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MINIMIZING SULFUR CONTAMINATION AND RINSE WATER VOLUME REQUIRED FOLLOWING A SULFURIC ACID/HYDROGEN PEROXIDE CLEAN BY PERFORMING A CHEMICALLY BASIC RINSE[*]

P. J. Clews, G. C. Nelson, C. A. Matlock[a], P .J. Resnick, C. L. J. Adkins
Sandia National Laboratories, Albuquerque, NM 87185

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 contamination on the wafer surface was measured. The addition of small amounts of a chemical base such as ammonium hydroxide to the rinse water has been found to be effective in reducing the surface concentration of sulfur and also mitigates the particle growth that occurs on SPM cleaned wafers. The volume of room temperature water required to rinse these wafers is also significantly reduced.

INTRODUCTION

Sulfuric acid/hydrogen peroxide mixtures (SPM), also commonly referred to as a piranha clean, are widely used in the semiconductor industry for removing organic contamination from wafer surfaces. This viscous mixture is difficult to rinse 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. The residual contamination remaining on the wafer surface after a SPM clean results in particle growth on the wafer surface after the wafers have been stored in the clean room environment for a period of time. 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. Over time the residual acid grows large enough to be detected as particles [1] Other researchers suggest that contamination is trapped in the SPM chemical oxide, diffuses to the wafer surface

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[a] Present address: FSI International, Surface Conditioning Division, Chaska, MN 55318

and coalesces forming micro-crystals during storage. Given enough time, most of the contaminants diffuse to the surface and a simple water rinse step can remove it preventing further particle formation [2].

Methods to eliminate or significantly reduce particle growth on SPM cleaned wafers are also reported in the literature [1-5]. These methods are effective but they require hot deionized (DI) rinse water, addition of HF to the SPM tank, or additional processing tanks so wafers can be exposed to HF, SC1 or IPA solutions after the SPM clean to remove the contamination. The objective of this study was to: 1) better understand the particle growth that occurs on SPM cleaned wafers; 2) minimize the amount of rinse water required to rinse SPM cleaned wafers; and 3) minimize the amount of sulfur contamination remaining on the wafer surface after the SPM clean.

In previous work [6] we 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 or eliminate the time-dependent SPM particle growth. We also demonstrated that SPM particle growth correlates with the relative amount of sulfur contamination on the wafer surface after a SPM clean. Higher sulfur concentration on wafers cleaned in SPM is correlated with faster particle growth.

In this paper we present information on the shape and composition of the SPM particles and wafer storage conditions that alter the growth rate of these particles. We also present additional rinsing experiments that investigate the effects of extended rinse times and adding chemicals to the rinse water. We demonstrate that addition of a chemically basic material to the rinse water reduces the amount of water required to rinse SPM cleaned wafers and also reduces the amount of sulfur contamination remaining on the wafer surface following a SPM clean. As a result, the time dependent SPM particle growth is mitigated. Based on our results we suggest a mechanism for SPM particle growth.

EXPERIMENTAL DETAILS

Rinsing studies were performed using 6-inch n-type (100) bare 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) SC-1 clean, a 5:1:1 (H_2O:H_2O_2:HCl) SC-2 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 constant 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. The ambient rinse water temperature for all experiments was approximately 25°C. Light point defect (LPD) measurements were made to monitor particle growth 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 light scattering from particles or haze on the wafer surface overwhelms the PMT at a given gain setting. Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) and/or Total Reflectance X-Ray Fluorescence Spectroscopy (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 [6].

EXPERIMENTAL RESULTS

Composition and Shape of SPM-Derived Particles

Scanning electron microscopy (SEM) images of SPM-derived particles (particles which are formed from residual SPM contamination) are shown in Figure 1. The morphology of the SPM-derived particles depends on the concentration of H_2O_2 in the SPM solution. Particles derived from 10:1 SPM are crystalline but the 5:1 SPM-derived particles have no distinct shape. In order to obtain these images, the samples had to be carbon coated. TOF-SIMS negative and positive ion image maps of the SPM-derived particles, shown in Figure 2, indicate that the particles are composed of SO_x^- and NH_4^+.

