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EVALUATION OF POST-ASHED PHOTORESIST CLEANING USING  
OXIDIZING CHEMISTRIES\*

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ABSTRACT

The use of sulfuric acid based chemistries for the removal of photoresist ashing residue was investigated. Samples were prepared by ion-implanting patterned, UV-hardened photoresist. The efficacy of post-ash cleaning was determined by measuring organic, metallic, and particulate surface concentrations. Sulfuric-nitric mixtures and sulfuric-hydrogen peroxide mixtures were highly effective for the removal of metallic contaminants. Neither chemistry was very effective for particulate and organic residue. Highly effective overall cleaning was observed when a sulfuric acid based clean was followed with an RCA-type process sequence. Redundant cleans provided no additional benefit. Post-ash cleaning may be simplified by either reducing the number of sulfuric acid based cleans, or for certain post-ash applications, by replacing them with RCA-type processes.

INTRODUCTION

Oxidizing chemistries have been used for many years to strip photoresist and as a post-photoresist ashing clean. These oxidizing chemistries are typically based on sulfuric acid, combined with a strong oxidizer such as hydrogen peroxide or nitric acid. Although numerous studies have been performed to assess the efficacy of these sulfuric acid based chemistries for the removal of photoresist, relatively little information exists in the open literature regarding the use of these chemistries for post-ash cleaning. Much of the previous work on photoresist stripping has focused on optimizing the mixing ratio of the sulfuric chemistry to achieve a maximum adiabatic temperature (1,2). Such an optimization technique may be appropriate for the removal of bulk photoresist, but it is

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likely to have little value for the study of post-ash cleaning. Typically, oxygen plasma ashing is used to remove photoresist in front-end-of-line operations, rather than wet chemical stripping. However, these oxidizing wet chemistries are commonly used following front-end-of-line ashing steps as an additional safeguard against residual organic contamination, as well as a means to remove post-ash metallic contamination. Often these cleaning chemistries will be used at the end of a photolithography, implant, or etch process route, as well as at the beginning of a subsequent diffusion or CVD route. This type of process flow results in redundant cleaning steps. Although there is no reason to believe that such redundancy would have a deleterious effect on device fabrication or performance, there may be little or no value added by performing redundant cleans. Finally, the sulfuric acid based cleans are often used in combination with other cleaning chemistries such as SC-1 ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ ) and SC-2 ( $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ ). The combination of these cleaning steps must be considered during an optimization of a post photoresist ashing clean sequence.

The objective of this study was to evaluate the efficacy of post-ash cleaning. The primary focus was on sulfuric acid based cleans. The efficacy of both sulfuric acid-hydrogen peroxide mixtures (SPM) and sulfuric acid-nitric acid mixtures (SNM) was evaluated. The value added by performing multiple cleans was investigated, as was the overall cleaning efficacy of process sequences that included RCA-type cleans. Process simplifications are proposed.

## EXPERIMENTAL

### Sample Preparation

Many factors are either known to affect or are believed to affect the efficacy of photoresist ashing (3). These factors include implant species and dose, photoresist thickness and track bake conditions, UV stabilization parameters, and perhaps most of all, the tool and process parameters that are used to perform the photoresist ash. All of the wafers that were prepared for this study were 150 mm monitor grade silicon, on which a 10 nm screen oxide had been grown. Following oxidation, photoresist was spun on, exposed on an I-line stepper using either a reticle test structure mask or a CMOS process layer mask, and track developed. Finally, the wafers were cured in a UV stabilizer, implanted with either  $^{75}\text{As}^+$  or  $^{31}\text{P}^+$  at various doses and energies, and ashed in a downstream oxygen plasma asher.

Two sets of samples were prepared. The first sample set was prepared for a screening experiment to examine metrology techniques and the effect of implant dose. A non-optimized ashing recipe was used following an  $^{75}\text{As}^+$  implant ( $1.4\text{E}14$  @ 160 keV) to create a "worst case" contamination challenge. The second sample set was used to evaluate the post-ash clean following an n-well implant ( $^{31}\text{P}^+$ ,  $1.7\text{E}13$  @ 900 keV) used in

CMOS device fabrication. These samples were processed through an optimized ash, and possess contamination levels that are representative of typical post-ash processes.

