How Low Can the Detection Limit Go With VPD-TXRF?

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Abstract

The detection limit for synchrotron radiation total reflection x-ray fluorescence (SRTXRF) that can routinely be achieved for transition metals is about 8E7 atoms/cm^2 for a standard 1000 second counting time. Theoretically, the SRTXRF detection limit of 8E7 atoms/cm^2 could be further reduced to 3.6E4 atoms/cm^2 by using a pre-concentration process such as vapor phase decomposition (VPD). In VPD process, the contaminants on the wafer surface will be collected into a single droplet and the droplet will be dried on the wafer surface for TXRF analysis. During the process, however, impurities in the UPW (ultra pure water), chemicals or from handling cannot be ignored. Our investigation of wafers subjected to different cleaning processes has revealed that background signals on the dry spot could arise from the VPD process itself. Therefore, the baseline determined by the purity of the UPW and starting chemicals limits the detection limits of VPD-SRTXRF.

Introduction

Metallic contaminants 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. As the feature size of the ULSI continues shrinking, cleaner and cleaner wafer surface is demanded and lower and lower detection limits of the analytical techniques are required.

The detection limit for synchrotron radiation total reflection x-ray fluorescence (SRTXRF) that can routinely be achieved for transition metals is about 8E7 atoms/cm^2 for a standard 1000 second counting time [2]. The detection limits can be further improved by combining SRTXRF and VPD (vapor phase decomposition) technique [3,4]. In the VPD process, 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 (e.g. ultrapure water, diluted HF, HF/H_2O_2 or others). The droplet can be dried on the

wafer surface for TXRF or SRTXRF analyses. Because the VPD process pre-concentrates the contaminants from the entire wafer surface onto a single dry spot, the sensitivity enhancement of VPD-TXRF over TXRF is estimated from the ratio of the total wafer surface area to the instrumental sampling area on the wafer. For example, a 200mm wafer with 5mm-edge exclusion has a total surface area of 283.5 cm^2. Assuming a sampling area of 0.126 cm^2 for the SRTXRF instrument at the Stanford Synchrotron Radiation Laboratory (SSRL) the gain in sensitivity for the VPD-SRTXRF technique will be 2250. This means, theoretically, that the SRTXRF detection limit of 8E7 atoms/cm^2 could be further reduced to 3.6E4 atoms/cm^2 (8E7/2250) by applying the VPD technique. During the VPD process, however, impurities in the UPW (ultra pure water), chemicals or from handling cannot be ignored. In this paper, an investigation of wafers subjected to different cleaning processes has revealed that background signals on the dry spot could arise from the VPD process itself. Therefore, the baseline determined by the purity of the UPW and starting chemicals or perhaps some other factors limits the detection limits of VPD-SRTXRF. The detection limits based on the dry spot on the wafer surface after VPD process are estimated. Some potential sources of contaminants are discussed.

Experimental

Four wafers were shipped from Lucent Technologies, Murray Hill, New Jersey. Wafer #1 was used as a control. The control wafer was from the same source as others but did not go through any cleaning process. Wafer #2 went through PCL/HF cleaning (Piranha followed by HF cleaning). Both wafers #3 and #4 went through RCA cleaning; All of these wafers were prepared by VPD, droplet scanning and drying under a class 10 mini-environment within a class 100 cleanroom (ISO 5). The preparation procedures are listed below:

(1) Wafer #1 (control): VPD was performed. The wafer surface was scanned by a droplet of solution of HF/H_2O_2 for collecting contaminants. Then the droplet was dried on the wafer surface under nitrogen purge at room temperature.

(2) Wafer #2 (PCL/HF cleaning): The same process as wafer #1 was performed.

(3) Wafer #3 (RCA cleaning): The same process as wafer #1 was performed.

(4) Wafer #4 (RCA cleaning): First, a VPD process was performed. The wafer surface was scanned by a droplet of HF/H_2O_2 solution. Then the scanning solution was removed and discarded. After that, a VPD was carried out a second time on the same wafer and the wafer

surface was then scanned by a droplet of solution of HF/H_2O_2 for collecting contaminants. The droplet was dried on the wafer surface under nitrogen purge at room temperature.

