MICRO
Defect Reduction and Yield Enhancement Strategies
for Semiconductors and Advanced Microelectronics

Removing postash polymer residue from BEOL structures using inorganic chemicals

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A research project investigates the use of a sulfuric acid/peroxide/hydrogen fluoride mixture in place of organic chemicals to remove postash polymer residue from BEOL structures.

A*s the semiconductor industry* continues to expand design and process boundaries, especially at cutting-edge device nodes below 0.1 µm, IC manufacturers and capital equipment vendors have been under considerable pressure to develop new and cost-effective process methods to meet the new challenges. The transition from 200- to 300-mm wafer processing has compounded this problem. New tool sets must be developed, and either 200-mm processes must be adapted to the demands of 300-mm manufacturing or completely new processes must be designed. Innovative applications that offer IC manufacturers value-added solutions must be developed as the demands of semiconductor processing increase.

Among the many challenges facing the semiconductor industry are those associated with postash polymer residue removal in both front-end-of-line (FEOL) and back-end-of-line (BEOL) processing. In BEOL processing, the removal of residue from both metal lines and contact/via structures is critical. This article discusses research conducted by SEZ on the development of a novel inorganic chemistry for removing postash polymer from BEOL structures.

Reducing Chemical Costs

The main impetus for exploring whether inorganic chemicals can be used to remove polymer residue from BEOL structures came from a major IC

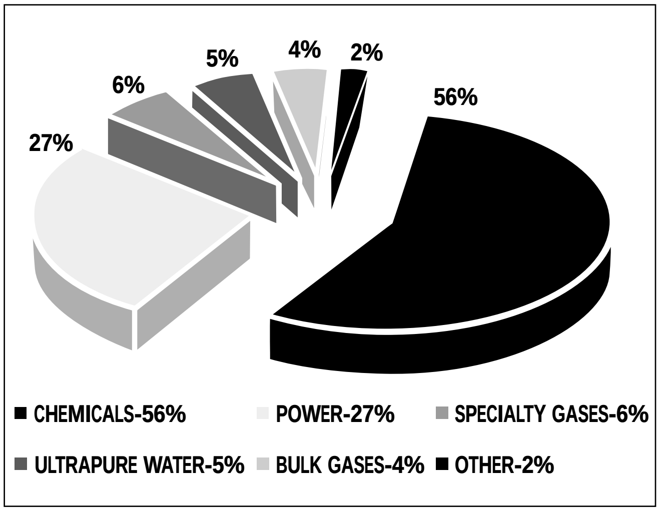


Figure 1: Breakdown of running costs associated with semiconductor manufacturing expenditures.

manufacturer in the process of shifting from 200- to 300-mm DRAM production. The manufacturer's primary concern was how to make the transition to 300-mm production while maintaining costs at or close to existing 200-mm levels. That is no easy feat, given the initial capital construction and equipment costs of shifting to 300-mm production. As part of an overall cost-reduction strategy, the company has evaluated how to decrease manufacturing costs, which requires a reduction in both FEOL and BEOL costs per die and, wherever possible, an increase in effective yields.

The cost breakdown in Figure 1 reveals that fabs spend more money on chemicals than on any other items of daily use. Although several successful chemicals are available for postash residue removal, all of them have similar problems: First, the use of organic compounds in residue-stripping chemicals increases production and disposal costs. Second, organic chemicals are environmentally unfriendly, prompting many IC manufacturers to find ways to limit their use. Third, the vast majority of residue-stripping chemicals on the market are proprietary, which can lead to higher costs and supply bottlenecks. Because many such products are available from only one vendor, fabs can be crippled when supplies run short, as occurred with hydroxylamine last year.

These issues have spurred the search for a complete postash residue application combining spin processing and a nonproprietary dilute inorganic mixture containing chemical components readily available in any fab.

Using a DSP Spin-Processing Technique to Remove Postash Residue

Some companies have attempted to use dilute inorganic acid mixtures to remove polymer residues.[1,2] In one case, a manufacturer tried to use a conventional wet bench to remove polymer from both metal and contact/via structures with a dilute sulfuric acid/hydrogen peroxide (DSP) mixture containing parts-per-million concentrations of hydrogen fluoride (HF). It was discovered that the effectiveness of this mixture depends on HF concentration. When used in a wet bench, there is only a 2-ppm process window for HF concentration. While insufficient cleaning takes place below the lower control limit, excessive etching of the underlying material takes place above the upper control limit. Both of these effects result in poor electrical performance.