### Metrology

Multiple metrology techniques were employed to assess the effectiveness of the post-ash cleaning sequence. Because the wafers were photopatterned, a semi-quantitative laser light scattering technique could be employed to detect residual photoresist following the cleaning steps (4). This type of measurement, which allows for the detection of periodic defects that are easily identified as residual photoresist, as well as random defects, was performed on both a Tencor Surfscan 7700 and a Surfscan 6200. Residual metallic contamination was quantified by either total x-ray fluorescence (TXRF) spectroscopy or heavy ion backscattering (HIBS) spectroscopy. HIBS is most effective for detecting high-Z elements, and as a result was used sparingly during this study. Finally, residual organic contamination was quantified by using time-of-flight secondary ion mass spectrometry (TOF-SIMS). To quantify the TOF-SIMS data, organic species peak heights were normalized to the abundant and constant  $^{28}\text{Si}$  peak. TOF-SIMS and TXRF were performed on one wafer per experimental split. TXRF was performed on a single spot, and TOF-SIMS was performed on three spots per wafer.

### Cleaning Experiments

Wafers were measured on a Tencor Surfscan 7700 immediately after the plasma ashing step. Where defect levels were sufficiently low, high sensitivity measurements (light point defects  $> 0.15 \mu\text{m}$ , latex sphere equivalent) were also made on a Surfscan 6200. Following the initial measurement, samples were processed through various post-ash cleaning chemistries. Table I provides details on the individual cleaning chemistries and process conditions that were used throughout this study. Post-clean light scattering defect measurements were performed prior to off-line analytical work for measuring organic and metallic contamination.

The cleaning splits were chosen to evaluate the efficacy of individual sulfuric acid based chemistries, as well as the overall efficacy of cleaning sequences that include both sulfuric acid chemistries and RCA processes. These splits were conducted in three separate cleaning experiments, using a minimum of three wafers per split.

**Table I. Parameters for individual process steps**

Chemistry	Mixing Ratio	Temperature (°C)	Process Time (min.)
$\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (SPM)	5:1	90	10
$\text{H}_2\text{SO}_4:\text{HNO}_3$ (SNM)	10:1	150	10
$\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (SC-1)	1:4:64	45	10
$\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (SC-2)	1:1:6	45	5
$\text{HF}:\text{H}_2\text{O}$ (HF)	1:15	24	0.5

## RESULTS AND DISCUSSION

In the initial screening experiment, wafers were photopatterned with a reticle test structure mask, implanted with arsenic at various doses, and stripped using a non-optimized ashing recipe. Following the ash, wafers were processed through a 5:1 SPM chemistry. This resulted in no substantial change in light scattering event count, as measured on a Tencor Surfscan 7700. Following the SPM clean, a dilute SC-1 megasonic clean was also performed. This produced a substantially cleaner surface, although numerous defects associated with certain mask structures still remained. Representative wafer maps are shown in Figure 1. Scanning probe microscopy analysis of the wafers following the ash revealed that the defects that remain were indeed artifacts of the original patterned photoresist. The morphology of these defects was similar to that which has been reported in the literature previously for ashed photoresist samples. (4). Carbonization of photoresist (e.g., a C/O ratio greater than 10) has been reported to render SPM chemistries ineffective (3). Post-ash photoresist presumably possesses a high C/O ratio, and therefore may be inert to oxidizing chemistries. The physical action of megasonics was significantly more effective than the purely chemical action of the SPM for the removal of bulk ash residue.

The remaining experiments were performed on a short loop product that was processed through n-well photolithography and implant, followed by an optimized ashing step. This short loop structure was used to evaluate post-ash cleaning on samples that possessed a realistic contamination challenge.

First, the post-ash cleaning efficacy of 5:1 SPM was compared to that of 10:1 SNM. These cleans were found to be equally efficacious. Both cleans performed very well with respect to metallic contamination removal; neither chemistry performed well with respect to particulate or organic contamination removal. Other researchers have also found that SPM, as a stand-alone process for post-ash cleaning, does not perform well with respect to particle contamination (5). Results for residual metallic contamination levels are shown in Figure 2. It is interesting to note that metallic contamination levels on the control group (wafers that received no subsequent clean following the ash) are relatively low. By comparison, surface concentrations in the mid  $10^{11}$  atom/cm<sup>2</sup> range for transition metals such as iron are not uncommon following an SC-1 clean (6).