All wafers were placed in a wafer cassette sealed with cleanroom tape and were shipped to Stanford Synchrotron Radiation Laboratory (SSRL) for SRTXRF analyses at a focussed wiggler beamline (6-2) using a double-reflection multilayer monochromator.

Results and Discussion

Figure 1 shows spot surface concentrations of 6 transition metals, *i.e.* chromium (Cr), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn), vs. SRTXRF beam position as it scanned across the wafer. The spot surface concentrations are defined as the number of transition metal atoms on an area of 0.126 cm^2 (*i.e.* sampling area of instrument detector). When the x-ray beam/detector sampling area is moving close to the dry spot, signal intensity increases. When the x-ray beam/detector sampling area covers the entire dry spot, a maximum intensity is reached.

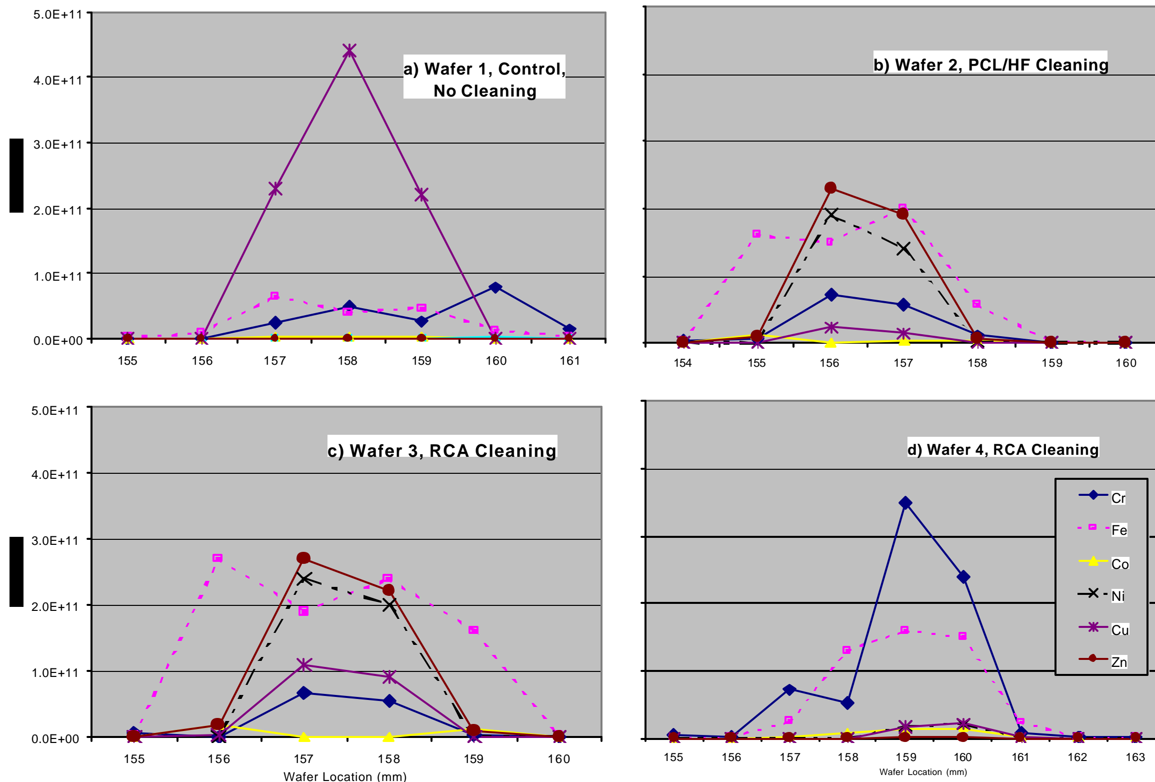

Figure 1. Spot surface concentrations of 6 metals vs. SRTXRF beam position scanned across the wafer. When the x-ray beam/detector sampling area is moving close to the dry spot, signal intensity increases. After reaching a maximum, the signal intensity decreases when the x-ray beam/detector sampling area is moving away from the dry spot. The spot surface concentrations are defined as the number of contaminant atoms on an area of 0.126 cm^2.

