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SULFURIC ACID/HYDROGEN PEROXIDE RINSING STUDY*

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ABSTRACT

Sulfuric acid hydrogen peroxide mixtures (SPM) are commonly used in the semiconductor industry to remove organic contaminants from wafer surfaces. This viscous solution is very difficult to rinse off wafer surfaces. Various rinsing conditions were tested and the resulting residual acid left on the wafer surface was measured. Particle growth resulting from incomplete rinse is correlated with the amount of sulfur on the wafer surface measured by Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS). The amount of sulfur on the wafer surface after the rinse step is strongly affected by the wafer film type and contact angle prior to the SPM clean.

INTRODUCTION

Sulfuric acid/hydrogen peroxide mixtures (SPM) are widely used in the semiconductor industry for removing organic materials such as photoresist from wafer surfaces. This viscous mixture is not readily rinsed off the wafer surface even when using copious amounts of water. Conservation of water in semiconductor fabrication is becoming an important issue, especially in areas that do not have abundant water supplies. Reducing the amount of water required for wet processing can significantly reduce the cost-of-ownership of wet processing equipment.

Residual SPM contamination results in the growth of particles on the wafer surface after the wafers have been stored in a clean room environment for a period of time. These particles are easily rinsed off the wafer surface with deionized (DI) water. The particles will not regrow if they are given enough time to fully develop before they are rinsed off the wafer with water. If the particles are only allowed to grow for a short time, they will rinse off the wafer but new particles will regrow. It is not practical in a manufacturing environment to sufficiently delay rinsing wafers so that particles will not regrow because the delay increases cycle time. Wafers processed through ammonium hydroxide, hydrogen peroxide, water (SC1) or dilute hydrofluoric acid (HF) processes after the SPM clean

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do not exhibit particle growth. HF or SC1 processing may not be practical due to extra processing equipment required. HF and concentrated SC1 solutions etch oxide which may not be acceptable in some manufacturing applications. Since processing in SPM last may be desirable in some applications, the SPM particle growth problem must be addressed using other means.

Several options to eliminate this residual contamination and reduce water usage have been reported in the literature. Adding small amounts of HF to the SPM mixture causes the silicon wafer surface to be hydrophobic after the clean. These wafers do not exhibit particle growth over time [1-2]. Rotondaro *et al.* reported that if SPM-cleaned wafers are placed in a isopropyl alcohol (IPA) bath prior to the DI water rinse step, particle growth is significantly reduced. It can be further reduced by heating the wafers with an infrared (IR) exposure to enhance particle growth, followed by a DI water rinse to remove the particles. No increase in particles is observed after one month of storage following the IR exposure and subsequent rinse step [3].

Methods to eliminate or reduce the particle growth on wafers cleaned in SPM without altering the chemicals the wafers are exposed to have also been investigated. M. Hall *et al.* [4] have demonstrated, by bulk resistivity measurements taken in the rinse tank, that megasonic power applied during an overflow rinse reduces the amount of water required to rinse wafers cleaned in a SPM. They also report that there is no advantage of using megasonic power during the rinse step of wafers cleaned in a SPM if the wafers are dump rinsed for 3 to 4 cycles prior to the overflow rinse. This work also demonstrated that megasonic power applied during an overflow or a dump rinse operation does not eliminate time-dependent particle growth on wafers cleaned in SPM. These researchers were able to significantly reduce time-dependent particle growth on wafers cleaned in a SPM by rinsing them in hot DI water [4].

The mechanism for particle growth and the composition of these particles are not well understood. Some researchers suggest that the particles are formed when residual acid on the wafer surface reacts with moisture from the air and over time the residual acid grows large enough to be detected as particles [4]. Other researchers suggest that contamination is trapped in the SPM chemical oxide, diffuses to the wafer surface and coalesces forming micro-crystals during storage. Given enough time most of the contamination diffuses to the surface and a simple rinse step can remove it preventing further particle formation [3]. We will refer to this as the SPM diffusion theory throughout this paper.

