TXRF TO MONITOR FOR HIGH K DIELECTRIC MATERIAL CONTAMINATION IN A SEMICONDUCTOR FAB

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Abstract

A silver tube anode was used for total reflection x-ray fluorescence (TXRF) spectroscopy to analyze for zirconium contamination on silicon wafers. There was good correlation between results obtained by TXRF and results from vapor phase decomposition inductively coupled plasma mass spectrometry (VPD-ICP-MS) until the detection limits of the TXRF were reached at ~1E10 atoms/cm². Calibration with either a nickel or a zirconium standard wafer was acceptable. The measurement precision using the silver anode was also acceptable (< 5% RSD).

Introduction

As new materials are introduced into semiconductor device manufacturing lines, analytical techniques must be developed or modified to insure the ability to measure any contamination that may arise. Recently, ZrO₂ films were introduced as a high k gate dielectric (testing the feasibility of replacing SiOₓNᵧ) in the manufacturing line of International SEMATECH [1]. Prior to introduction of this new material, a majority of the process tools in the fab were baselined for elemental contamination with monitor wafers. The baseline covered zirconium as well as other metals that are potential candidates for a high k gate dielectric. Periodic process tool monitoring for contamination was also put in place.

There are two primary pathways to wafer cross contamination. The first is mechanical transfer of contamination; that is, a wafer leaves behind contamination that is then transferred to the next wafer or set of wafers that come into contact with the contamination. An example would be contamination left on a handling robot or process equipment chuck. The second is a tool process environment type of contamination. In this case there is contamination in the wafer processing equipment that ends up contaminating a set of wafers as that particular process step occurs. Examples of this type could be particles moved around by gas flow in a chamber or a plasma sputtering contamination off the walls of a process chamber onto the wafer. We have found examples of both types of contamination while monitoring the process equipment toolset in our fab. Typical monitoring of tools involves analysis of two monitor wafers cycled after potential contaminating wafers. Figure 1 is an example of mechanical type of contamination. The zirconium values near 1E11 atoms/cm² were determined to be...
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instances where the proper decontamination protocol was not followed. Figure 2 is an example of process environment type of contamination. In this case, experiments were done to test the ability to clean up a process tool after contamination (note zirconium contamination drops from E13 to mid E10 atoms/cm² around wafer number 15).

Figure 1: Example of mechanical transfer of contamination.

Vapor phase decomposition inductively coupled plasma mass spectrometry (VPD-ICP-MS) was initially used as the analytical technique to monitor for elemental contamination on the wafers as it had the required sensitivity and a reasonable sample throughput [2, 3]. As baselining activities increased, a search for alternative techniques to improve sample throughput was conducted. To streamline the contamination monitoring, analysis by
TXRF was considered. The high level of automation available on a commercial TXRF makes it ideally suited for contamination monitoring in a semiconductor manufacturing environment. A TXRF equipped with a silver tube anode as well as a tungsten rotating anode, was brought into the lab. The Ag K\(\alpha\) line at 22.101 keV from the silver anode is ideally suited for zirconium analysis (Zr adsorption edge = 17.998 keV).

**Experimental**

TXRF: A Technos model 630T TXRF was used in this analysis. The silver tube was operated at 1.4 kW with the incident angle set to 0.05 degrees. Bare silicon monitor wafers, 200 mm diameter, were used for all the samples. Each wafer was analyzed at five points per wafer.

VPD-ICP-MS: The wafers were prepared by VPD in a Mesa-Tek HF reaction chamber. The wafers were exposed to 49% hydrofluoric acid vapors for approximately 20 minutes, then scanned twice (either manually or with a Mesa-Tek fluid scanner) with an acidic collection solution. The total volume of the sample solution was 1.00 mL for analysis by ICP-MS. A Hewlett Packard model 4500 ICP-MS was operated under normal plasma conditions for analysis of the high k type contamination. The sample solution was nebulized by a self-aspirating, low flow Teflon nebulizer (100 µL/min PFA from ESI).

