SAND96-2167C
CONF-9609107--3
SAND--96-2167C

Mechanistic Studies of SC-1 Particle Removal and Post Piranha Rinsing*

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1.0 INTRODUCTION

SC-1 ($NH_4OH/H_2O_2/H_2O$) and piranha (H_2SO_4/H_2O_2) cleans have been used for many years to remove particulate and organic contamination. Although the SC-1 clean, often used with applied megasonic power, is known to be highly effective for particle removal [1,2], the removal mechanism remains unclear. For the removal of heavy organic contamination, the piranha cleaning chemistry is an effective process; however, post-piranha residue adheres tenaciously to the wafer surface, causing a particle growth phenomenon [3]. A series of experiments have been performed to help understand the interaction of these processes with silicon surfaces.

2.0 EXPERIMENTAL

2.1 SC-1/Megasonic

Two surface sensitive techniques, open circuit potential (OCP) and optical haze measurements, were used to study the etching/passivation of silicon surfaces with SC-1 chemistry under various process conditions. All wafers were pre-cleaned in a dilute SC-1 chemistry, giving rise to a hydrophilic surface. OCP measurements were performed in a single-wafer electrochemical cell, using a saturated calomel reference electrode. Detailed OCP data have been presented elsewhere [4]. Haze measurements were performed using the haze channel on a Tencor Surfscan® 6200. To evaluate the role of surface activity on cleaning performance, these results were then compared to silicon nitride particle removal efficacy (> 0.15 µm Si_3N_4 deposited from an aerosol). In addition to studying the effects of SC-1 chemistries, computational and experimental modeling is also being performed to understand the physical component of particle removal in acoustically assisted cleaning. The effect of the acoustic pressure field, as well as the effect of cavitation intensity and distribution are being studied.

*This work was performed at Sandia National Laboratories, which is operated for the U.S. Department of Energy under contract no. DE-AC04-94AL85000. This work was funded by the Contamination Free Manufacturing Research Center through a cooperative research and development agreement with SEMATECH.

DISCLAIMER

2.2 Sulfuric Peroxide (Piranha) Rinsing

To evaluate the amount of sulfur remaining on a wafer after a piranha clean, 150 mm n-type bare silicon and thermally oxidized wafers were processed through either 5:1 or 10:1 (H_2SO_4:H_2O_2) piranha at 95°C for 10 minutes. Following various modifications to the rinse process, time-of-flight secondary ion mass spectrometry (TOF-SIMS) and total reflection X-ray fluorescence spectrometry (TXRF) were used to measure residual sulfur. Light point defects (LPDs) were also measured as a function of time after wafers were rinsed and dried, as post piranha processed wafers have been shown to exhibit a particle growth phenomenon. The data from these analytical techniques were used to assess the efficacy of various rinsing techniques.

3.0 RESULTS AND DISCUSSION

3.1 SC-1/Megasonic

In the study of SC-1 chemistries, no correlation between the cleaning efficacy and either the measured open circuit potential or the haze delta was evident when dilute SC-1 chemistries were used. LPD removal efficiency, based on the removal of Si_3N_4 particles is shown in Figure 1. These experiments were performed under conditions known to effect silicon etching (both n and p-type Si<100>, with and without illumination). The box plot of Figure 2 shows haze delta data for the same process conditions. Haze values can be related to surface roughness [5], which is caused by preferential Si{100} etching in basic media. It can be seen that conditions conducive to increased haze, and thus etching, do not correlate with increased particle removal efficiencies (see Figure 1). When sufficiently dilute aqueous ammonia solutions with no H_2O_2 are used on hydrophilic wafers, alkaline attack and roughening of the silicon is minimal, yet effective particle removal is still

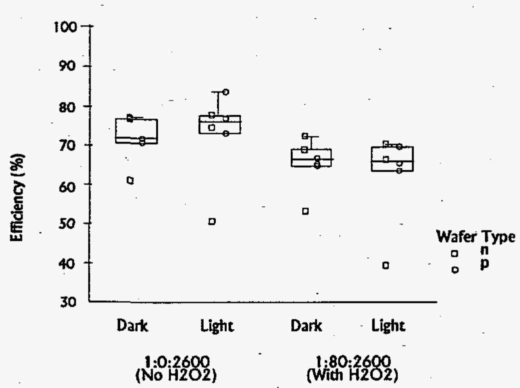

Figure 1. LPD removal as a function of wafer type and lighting conditions.

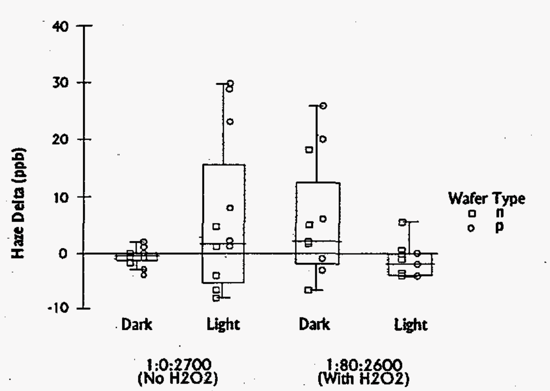

Figure 2. Delta haze as a function of wafer type and lighting conditions.

obtained. A measurable increase in haze was noted when hydrophobic bare silicon wafers were processed through the dilute aqueous ammonia solutions. It appears that the thin chemical oxide resulting from an SC-1 preclean step is sufficient to suppress alkaline etching of the silicon surface in very dilute aqueous ammonia. These data suggest that etching of silicon is not requisite to an effective clean.