The purpose of our work is to gain a better understanding of the particle growth mechanism on SPM-cleaned wafers. We have demonstrated that megasonic power applied during the rinse step following a SPM clean removes particles added during the clean but does not aid in the removal of sulfur (S) contamination from the wafer surface. Comparison of Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) and/or

Total Reflectance X-Ray Fluorescence Spectroscopy (TXRF) measurements with particle measurements shows a correlation between sulfur concentration and particle growth. Higher sulfur concentration on wafers cleaned in SPM is correlated with faster particle growth. We found that hydrophobic thermal oxide wafers cleaned in SPM do not exhibit particle growth but hydrophilic oxide and hydrophobic or hydrophilic silicon wafers do. We suggest another mechanism for SPM particle growth.

EXPERIMENTAL DETAILS

Rinsing studies were performed using 6-inch n-type (100) silicon wafers and 100 Å thermally oxidized silicon wafers. The contact angle of the thermal oxide and silicon wafers was altered prior to the SPM clean by processing these wafers through either a 100:1 HF dip, a 64:4:1 (H_2O:H_2O_2:NH_4OH) SC1 clean, a 5:1:1 (H_2O:H_2O_2:HCl) SC2 clean, or a combination of these chemistries. A full cassette of wafers was cleaned in a 5:1 or 10:1 (H_2SO_4:H_2O_2) SPM solution at 95°C for 10 minutes. The SPM temperature and time were standard for all experiments. Wafers were rinsed in a Verteq Turbo Sunburst Quick Dump Rinse (QDR) tank. The rinsing parameters used for each experiment are described in the experimental results section. Bulk resistivity of the water was monitored during the rinsing process. Light point defect (LPD) measurements, to monitor particle growth, were made on these wafers using a Tencor SFS-6200. Wafers were measured periodically until the SFS-6200 failed to scan the entire wafer. The SFS-6200 will fail to scan a wafer if there are too many particles on the wafer surface. TOF-SIMS and/or TXRF measurements were taken to compare LPD growth with the amount of sulfur left on the wafer surface. These data were used to evaluate the effectiveness of the rinse step.

EXPERIMENTAL RESULTS

Effect of Megasonic Power on Surface Contamination

Multiple experiments rinsing SPM-cleaned wafers with and without megasonic power were performed. The 6-inch silicon wafers used in these experiments were precleaned in a SC1 solution followed by a 100:1 HF strip to remove the chemical oxide formed during the SC1 clean. This procedure established the same initial starting condition on all wafers. A fresh 5:1 SPM solution was poured for each experiment to eliminate any differences that might result due to aging of the SPM solution. A full cassette of wafers was cleaned in the 5:1 SPM solution and rinsed in the Verteq QDR using 5 dump cycles with spray followed by an overflow rinse for 20 minutes of total rinse time. Duplicate runs with and without megasonic power applied during the rinse step were performed.

TXRF data shown in Figure 1 indicate that the concentration of sulfur on the wafer surface is approximately the same for all wafers rinsed with or without megasonic power. The TOF-SIMS S/O_2 peak height ratio data, shown in Figure 2, also indicate that megasonic power applied during the rinse step does not reduce the amount of residual sulfur on the wafer surface. However, the number of light point defects measured immediately after the SPM clean, shown in Figure 3, indicates that megasonic power applied during the rinse step significantly reduces the amount of particulate contamination added to the wafers during this cleaning step. All wafers used in these experiments failed the SFS-6200 scan less than 24 hours after the SPM clean. This failure indicates that megasonic power applied during the rinse step does not eliminate the growth of particles on wafers cleaned in SPM. Nor does resistivity data taken during the experiment indicate an advantage of using megasonic power during the rinse. These data are consistent with that presented by Hall *et al.* [4]. If contamination remains bound to the surface and therefore does not contribute to the conductivity of the water, a high resistivity will not necessarily be indicative of a clean wafer surface. In summary, megasonic power applied during the rinse step of SPM-cleaned wafers removes particles added during the clean but does not aid in the removal of sulfur contamination from the wafer surface.