**Results and Discussion**

Figure 3 shows the spectra obtained with a silver anode on a clean silicon wafer. Figure 4 shows one point of a wafer contaminated with zirconium (1.8E12 atoms/cm\(^2\)).
It was discovered that this process environment contaminated wafers left a fairly uniform distribution of zirconium contamination over the monitor wafer. We took advantage of this fact and had several wafers created for correlation purposes between VPD-ICP-MS results and TXRF results.

Figure 5 shows the correlation between the zirconium concentrations as analyzed by both TXRF and VPD-ICP-MS for individual wafers. There is good agreement between the results of the two techniques until the detection limit of TXRF is reached. The detection limit of TXRF with a silver anode for zirconium is approximately $1 \times 10^{10}$ atoms/cm$^2$. There are error bars (representing zirconium distribution on the wafer) shown for the TXRF results except when the points on the wafer were below the detection limits. However, note that there are no error bars shown for the wafers measured by VPD-ICP-MS, as there is only one measurement, which is the average concentration for the wafer’s surface. The zirconium was distributed so evenly on the wafers in the E12 range that the errors bars are relatively small for the measured five points, though there must be some variation (perhaps, particulate) that whole wafer analysis by VPD-ICP-MS measured.

Also evident in Figure 5 is the superior detection limits provided by the VPD technique as you are concentrating the entire surface contamination of the wafer into a single measurement. Typical detection limits for zirconium by VPD-ICP-MS are $1 \times 10^8$ atoms/cm$^2$. Wafers that had been through VPD sample preparation showed no measurable zirconium when they were re-analyzed by TXRF.
Six zirconium contaminated wafers were evaluated against both a nickel standard wafer and a zirconium standard wafer (150mm standard wafers supplied by GeMeTec). The results are shown in Figure 6.

As shown by the slope of 1, there is excellent correlation between the values obtained by processing the data with either nickel or zirconium standards. This was a pleasant surprise since nickel’s adsorption edge (8.331 keV) is much further away from silver as compared to zirconium’s adsorption edge (17.998 keV) and is therefore less sensitive to excitation by the silver source (22.101 keV).

Table 1 shows the reproducibility of the zirconium measurement by the silver anode. The static wafer test consisted of measuring the same spot on the wafer ten times without moving the wafer. The dynamic wafer test included moving the wafer to different

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**Figure 5:** Comparison of zirconium concentrations by TXRF and VPD-ICP-MS, units are atoms/cm².

**Figure 6:** Comparison of concentrations calculated against different standards, units are E10 atoms/cm².
analysis spots and unloading/loading the wafer from the TXRF. Even with a 500 second acquisition and the dynamic wafer test, a precision of 5% is quite reasonable.

<table>
<thead>
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<th>measurement</th>
<th>Static wafer test</th>
<th>Dynamic wafer test</th>
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<tr>
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<td>1000s 500s</td>
</tr>
<tr>
<td>% relative standard deviation</td>
<td>1.54 3.69</td>
<td>2.96 4.72</td>
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Table 1: Precision of a 1E12 atoms/cm² zirconium signal measured with silver anode

Conclusions

TXRF with a silver anode was shown to be a viable technique to analyze for zirconium contamination on silicon wafers. The agreement between VPD-ICP-MS and TXRF results will allow International SEMATECH to correlate the results of the baseline to continued monitoring of the equipment process line. One advantage to TXRF is the ability to see contamination distribution across the wafer, something that was not possible with VPD-ICP-MS. A second advantage to monitoring for high k contamination by TXRF is quicker access to results for the fab engineers. A downside to the TXRF analysis is lack of sensitivity as compared to VPD-ICP-MS. For the best picture of the condition of contamination in process equipment, these two techniques are quite complementary.

This work will be expanded to include other metals that are potential candidates for high k gate dielectrics; for example, ruthenium, hafnium, yttrium, and lanthanum.

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References