Next, experiments were performed to determine if redundant cleaning operations following the photoresist ash step provide any benefit. The cleaning sequence that is currently used for post n-well implant and photoresist ashing of a 0.5  $\mu$ m CMOS technology at Sandia Laboratories was used as a benchmark for these studies. This sequence, which includes numerous sulfuric acid based cleans, RCA cleans, and an HF dip, was adopted from a product flow used by a major U.S. chipmaker. Figure 3 shows Surfscan light point defect (LPD) data for redundant cleaning steps. The first two sulfuric acid based cleans are fairly ineffective. The LPD count is significantly reduced when

RCA and HF cleans are included in the process sequence. The TOF-SIMS data, shown in Figure 4, show a similar behavior -- the sulfuric acid based cleans appear to be ineffective for removal of organic material (m/z 41-74), but the addition of RCA/HF steps significantly reduces the amount of organic contamination detected on the surface. TXRF analysis of redundant cleaning steps was somewhat ambiguous, presumably due to an environmental contamination source. This analysis was repeated during the study of simplified process flows, discussed below.

Finally, it was of interest to determine if a simplified process flow has any measurably deleterious effects. Based on the results from the previous experiments, simplified process flows were created and compared to the benchmark cleaning sequence. LPD data for simplified product flows are shown in Figure 5. Although the benchmark cleaning sequence exhibited the lowest LPD count, there was no substantial difference between the splits (excluding Split #0, which received no post-ash clean), and all of the cleaning splits reduced the LPD levels to the original levels following oxide growth, or lower. The metallic contamination data, shown in Figure 6, showed that the most simplified split (Split #1b in Figure 6) possessed a slightly higher zinc level than the other splits. Calcium contamination levels (not shown in Figure 6) were also slightly elevated in the most simplified cleaning split. Iron contamination levels were below the practical lower detection limit in all of the cleaning splits. The other transition metals were all near or below the detection limit for each of the cleaning splits. Finally, TOF-SIMS data, shown in Figure 7, indicate that all of the cleaning splits performed equally well for the removal of organic contamination. Aluminum, not shown with these data, was slightly elevated in the most simplified cleaning split (Split #1b in Figure 7).

## CONCLUSIONS

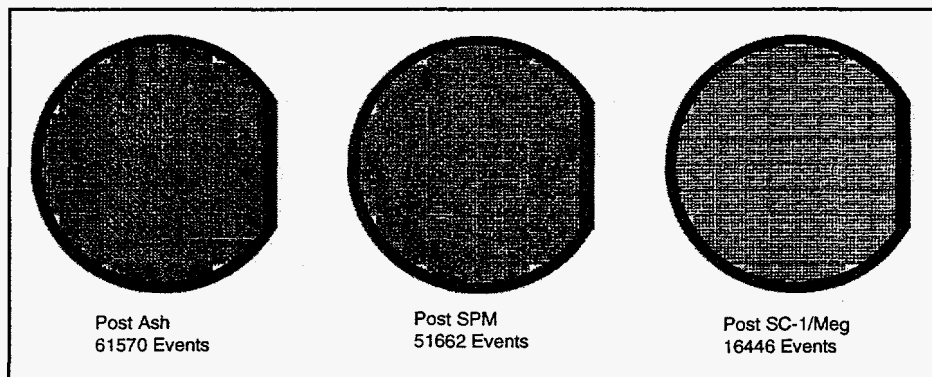
The considerations involved in optimizing post-ash cleaning are substantially different than those used to optimize photoresist stripping. For post-ash cleaning, it is the removal of trace metallic contamination, particulates, and molecular organics that is desired, rather than the removal of bulk heavy organic material. Sulfuric acid based chemistries are often used following photoresist ashing, and in fact, are often performed repetitively and with other cleaning chemistries. Because these cleans are effective for removing metallic contamination, they provide benefit for post-ash cleaning. However, such benefit may also be derived by using mineral acid cleaning chemistries such as HF, HCl or SC-2 for metallic contamination removal. Redundant cleans however, do not appear to have any added value. Simplified process flows that either reduce the number of sulfuric acid based cleans, or eliminate them entirely, appear to be viable alternatives for cleaning wafers after ashing hardened photoresist.