Effect of Si and SiO_2 Wafer Contact Angle Prior to SPM Clean on Ease of Rinse

In order to determine if the diffusion of contaminants trapped in the chemical oxide grown during the SPM clean is the cause of particulate growth, both Si and SiO_2 wafers were cleaned in the same 5:1 SPM solution and then rinsed together. No chemical oxide should be grown on thermally oxidized wafers during an SPM clean. These oxide wafers should not experience growth of particles if the SPM diffusion theory [3] is correct. The contact angle, and therefore surface termination, of the wafers prior to the SPM clean was varied by exposing the wafers to SC1, SC2, HF, or a combination of these solutions. The SiO_2 wafers were exposed to either 1) an SC1 clean, 2) an SC2 clean, 3) an SC1 followed by an SC2 clean, or 4) a 1 second HF dip to remove approximately 8 Å of oxide. One group of thermally oxidized wafers did not receive any post furnace processing. Silicon wafers were exposed to 1) an SC1 clean, 2) an HF dip followed by an SC2 clean, or 3) an SC1 followed by an SC2 clean. Wafers of each type were evenly spaced throughout the cassette. This full cassette of wafers was cleaned in a 5:1 SPM solution and rinsed with no megasonic power for 5 dumps followed by an overflow rinse for a total rinse time of 10 minutes.

Sulfur concentration on the wafers used in this experiment was measured by TXRF. The results are shown in Figure 4. The thermally oxidized wafers that received no post-furnace processing (SiO_2+none) and the ones that received only an SC2 process (SiO_2+SC2) prior to the SPM clean have significantly less sulfur on the wafer surface than the other wafers processed in this experiment. These wafers were hydrophobic prior to the SPM clean and had a water contact angle of 33° and 19°, respectively. These wafers also did not exhibit SPM particle growth even after one month of storage. The remaining wafers in this experiment were hydrophilic prior to the SPM clean. All had significantly more sulfur on the wafer surface than the SiO_2+none and SiO_2+SC2 wafers. They also exhibited SPM particle growth that caused the SFS-6200 to fail to scan these wafers within 17 hours after the SPM clean.

These data indicate that the SPM diffusion theory [3] does not fully explain particle growth. A chemical oxide should not have grown on thermally oxidized wafers cleaned in a SPM and therefore particles should not have grown if diffusion from an SPM oxide is the source of sulfur. It appears that the SPM residual contaminant is more tightly bound to the surface of hydrophilic SiO_2 than to hydrophobic SiO_2 wafer surfaces.

Hydrophobic Si wafer surfaces were not included in this experiment although they were included in the megasonic rinsing experiments described earlier. Silicon wafers dipped in HF to make the wafer surface hydrophobic prior to the SPM clean were used in the megasonic experiment. Hydrophobic silicon wafers exhibited particle growth within 24 hours after the SPM clean. Sulfur concentrations on hydrophobic Si wafers, shown in Figure 1, are comparable to the sulfur concentrations on the hydrophilic Si wafers shown in Figure 4. Since the sulfur concentration is similar and since both hydrophobic and hydrophilic Si wafers exhibited SPM particle growth, one can conclude that contact angle on Si wafers prior to the SPM clean does not significantly influence the effectiveness of rinsing SPM-cleaned silicon wafers.

Correlation of Sulfur Concentration and Particle Growth

The Si/SiO_2 contact angle experiment described above suggests that particle growth is caused by elevated sulfur concentrations on the wafer surface. We performed an additional experiment to confirm this apparent correlation. Si wafers precleaned in an SC1 solution and SiO_2 wafers with no post furnace processing were cleaned in a 10:1 SPM solution at 95°C for 10 minutes. Wafers were rinsed with no megasonic power for 5 dumps followed by an overflow rinse. Wafers of each type were removed after 5 minutes and 20 minutes of total rinse time. Table I indicates that as the TOF-SIMS S/O_2 peak height ratio increases there is a corresponding increase in the number of light point defects (LPD) added to the wafers 17 hours after the SPM clean.

Table I. TOF-SIMS and LPD measurements on 10:1 SPM-cleaned wafers.

Wafer Type	Rinse Time (minutes)	TOF-SIMS S/O_2 peak height ratio	SFS-6200 LPD increase 17 hours after SPM clean (SPM particle growth)
SiO_2 + none	5	0.06	22
SiO_2 + none	20	0.07	40
Si + SC1	20	0.50	137
Si + SC1	5	0.63	7551

Caution must be exercised when using SFS-6200 measurements for evaluating the effectiveness of the rinse process because we have found that altering the storage conditions of the wafers can drastically alter the particle growth. For example, wafers stored in a very humid environment (storage box with small amount of DI water in the bottom) do not exhibit particle growth for as long as two weeks after the SPM clean. However, once the humid wafers are exposed to the clean room air, particles begin to grow very quickly. Wafers cleaned and rinsed at the same time as the wafers stored in the humid environment but stored in the normal clean room air exhibited particle growth and failed the SFS-6200 scan less than 24 hours after the SPM clean.