Effect of Wafer Storage Environment on SPM-Derived Particle Growth

Altering the storage conditions of SPM cleaned wafers can drastically alter the particle growth behavior. Data in Table I indicate that 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 cleanroom air, particles begin to grow very quickly. Although wafers stored in humid environments do not exhibit particle growth, we speculate that the reaction to form SPM-derived particles is still occurring, but the particulate matter is dissolved in the monolayers of water present on the wafer surface. When the wafers are removed from the humid environment, excess moisture evaporates and the particles form. Wafers cleaned and rinsed at the same time as the wafers stored in the humid environment but stored in the normal cleanroom air (in an open cassette) exhibited particle growth and failed the SFS-6200 scan less than 24 hours after the SPM clean. Wafers stored in a closed storage box, with no water in the bottom of the box, took longer to fail the SFS-6200 scan than the wafers stored in the open cassette. This indicates that SPM-derived particle growth depends on cleanroom air exposure.

Table I: Effect of Wafer Storage Environment on SPM-Derived Particle Growth

Storage Condition	X = Time to Fail SFS-6200 Scan ($> 0.13\mu m$)
Open cassette	$15 < X < 22$ hours
Closed storage box	$41 < X < 112$ hours
Humid storage box	> two weeks
Humid wafers moved to dry storage box	$2 < X < 5$ hours after move

Extended Rinse Times

The TXRF and SFS-6200 data shown in Figure 3 indicate that extended room temperature rinse times do not eliminate SPM-derived particle growth on bare silicon wafers. Wafers from this 5:1 SPM clean were removed from the rinse bath after 10 minutes and after 20 hours of total rinse time. Room temperature rinse water was flowing into the QDR during the entire 20 hour rinse.

Addition of Chemicals to the Rinse Water

The extended rinse time data presented above and megasonic rinse data presented in prior work [6] indicate that the sulfur contamination remaining on silicon wafer surfaces after a SPM clean is chemically bound to the wafer surface. A chemical reaction is required to break the sulfur/silicon bond so that the sulfur contamination can be removed from the wafer surface. The TOF-SIMS particle image maps, shown in Figure 2, indicate that SPM-derived particles are composed of NH_4^+ and SO_x^-. This knowledge led to the discovery that adding small amounts of NH_4OH directly to the SPM wafer rinse water significantly reduces SPM-derived particle growth. The addition of ammonium salts such as ammonium chloride and ammonium persulfate did not reduce SPM-derived particle growth; however, the addition of KOH, or another chemically basic material, to the room temperature rinse water did.

Figure 4 shows plots of the number of LPDs measured on 5:1 SPM cleaned wafers which were rinsed using either the standard rinse process or with the addition of KOH or NH_4OH to the rinse water. Sulfur concentration on these wafers is shown in Figure 5. All runs illustrated in these figures were performed on a full boat of wafers and were rinsed with approximately 60 liters of room temperature water. Wafers were rinsed for 5 dump cycles to remove most of the acid before the KOH or NH_4OH was added to the rinse water. The pH of the rinse water after the addition of KOH or NH_4OH was 10.4. Only 5 ml of NH_4OH and 3 g of KOH was added to the rinse water for these runs. Wafers were stored on a shelf and exposed directly to the cleanroom air to accelerate particle growth rate. Wafers rinsed using the standard process had significantly higher sulfur concentration on the wafer surface than the wafers which were rinsed with NH_4OH or KOH. The standard rinsed wafers failed the SFS-6200 scan one day after the SPM clean. The KOH and NH_4OH rinsed wafers were still passing the SFS-6200 scan 3 weeks after the clean. The KOH wafers have a higher initial count because they were rinsed in a different ("KOH contaminated") wet bench. A slight increase in the number of LPDs on the NH_4OH rinsed wafers appeared after 3 weeks of storage.