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**Figure 1. Tencor Surfscan 7700 event maps following photoresist ash (non-optimized), SPM processing, and dilute SC-1 with megasonics.**



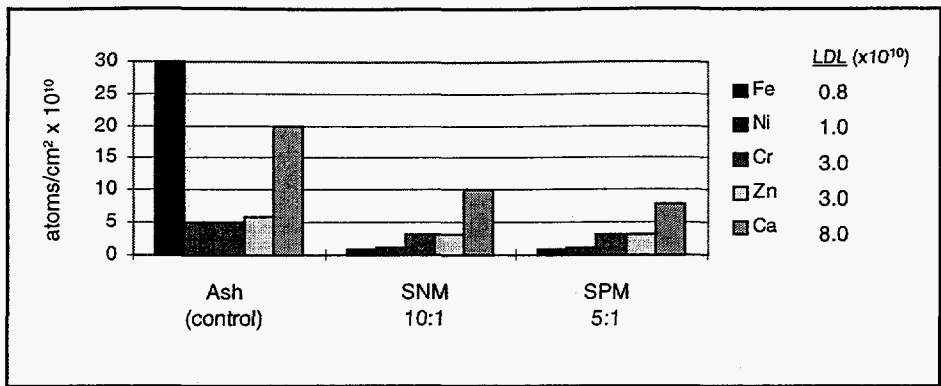


Figure 2. Metallic contamination following photoresist ash, sulfuric-nitric mixture, and sulfuric peroxide mixture processes (LDL = Lower Detection Limit).

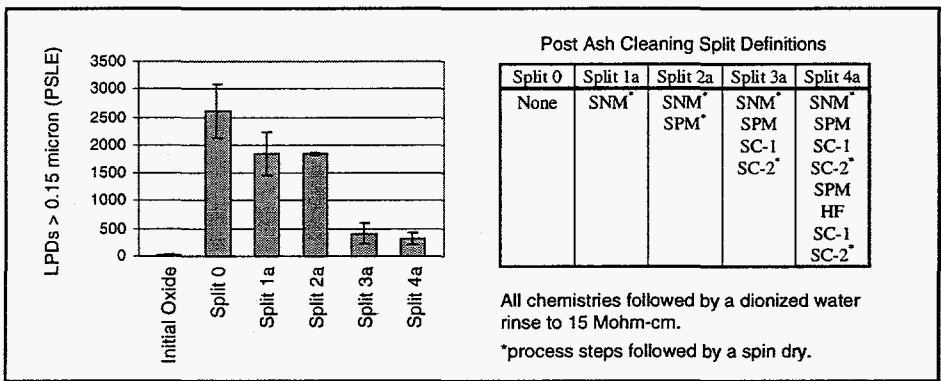


Figure 3. Effect of redundant cleaning on LPD count.

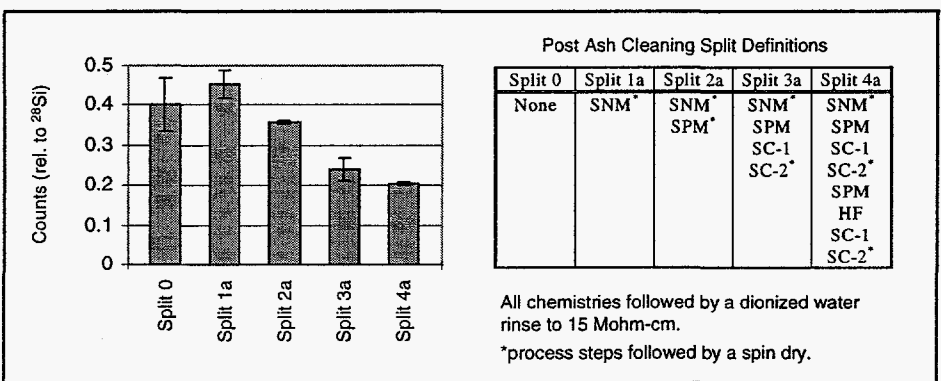


Figure 4. Effect of redundant cleans on organic contamination levels.