The signal intensity decreases when the x-ray beam /detector sampling area is moving away from the dry spot. As mentioned earlier, both wafers #3 and #4 went through RCA cleaning. The surface contamination on these two wafers should be similar. However because first VPD was performed on wafer #4 and the HF/H_2O_2 scanning solution was discarded, most of the contaminants on the wafer surface are probably removed. The wafer becomes cleaner, thus SRTXRF result of wafer #4 from the second VPD dry spot is expected to be lower, compared to that of wafer #3, on which VPD and droplet scanning was performed only once. As can be seen from signals of wafers #3 (figure 1c) and #4 (figure 1d), it is true for Zn, Cu and Ni because results of wafer #4 are lower than that of wafer #3. But it is untrue for Cr because the result of Cr from wafer 4# is even higher than that of wafer #3. Furthermore, SRTXRF results of wafer #2 (figure 1b) are similar to that of wafer #3, but higher than that of wafer #1 (control, figure 1a) except Cu. It seems that Cu has been significantly reduced during either RCA or PCL/HF cleaning process. However, some contaminants are either unchanged (e.g. Co) or increased (*e.g.* Fe and Cr) after VPD and droplet scanning. Based on the above discussion, it is believed that some contaminants (*e.g.* Cr and Fe) may have been introduced onto the dry spot during the VPD and droplet scanning process.

It should be noted that the spot surface concentration (*i.e.* Fe, ~5E10 atoms/cm^2 in figure 1a) is calculated based on the dry spot within the detector sampling area of 0.126 cm^2. If this spot surface concentration converts to entire wafer surface area, the level of Fe contamination would be negligible. For example, Fe spot surface concentration of 5E10 atoms/cm^2 on wafer #1 can be converted to 2.2E7 atoms/cm^2 on an entire 200mm wafer: (5E10 atoms/cm^2 * 0.126 cm^2)/ 283.5 cm^2 = 2.2E7 atoms/cm^2. Notice that the surface concentration of 2.2E7 atoms/cm^2 is well below the detection limit of SRTXRF for a 1000-second counting time (*i.e.* 8E7 atoms/cm^2). In other words, Fe on wafer #1 can not be detected at all by SRTXRF without a VPD process. This is a good example to demonstrate the benefit of VPD-SRTXRF.

Some potential contamination sources during VPD process are listed below:

1. Contaminants contributed to the droplet by ultra pure water (UPW) and chemicals

During the VPD process, 100 µL (~0.1g) of HF/H_2O_2 solution was used to scan the wafer surface. The total weight of Fe in a dry spot (*e.g* wafer #1, figure 1a) will be: (5E10x0.126x58.85)/6.022E23 = 6.2×10^{-13} g, where 6.022E23 atoms/mole is Avogadro's

number; 58.85 is atomic weight of Fe; 0.126 cm^2 is the sampling area of SRTXRF. The Fe concentration in 100 µL of solution would be $6.2x10^{-13}$ g/0.1g = 6.2 part per trillion (ppt). Based on our knowledge, 10 part per trillion Fe (or other contaminants) is possible in both chemicals and ultra pure water. In fact, a solution containing contaminant below 10 ppt is considered to be extremely clean. The amount in the solution, however, is generally below the method detection limit (MDL) by inductively coupled plasma mass spectrometry (ICP-MS) for UPW and definitely below the MDL for chemicals. Therefore, if the scanning solution contains 6.2 ppt Fe, the result of SRTXRF on the dry spot will show 5E10 atoms/cm^2.

2. Contaminants contributed to the droplet by particles

If particles land on wafer surface during shipping or sample preparation, since no particle measurement are done before sample preparation, these particles would be included in the results and could affect the detection limit. For example, based on a calculation, five 1-µm particles would generate 6.3 part per trillion (ppt) to the droplet and the dry spot would be equivalent to 5E10 atoms/cm^2 as discussed earlier. The results would essentially be the same if these were ten 0.5-µm or even twenty 0.25-µm particles. Without particle measurement on the wafer before sample preparation, the added concentration is an unknown value.