Despite the difficulties of using DSP on a wet bench, the results of these experiments showed promise. After further investigation, it was decided to try DSP on a spin processor to determine whether spin-processing fluid dynamics avoid the problems associated with the classical wet bench. Experimental work performed at SEZ's Phoenix research lab and at customer sites demonstrated that a special DSP mixture known as DSP+ from Kanto (Portland, OR) can successfully remove postash polymer residue from wafers and that when used in a spin processor, the process window of that mixture is significantly larger than when used on a wet bench. When HF concentrations of between 5 and 1000 ppm were investigated during preliminary work, it was determined that the allowable

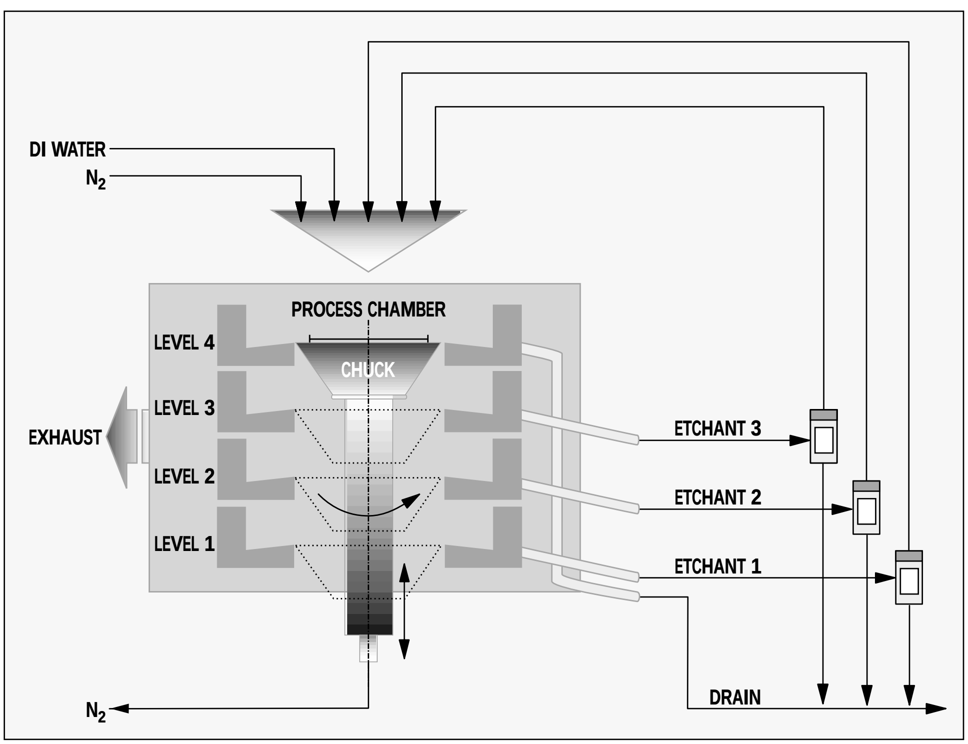


Figure 2: Schematic drawing of the spin-processor chamber.

HF concentration on the spin processor is about two orders of magnitude larger than that on a wet bench.

Equipment and Process Development

The process chuck of the spin processor used to conduct the HF tests relies on Bernoulli's principle to fix the wafer at a constant distance from the chuck surface on a bed of nitrogen (N_2). The wafer is held in place by six edge-contact-only pins that make contact at the wafer bevel with sufficient force to center the wafer on the N_2 bed and hold it in place while the chuck rotates. The chuck rests in a process chamber, as depicted in the schematic drawing in Figure 2.

The process chamber can have up to four independent process levels, three of which dispense different process chemicals (or chemical blends) and one of which is dedicated to DI-water rinsing and nitrogen drying. The process chuck rotates clockwise or counterclockwise within the process chamber while the medium is dispensed. The different chemistries are dispensed onto a spinning wafer at three dedicated process levels, allowing for tight process control and eliminating the risk of chemical cross-contamination.