In order to understand the physical mechanism of megasonics in particle removal, a predictive model of the acoustic pressure field in the cleaning bath is required. Using a ray-trace method, calculated one-dimensional pressure fields were compared to measured values, as shown in Figure 3. In order to obtain pressure measurements free of reflections, the experimental transducer was operated in pulsed mode using a pulse duration of about 50 microseconds. This modeling method, which shows good agreement with measured values, can be used to predict pressure fields in various bath geometries, and ultimately may be used to optimize cleaning bath geometries in future generation tools.

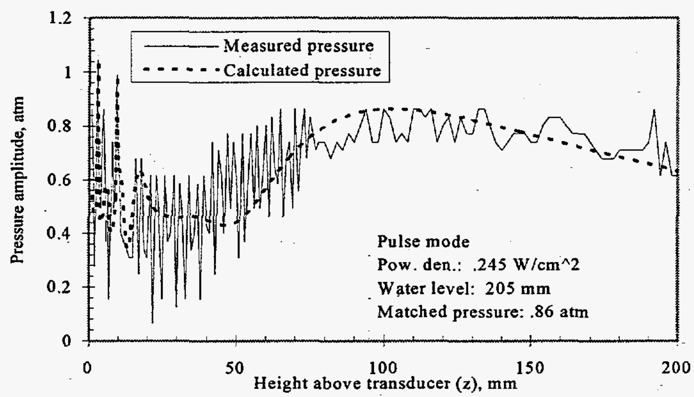

Figure 3. Predicted and measured pressure field. Pressure distribution along center axis above transducer midway between two wafers spaced 2 cm apart.

3.2 Sulfuric Peroxide (Piranha) Rinsing

Following a piranha clean, the residual sulfur contamination left on the wafer after rinsing adheres tenaciously to the silicon surface. This residual sulfur generates particle contamination with time when the wafers are exposed to cleanroom air. Indeed, the extent of the particle growth is indicative of the level of residual sulfur contamination on the wafer surface [6]. TOF-SIMS negative and positive ion image maps of the piranha-cleaned wafers shown in Figure 4 indicate that the particles are comprised of SO_x^- and NH_4^+. The addition of small amounts of ammonium hydroxide (*e.g.*, sufficient to achieve pH = 10) to the post-piranha rinse bath has been found to be effective in reducing the surface concentration of sulfur, as well as mitigating the piranha induced particle growth. Sulfur concentration, measured by total reflectance x-ray fluorescence (TXRF), is shown in Figure 5 for both basic rinsing and rinsing in deionized water. The addition of ammonium salts to the rinse bath did not reduce the surface sulfur concentration, while the addition of other bases such as potassium hydroxide were effective. The hydroxyl ion is clearly the active species with respect to sulfur removal.

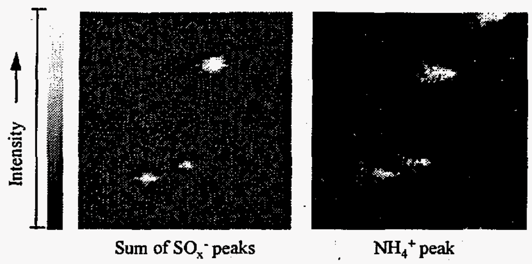

Figure 4. TOF-SIMS negative (left) and positive (right) ion maps.

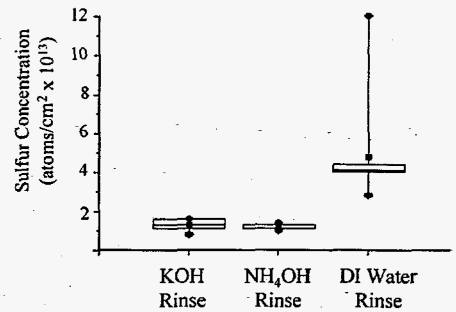

Figure 5. Surface sulfur concentration following basic and DI water rinsing.

4.0 CONCLUSIONS

Surface sensitive techniques were used to study SC-1 chemical effects on silicon wafers. Particle removal efficacy does not necessarily depend on surface modification phenomena such as etching or passivation. To study the physical effects of megasonic cleaning, computational and experimental models are being developed. Such models will allow bath manufacturers to calculate cleaning performance based on first principles.

Sulfur residue remains on silicon wafer surfaces following a piranha clean and rinse sequence. This residue forms particulate matter when the wafers are stored in a cleanroom environment. TOF-SIMS was used to identify these particles as ammonium sulfate. The use of an alkaline rinse (*e.g.*, pH = 10) following piranha is effective in reducing the residual sulfur concentration, and thereby suppressing the time dependent particle formation.

5.0 REFERENCES

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