3. Contaminants contributed to the droplet from wafer itself

If a 200mm wafer contains 2.2xE7 atoms/cm^2 Fe, and if the contamination from the solution or from handling are negligible, after VPD, the dry spot will have a spot surface concentration of 5E10 atoms/cm^2 because of a pre-concentration factor of 283.5cm/0.126cm. However, do we really know if a wafer contains Fe at 2.2*E7 atoms/cm^2 or less? Present techniques may not be able to give a certain answer. But one thing we are quite sure of is that we do not have an absolutely clean wafer. Certainly if we have a cleaner wafer to start with, we may be able to get a better detection limit.

Estimate detection limits

Since we do not know if the Fe result of 5E10 atoms/cm^2 comes from wafer itself, or from other sources, there is a limitation on the detection limit of VPD-TXRF or VPD-SRTXRF. The

limitation is due to the fact that some contamination sources may contribute to the dry spot during VPD and droplet scanning process. Thus, detection limits can be estimated by choosing

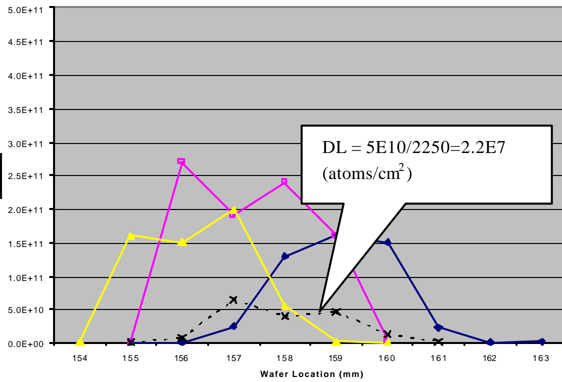

Figure 2. Spot surface concentration of Fe from different cleaning processes vs. SRTXRF beam position scanned across the wafer

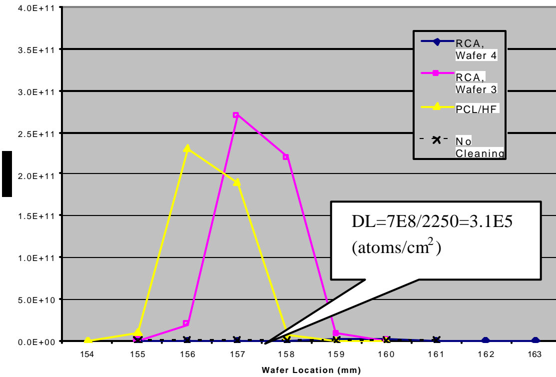

Figure 3. Spot surface concentration of Zn from different cleaning processes vs. SRTXRF beam position scanned across the wafer

the lowest blank level from the results of 4 wafers then divided by a pre-concentration factor of 2250. For example, Fe results from 4 wafers subjected to different cleaning processes are compared as shown in figure 2, the lowest Fe spot concentration is found to be 5E10 atoms/cm^2. A detection limit of 2.2E7 atoms/cm^2 can be obtained from 5E10 divided by 2250. In the same way, the detection limit for Zn is found to be 3.1E5 atoms/cm^2 as shown in figure 3. Estimated detection limits for 6 transition metals are listed in table 1.

Metals	Fe	Cu	Ni	Cr	Co	Zn
DL (atoms/cm^2)	2.2E7	9.8E6	6.7E5	2.7E7	1.2E5	3.1E5

Table 1 . Estimated detection limits of VPD-SRTXRF

Conclusion

The VPD-SRTXRF technique can improve detection limits for metals on wafers by 2-3 orders of magnitudes because of a pre-concentration process such as VPD. However, impurities in the UPW (ultra pure water), chemicals or from handling cannot be ignored. It is found that background signals on the dry spot could arise from the VPD process itself. Therefore these impurities pose a limited factor for further reducing detection limits. Detection limits by VPD-SRTXRF were estimated at a range of E5 to E7 atoms/cm^2, depending on the blank levels of elements in the dry spot. If we want to further improve detection limits, we should understand

that it is very critical for controlling contaminants from UPW, chemicals, and environment. A cleaner wafer as a blank is also a must.