Work on the use of inorganic chemicals for postash polymer removal has been conducted at facilities in Europe, while ongoing process development, including experiments with the DSP mixture, has been carried out at SEZ (Phoenix) and IC fabs in the United States. Process development has involved a variety of different BEOL device structures from several manufacturing partners. Wafer samples were provided by major U.S. and European manufacturers.

Initial tests performed on a 200-mm spin processor operating at room temperature focused on the cleaning of metal lines. These tests quickly revealed that it is possible to clean such structures in 30 seconds in a single-step process. Figures 3a and 3b are scanning electron microscope (SEM) images of an unidentified standard metal structure before and after cleaning with the DSP mixture. The large amounts of postash residue polymer evident in Figure 3a, especially on the large exposed areas off the metal line, are no longer present in Figure 3b.

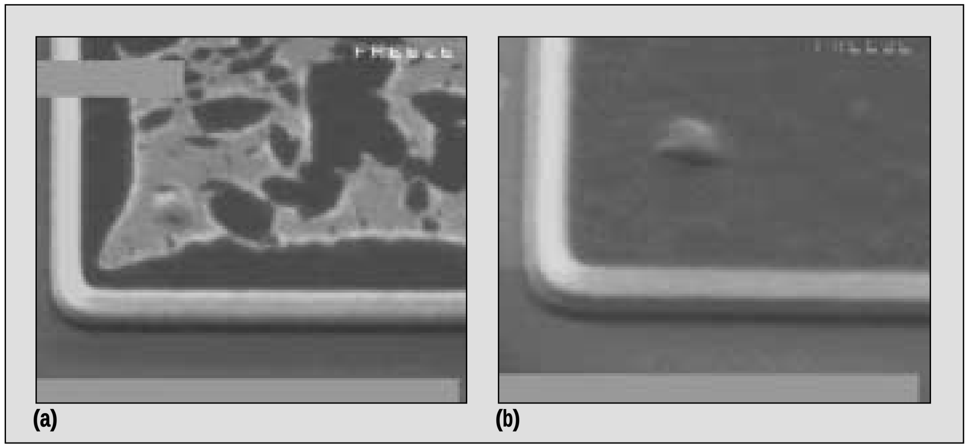


Figure 3: SEM images of a standard metal structure (a) before and (b) after cleaning with the DSP mixture.