DISCUSSION

Some of our data conflicts with the existing theories for particle growth. For example, wafers stored in a humid environment did not exhibit particle growth. This observation contradicts the theory that residual contamination on wafers cleaned in SPM grow by absorbing moisture from the air [4]. We demonstrated that SiO_2 wafers, which are hydrophilic prior to the SPM clean, exhibit particle growth. This indicates that for oxide films, diffusion of contaminants trapped in the chemical oxide grown during the SPM clean cannot be the mechanism for particle growth because oxide wafers will not grow a chemical oxide during the SPM clean.

Other researchers have also made observations that conflict with the SPM diffusion theory. For example, Christenson [5] has stated that in an inert spray tool, SPM-cleaned wafers do not exhibit particle growth when stored in the inert environment for one day after the SPM clean. Particles start to grow on these wafers after they have been exposed to clean room air for a short time. This would indicate that diffusion is not the mechanism because diffusion should occur even in an inert environment. Christenson stated that a very dilute 30 second SC1 clean applied immediately after the SPM rinse prevents the growth of particles. This indicates that diffusion is not the mechanism because a dilute SC1 clean will remove less than 1 Å of the chemical oxide grown during the SPM clean. Christenson also found that a hot DI water rinse following the SPM clean in this inert spray tool is not effective in eliminating SPM particle growth. However, Hall *et al.* [4] found that hot DI water is very effective in eliminating SPM particle growth.

From the experimental results presented in this paper and from discussions with other researchers, we suggest another possible explanation for particle growth on SPM-cleaned wafers. We speculate that chemical contaminants in the clean room air react with residual sulfur left on the wafer surface after a SPM clean and form water soluble particles that can then be easily rinsed off the wafer surface. This explanation is consistent with the observation that particles do not grow in an inert spray tool until wafers are exposed to the clean room air. We believe that the mechanism for particle growth is a surface effect which is consistent with the fact that hydrophilic SiO_2 wafers exhibit particle growth. The different hot DI water rinse results are explained by this mechanism. Contaminants in the clean room air could dissolve in the open tank hot DI rinse water and react with sulfur on the wafer surface forming a water soluble material which is then removed by the hot DI water. In the inert spray tool, the wafers and the hot rinse water are not exposed to the clean room air so this reaction can not take place to remove the sulfur contamination.

CONCLUSION

We have demonstrated that particle growth, as measured on the SFS-6200, correlates with the relative amount of sulfur on the wafer surface after a SPM clean. Megasonic power applied during the rinse step significantly reduces the amount of particles added to the wafer surface during the SPM cleaning process but does not reduce the amount of sulfur contamination on silicon wafer surfaces or eliminate the time-dependent SPM particle growth. We demonstrated that hydrophilic SiO_2 and hydrophobic and hydrophilic silicon wafers cleaned in a SPM exhibit growth of particles but hydrophobic thermal oxide wafers cleaned in the same SPM do not exhibit growth of particles. We have suggested another mechanism for SPM particle growth and are performing additional experiments to validate this theory.

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REFERENCES

1. "Reduction of Foreign Particulate Matter on Semiconductor Wafers", M. Fleming, Jr., W. Syverson, E. White, IBM Corporation, US Patent 5,294,570, March 15, 1994.
2. S. Verhaverbeke, R. Messoussi, T. Ohmi, UCPSS '94, Belgium, September 1994.
3. L.P. Rotondaro, H.F. Schmidt, M. Meuris, M.M. Heyns, C. Claeys and J. Mulready, UCPSS '94, Belgium, September 1994.
4. R.M. Hall, J.J. Rosato, P.G. Lindquist, T. Jarvis, T. Parry, J.D. Kelly, R.N. Walters, in Proceedings of Semiconductor Pure Water and Chemicals Conference 1995, M.K. Balazs (Ed), pp. 101-112.
5. Discussions with K. Christenson, FSI International.

