was dried on a wafer surface. It was found that in the analysis of Cu dry residue by TXRF, the results of Cu usually were lower than expected when the surface concentration of Cu was above a certain concentration. For example, a single droplet containing 1 ng Cu deposited on a wafer should have a surface concentration of 1890 E10 atoms/cm^2 (theoretical value) under a sampling area 0.5 cm^2. However, an average of 1612 E10 atoms/cm^2 from five replicates was found, indicating 15% lower than the theoretical result, as shown in figure 2. Similarly, a single droplet of 0.5 ng Cu deposited on the wafer surface should result in a surface concentration of 940 E10 atoms/cm^2. An average of 767 E10 atoms/cm^2 indicates 18% lower than the theoretical results. It is worth noting 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

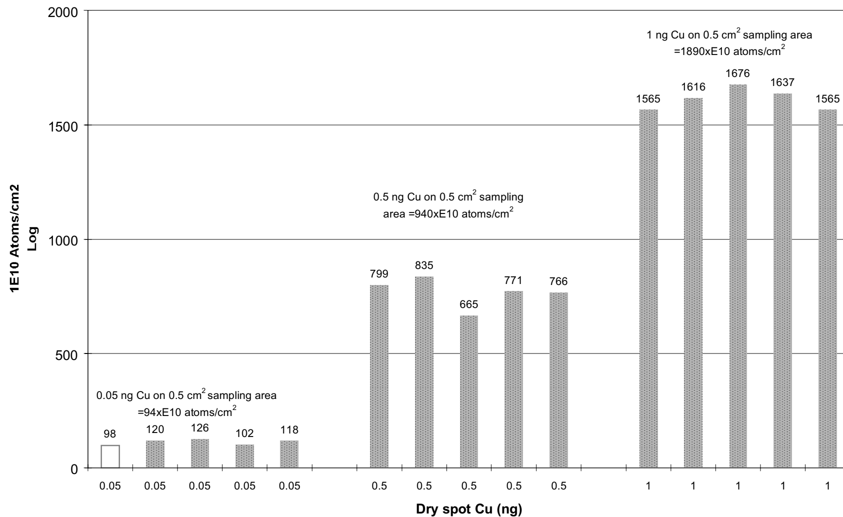

Figure 2. Cu result of TXRF vs. calculated surface concentration on Cu dry residue. The calculation is based on 0.5 cm^2 sampling area; each bar represents a dry residue analysis on the wafer surface. Average of 1612 E10 atoms/cm^2 for 1 ng Cu dry spot and average of 767E10 atoms/cm2 for 0.5 ng Cu dry spot were found from 5 replicates.

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 the spot of 1 ng Cu was equally distributed onto the entire 200-mm wafer surface as a reverse 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 [10,11,17] during the drying process remains debatable.

2. Dry spots of Cu/Ni solution on wafer surface by TXRF and ICP-MS:

For further investigation, a droplet of Cu/Ni mixed solution was deposited on a wafer surface. The dry spot was analyzed by TXRF. Then the dry spot was extracted twice with 0.5 mL solution of H_2O_2/HF. The extracted solutions were analyzed by ICP-MS. Figure 3a shows Cu recoveries by TXRF and ICP-MS. The Cu results of ICP-MS show consistent recoveries 100% ±10%. By contrast, the Cu recoveries of TXRF show ~ 80%. By taking into account that both TXRF and ICP-MS have Ni recoveries near 100%, as seen in figure 3b, the possibility of mis-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[17]. One of the possibilities for the discrepancy may attribute to different drying conditions. The mixed Cu/Ni droplet was dried in a chamber

at room temperature with nitrogen purge for this work; while the mixed elements solution was dried by using an IR heat lamp from that report. Nevertheless, the lower recovery of Cu by TXRF could be due to some unknown factors during the drying process. A detailed investigation is on the way.

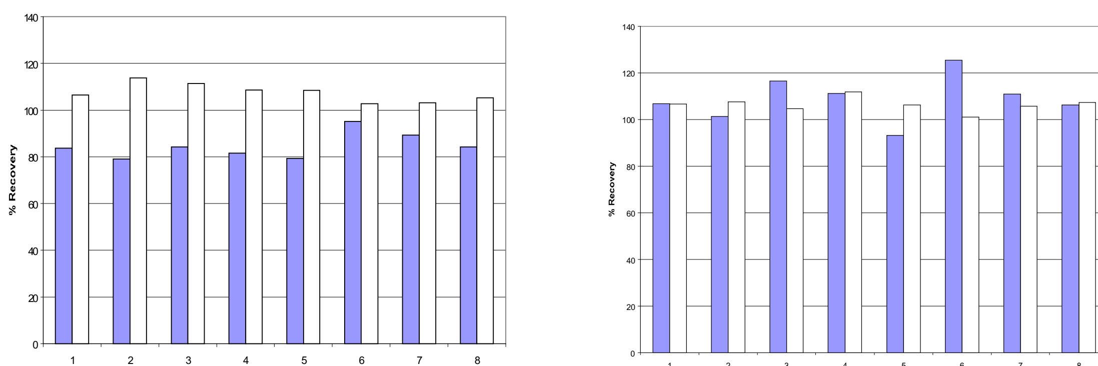

Figure 3. Recoveries of (a) Cu (left) and (b) Ni (right) by TXRF (dot bars) and ICP-MS (empty bars). Numbers on the x-axis represent results from replicate dry spots. A droplet of solution containing 1 ng of both Ni and Cu (diluted from NIST stock solution) was dried on the wafer surface and analyzed by TXRF. The dried spots were then extracted into a solution of H_2O_2/HF and analyzed by ICP-MS. The recovery is based on the analytical results vs. known 1 ng of Cu and Ni.