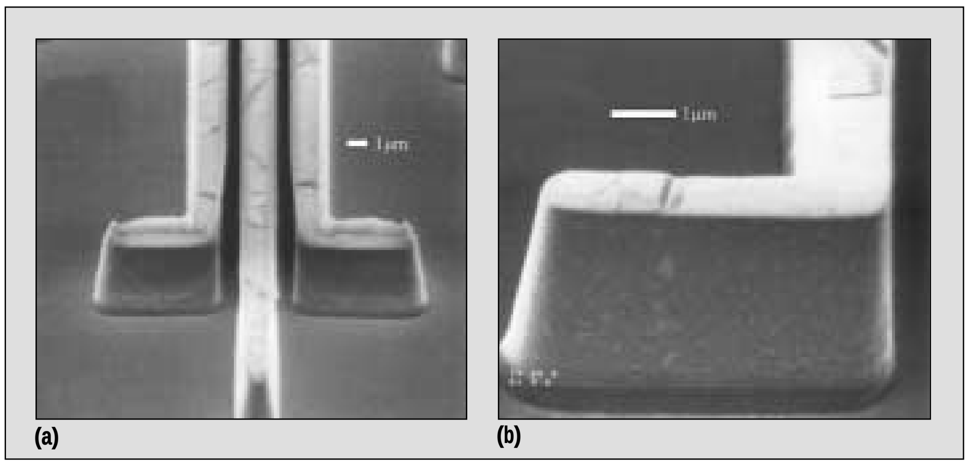
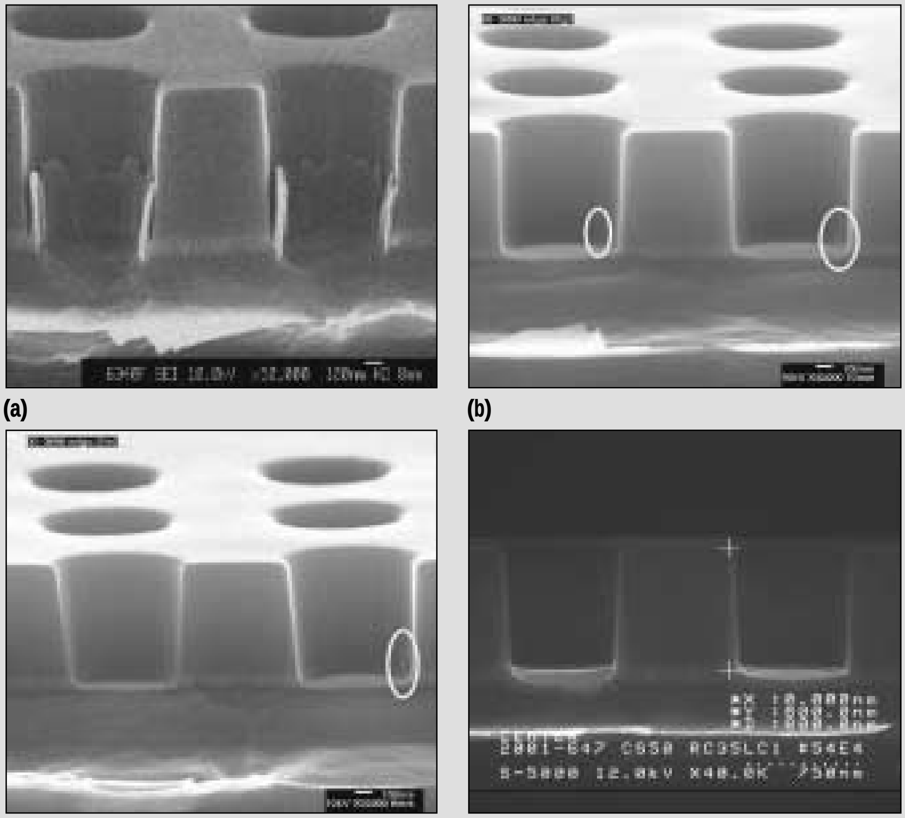


Figure 4: SEM images of a metal 6 stack (a) before and (b) after exposure to the DSP mixture.

Similar cleaning results were observed on other aluminum/copper structures. Figures 4a and 4b are SEM images of a metal 6 stack before and after exposure to the DSP mixture. In this example, the residue was removed in 25 seconds without the aluminum lines being etched.

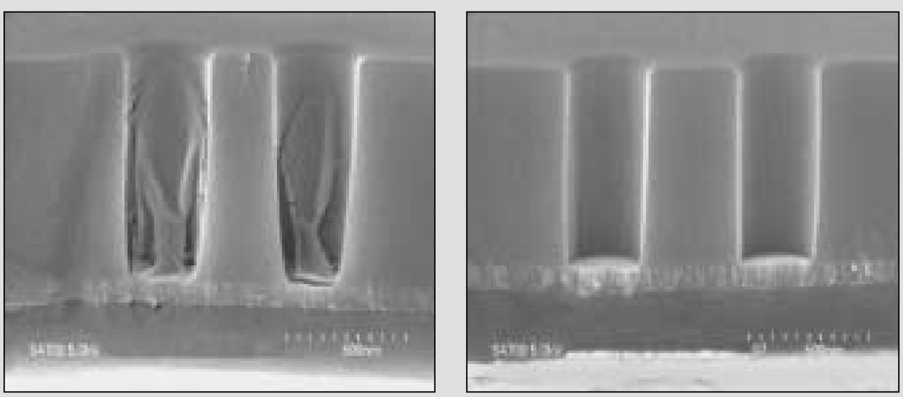
The DSP mixture also has proven successful in cleaning contact/via structures. However, the process protocols used on such structures are very different from those used on metal structures. Initially, contact/via structures were processed for up to 120 seconds, with less than conclusive results. Consequently, a series of design-of-experiment (DOE) process runs were performed to determine the optimum process conditions for cleaning such structures. The SEM images in Figures 5a through 5d present a synopsis of some of these experiments conducted on contact/via 6 structures, the most difficult structures to clean. The image in Figure 5a shows such a structure before residue cleaning, while the images in Figures 5b, 5c, and 5d depict different structures processed under differing conditions after the initiation of residue cleaning.