SPM-Derived Particle Growth Mechanism

Mechanisms for SPM-derived particle growth have been suggested in the literature [1-3]. The data presented above do not support these theories. Another mechanism is suggested here [6]. Ammonia gas in the cleanroom air absorbs into the monolayer of water present on the wafer surface forming ammonium hydroxide. The hydroxide ion reacts with the silicon surface, breaks the sulfur/silicon bond and ammonium sulfate particles form on the wafer surface. In humid environments, the ammonium sulfate remains dissolved in the monolayers of water on the wafer surface. When the wafers are removed from the humid environment, excess moisture evaporates and the particles appear. If hydroxide ions are introduced into the rinse water, this same reaction takes place except the ammonium sulfate can be removed by the water during the rinse step.

SUMMARY

Sulfur contamination tenaciously adheres to the silicon wafer surface after a SPM clean. Resistivity is not a good indication for rinse endpoint for SPM cleaned wafers because the contaminant is bound to the wafer surface and therefore cannot contribute to the conductivity of the water. Megasonic power applied during the room temperature rinse step of SPM cleaned wafers is not effective in removing SPM contamination. Room temperature rinse times as long as 20 hours do not eliminate SPM particle growth on bare silicon wafers. Scanning electron microscopy images of particles formed after SPM cleaning indicate the shape of the particles depends on the concentration of H_2O_2 in the SPM solution. Particles formed from 10:1 SPM are crystalline but the particles from 5:1 SPM are amorphous. TOF-SIMS negative and positive ion image maps of the SPM particles indicate the SPM particles are composed of SO_x^- and NH_4^+. The addition of small amounts of a chemical base such as ammonium hydroxide (e.g., sufficient to achieve pH = 10) to the SPM rinse water has been found to be effective in reducing the surface concentration of sulfur and mitigates SPM induced particle growth. The volume of room temperature water required to rinse SPM wafers can be significantly reduced by removing the majority of the sulfuric acid with a quick dump rinse step, followed by the addition of enough ammonium hydroxide to the rinse water to make the solution basic, and finally completing the rinse process with room temperature ultra pure rinse water. Additional process tanks to perform the SC1 clean or dilute HF dip are not needed. The water need not be heated, obviating energy-intensive heaters. Commercially available quartz equipment may be used to reprocess the H_2SO_4. Few chemicals are required which reduces the cost of both chemicals and waste disposal. Most important, the amount of water required for rinsing SPM cleaned wafers is reduced, and residual sulfur contamination is diminished. As a result, SPM derived particle growth is mitigated. Rinse tanks commonly used in semiconductor manufacturing can be easily modified to incorporate this rinsing technique.

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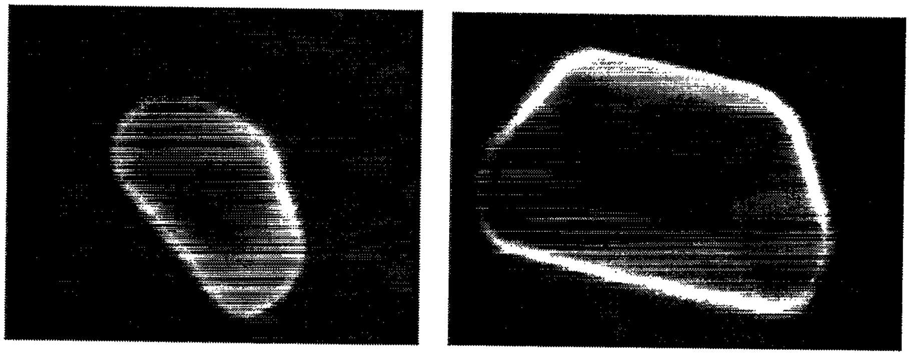

5:1 SPM **10:1 SPM**

Figure 1 SEM image of SPM-Derived particles.