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Biographies

Jiansheng (Jason) Wang, technical manager and research chemist, joined Balazs in January 1996. He received his B.S. in chemistry from South China Normal University, M.S. in organic analytical chemistry from Eastern Michigan University and Ph.D. in analytical chemistry from University of Cincinnati. Prior to joining Balazs, he worked as a staff chemist at the Midwest Research Institute (MRI).

Marjorie K Balazs is the founder and CEO of Balazs Analytical Laboratory in Sunnyvale, CA and Austin, TX. She has worked in the semiconductor Industry since 1968. Prior to her work in the semiconductor industry, she spent ten years at Stanford Research Institute and taught for six years at the University of San Francisco. She received her M.S. Degree in chemistry from the University of San Francisco and M.A. Degree in chemical education at Stanford University. She is a member of ECS, ASTM, and ACS. Outstanding honors including: Award from President Reagan in 1986 as an outstanding women entrepreneur in the United States; 1992 City of San Jose Small Business Award; And the 1993 SEMI Lifetime Achievement Award for North America, recognized her contribution in yield enhancement to the semiconductor industry over the past twenty-five years.

Piero Pianetta is a Professor in the Department of Electrical Engineering and Assistant Director at the Stanford Linear Accelerator Center for the Stanford Synchrotron Radiation Laboratory. He was born on October 19, 1949 in Santa Rosa California and obtained a B.S. degree from the University of Santa Clara in 1971. The M.S. and Ph.D. were obtained from Stanford University in 1973 and 1977, respectively. From 1977-78, Dr. Pianetta was a Research Associate at SSRL. From 1978-82, he was a member of technical staff at Hewlett-Packard Laboratories working in the area of III-V processing and devices. In 1982, he returned to Stanford as a staff scientist at SSRL and a Professor in Electrical Engineering. In 1985, he was appointed to his current position at SSRL. His current research interests include development of ultra-sensitive x-ray methods for contamination analysis on silicon wafers and understanding the surface chemistry of both metal oxide and semiconductor surfaces using electron spectroscopy techniques such as photoemission, photoelectron diffraction, surface EXAFS and x-ray standing waves.

Katharina Baur obtained her PhD in physics at the University of Bonn, Germany, and is currently working at the Stanford Synchrotron Radiation Laboratory as a visiting scientist.

Sean Brennan is a staff scientist at the Stanford Synchrotron Radiation Laboratory. He obtained his Ph.D. from the Materials Science Department at Stanford University in 1982. After a post doctoral research appointment at Exxon, he joined NIST working in the area of x-ray spectroscopy . In 1986, he joined the Stanford Synchrotron Radiation Laboratory and has been using glancing incidence x-ray scattering to study problems ranging from Si/SiO2 interface to crystal growth.

References

1. "How low can DLs go with VPD-TXRF?" J. Wang, M. Balazs, P. Pianetta, K. Baur, S. Brennan, T. Boone and J. Rosamilia, presented at the 8th TXRF Conference, Sept. 25-29, 2000, Vienna, Austria.
2. "Application of synchrotron radiation to TXRF analysis of metal contamination on silicon wafer surfaces", P. Pianetta, K. Baur, S. Brennan, D. Werho, and J. Wang, accepted by Thin Solid Films, 2000.
3. "Novel methods of TXRF analysis for silicon wafer surface inspection", L. Fabry, S. Pahlke, L. Kotz, P. Wobrauschek and C. Streli, Fresenius J. Anal. Chem (1999) 363: 98-102.
4. "Accurate calibration of TXRF using microdroplet samples". Fabry, L.; Pahlke, S.; Kotz, L., Fresenius' J. Anal. Chem. VOL. 354, NO. 3, Feb 1996.