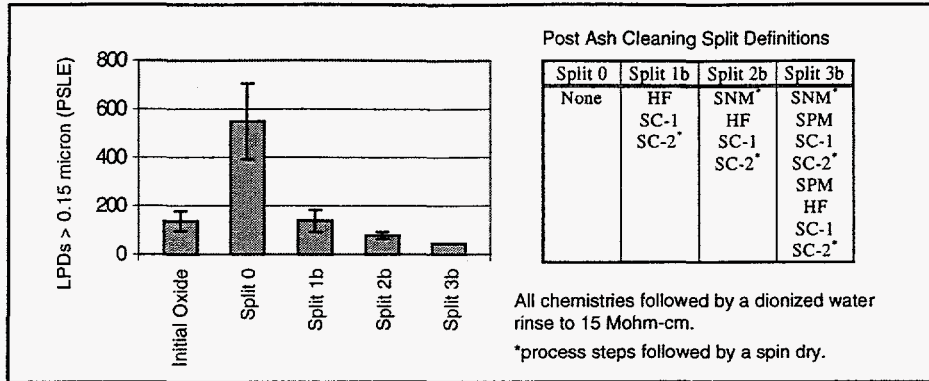


Figure 5. LPD counts after simplified clean sequences (splits 1b and 2b).

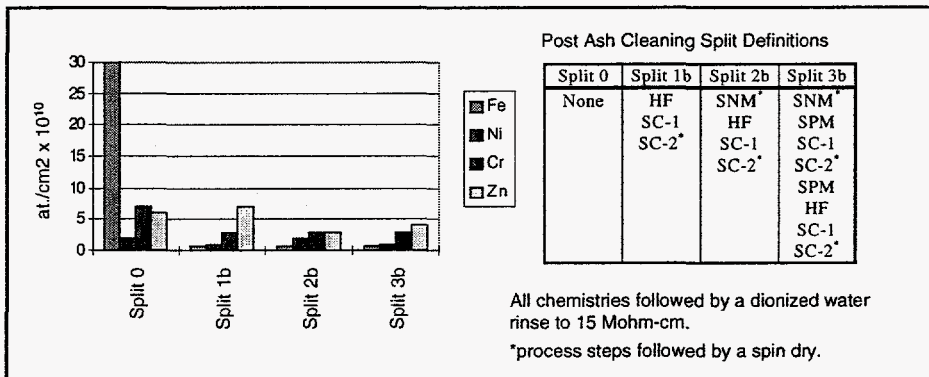


Figure 6. Metallic contamination levels after simplified clean sequences (splits 1b and 2b).

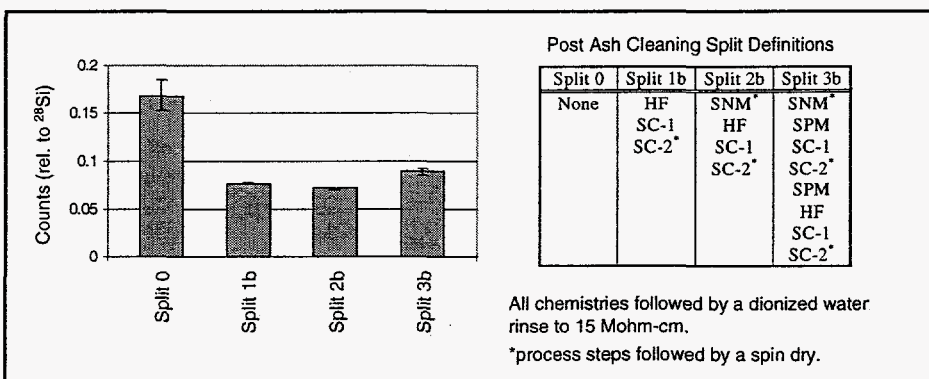


Figure 7. Organic contamination levels after simplified clean sequences (Splits 1b and 2b).