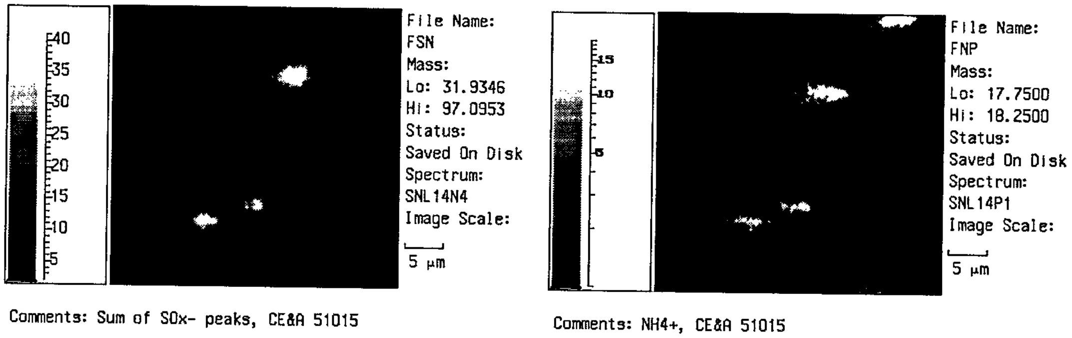

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Figure 2 TOF-SIMS ion image map of SPM-Derived particles.

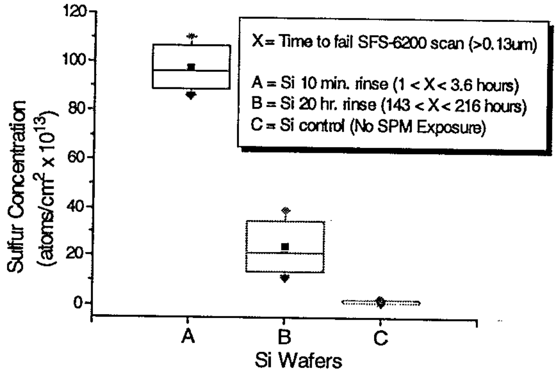

Figure 3 Box plot of TXRF S contamination levels measured on wafers processed through a 5:1 SPM and rinsed for a) 10 min. rinse; b) 20 hour rinse; c) Si control wafer not exposed to SPM solution.

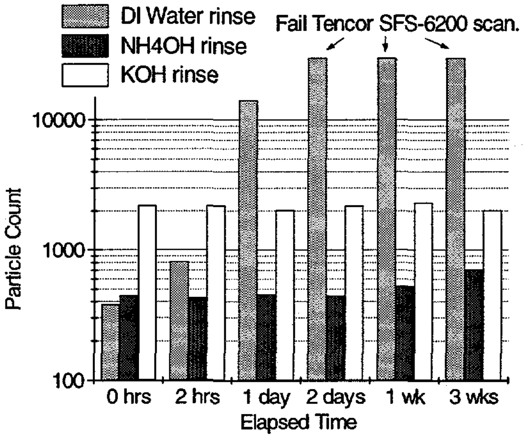

Figure 4 LPD average counts per wafer vs. elapsed time following a 5:1 SPM clean and rinse process. Wafers were rinsed using a) standard DI water rinse; addition of b) NH_4OH or c) KOH to the rinse water.

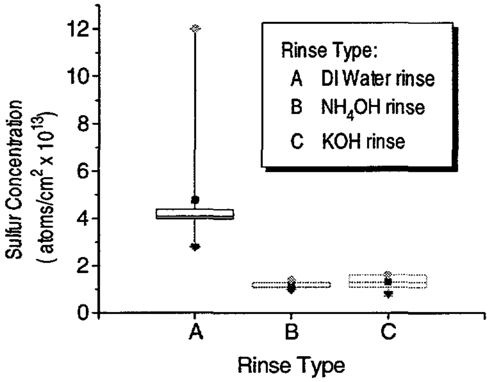

Figure 5 Surface sulfur concentration following basic and DI water rinsing. Wafers were rinsed using a) standard DI water rinse; addition of b) NH_4OH or c) KOH to the rinse water.