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

To quantify Cu at very low concentration by SR-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 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. Thus theoretical value of 0.1 pg Cu is 7.5 x 10^9 atoms/cm^2. Figure 4a shows that the Cu signal is plotted as a function of position vs. surface concentration as an area on the wafer is scanned through the SR-TXRF beam in steps of 0.5 mm. When the detector sampling area

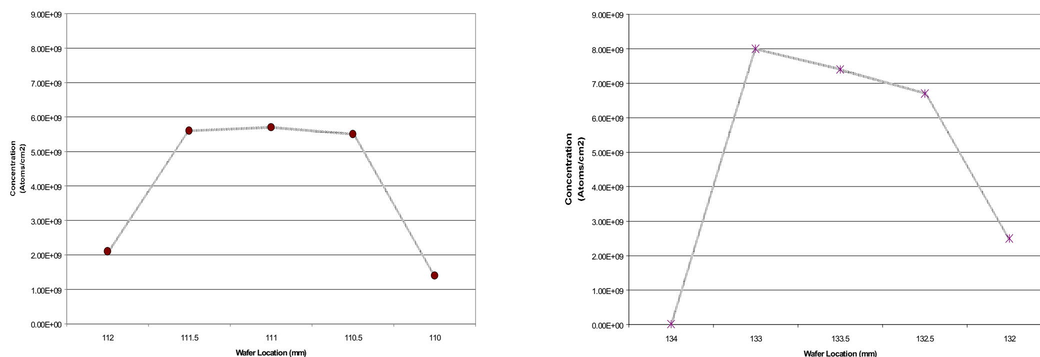

Figure 4a (left) and b (right): Cu surface concentration vs. the SR-TXRF beam position scanned across the wafer in steps of 0.5 mm.

covers 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 4a. Another spot shows a result of 8.0 x 10^9 atoms/cm^2 in Figure 4b. This provides an independent verification of the system calibration. It also confirms that the quantification problem is no longer an issue if the surface concentration is at a low level.

4. 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 the 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

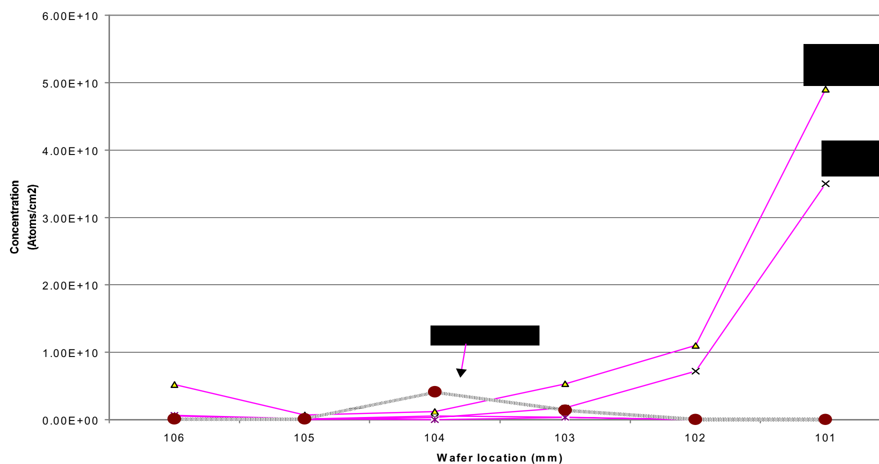

Figure 5. Cu, Ni and Co surface concentrations vs. the SR-TXRF beam scanned across the wafer in steps of 0.5 mm.

of the wafer was then extracted with H_2O_2/HF by scanning the wafer surface using a Padscan instrument (Programmable Automatic Droplet Scanner) for removing Cu residue. The wafer surface was then rinsed with ultra pure water (UPW). At that time, the resulting spot after Cu removal by H_2O_2/HF could barely be seen by eyes. It was found to be necessary that two marks by a marker pen be put on the both sides (10 mm apart) of the residue in order to locate the spot. The mark ink contains high levels of Fe and Co can be used as an indicator for estimating the location of the drop when the synchrotron x-ray beam is striking on the wafer.

Figure 5 shows the concentrations of Cu, Fe and Co plotted 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 to the marker and excites the ink materials. The maximum surface concentration of Cu was found to be 4E9 atoms/cm^2. It seems that even copper diffuses into Si substrate during the drying process, copper residue can be completely removed after H_2O_2/HF extraction because 4E9 is insignificant compared to a theoretical value of 7 E13 atoms/cm^2 (*i.e.* 1 ng Cu on an area of 0.126 cm^2). Carryover is only 0.006% by calculation in this droplet study.

Summary

We have made a comparison of TXRF, SR-TXRF, ICP-MS and VPD techniques to study the Cu concentration when a droplet is dried on a wafer surface. In general, direct measurement of trace elements on wafer surface by TXRF is quick and non-destructive. SR-TXRF has similar features to TXRF, but much better detection limits mainly due to the high flux. Measurement for low Z elements by TXRF and SR-TXRF are improving but are still in a developing process at the present time. VPD-TXRF and VPD-SR-TXRF improve the detection capability to various degrees. However, we found that some elements (e.g. Cu) may have recovery problems above a certain concentration. It is worth mentioning that many investigations have been conducted on detection limits on wafer surfaces by TXRF, but only a few have assessed recoveries. Therefore many issues concerning the quantification are still unknown. On the other hand, VPD-ICP-MS is a destructive technique because of dissolving the native oxide on wafers, but it can analyze most of the elements in the periodic table and especially well for low Z elements, e.g. B Na, Mg and Al. By using NIST standards for calibration, quantification can be verified relatively easily. All of these techniques can be complementary to each other and provide comprehensive analyses for the semiconductor industry.

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