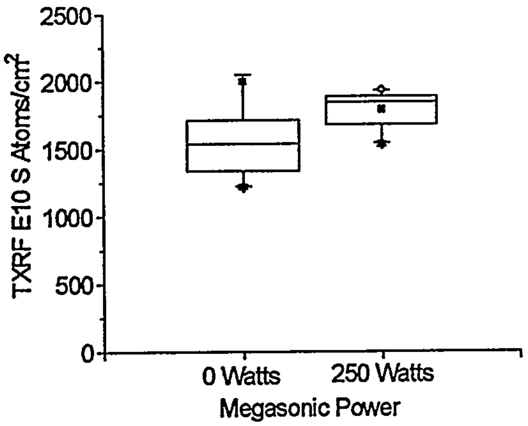

Figure 1. Boxplot of TXRF sulfur concentration on hydrophobic Si wafers cleaned in 5:1 SPM and rinsed with or without megasonic power.

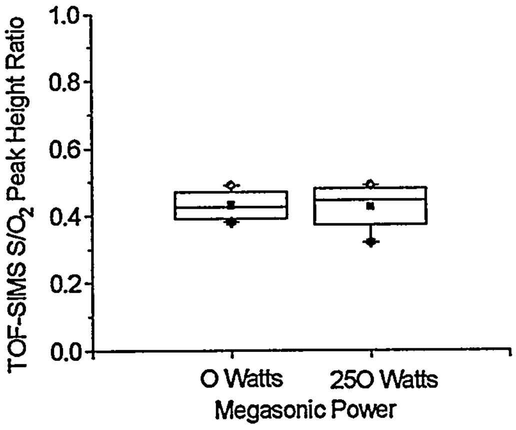

Figure 2. Boxplot of TOF-SIMS sulfur contamination on hydrophobic Si wafers cleaned in 5:1 SPM and rinsed with or without megasonic power.

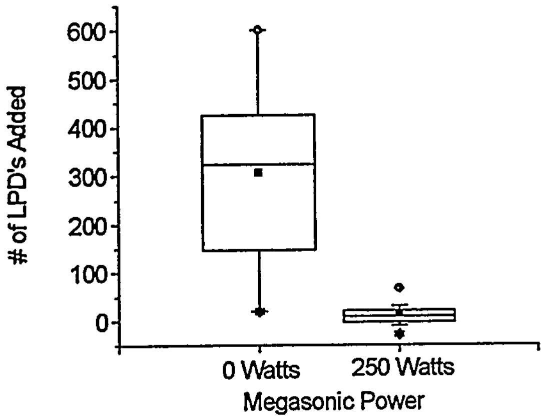

Figure 3. Boxplot of number of particles added to Si wafers cleaned in 5:1 SPM and rinsed with or without megasonic power. LPD measurements were made immediately following the SPM clean before measurable SPM particle growth could occur.

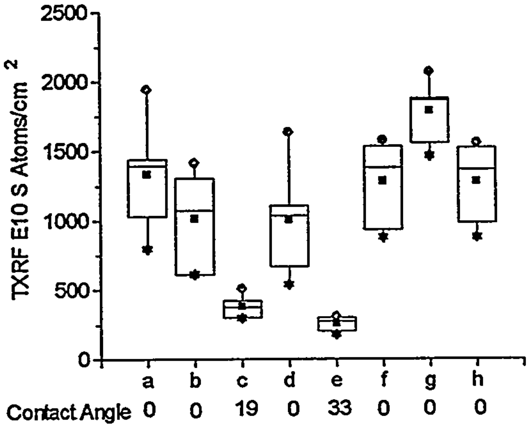

Figure 4. Boxplot of TXRF sulfur contamination levels measured on wafers processed through a 5:1 SPM and rinsed with no megasonic power. a) SiO_2 HF dip, b) SiO_2 SC1 clean, c) SiO_2 SC2 clean, d) SiO_2 SC1 + SC2 clean, e) SiO_2 no post furnace processing, f) Si SC1 clean, g) Si SC2 Clean, h) Si SC1 + SC2 clean.

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