Based on the knowledge gained from these experiments, further optimizations were performed in facilities in Europe and Asia. Figures 6a and 6b are images of a contact/via



(a) (b) (c) (d)

Figure 5: SEM images of contact/via 6 structures: (a) before cleaning; (b, c, and d) different structures processed under differing conditions after the initiation of residue cleaning.



(a) (b)

Figure 6: SEM images of a contact/via 6 structure cleaned with the DSP mixture for 90 seconds.

structure cleaned at SEZ's European lab in Villach, Austria. This structure was processed in 90 seconds. Although the process layer is unidentified, the conditions under which it was processed are typical for contacts/vias 1 through 4.

These experiments demonstrated that the application of the DSP mixture on a spin processor removes postash residue from wafers. However, because a variety of commercially available products also can be used on spin processors to remove polymer residues, it was necessary to compare the effectiveness of the DSP mixture with that of existing residue strippers containing organic chemicals. Although further testing is being conducted, some preliminary findings are available.

To determine the superior method for cleaning metal structures, first the DSP mixture and then a proprietary ammonium fluoride–based chemistry were used to strip wafers in a spin processor at temperatures ranging from 20° to 40°C. All other process conditions remained essentially the same throughout the experiment. The results of the test are shown in Figure 7. Figure 7a is an SEM image of a metal structure before cleaning, Figure 7b is an image of a metal structure after cleaning with the DSP mixture, and Figure 7c is an image of a metal structure after being cleaned with the ammonium fluoride–based chemistry. While the test demonstrated that both chemistries can be used successfully on a spin-processing system to clean metal structures, the chemistries' processing times differ markedly. The DSP mixture can remove surface residues in half the time it takes for the proprietary ammonium fluoride–based chemistry to remove residues.

Electrical Characterization

Scanning electron microscopy is typically used as a first-pass metrology test to determine the effectiveness of techniques for removing postash residues. However, the only truly reliable method for determining the effectiveness of cleaning techniques is to test the electrical characteristics of processed structures. Electrical characterization has been used extensively throughout the development of the DSP+ application.

The devices shown in Figure 7 underwent early electrical tests, the results of which are presented in Figure 8. The snake continuity (resistivity) measurements shown in that figure

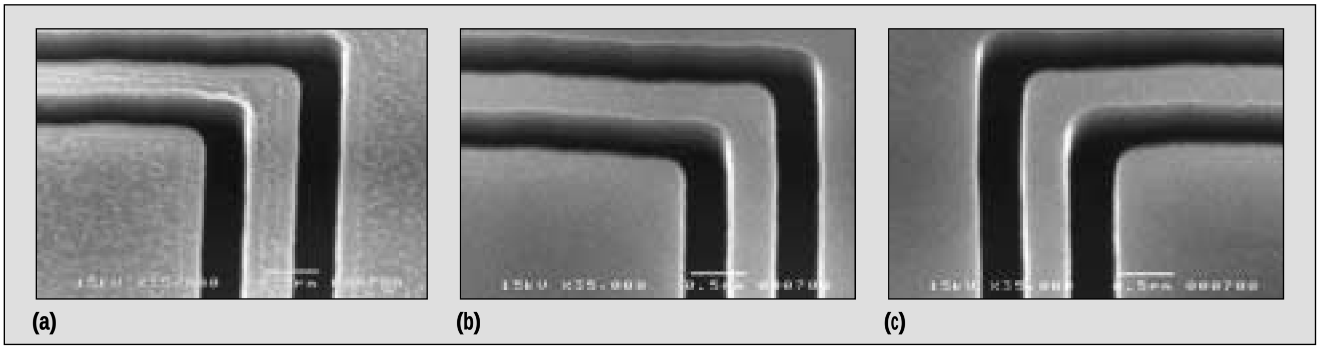


Figure 7: SEM images of a metal structure (a) before cleaning, (b) after being cleaned with the DSP mixture, and (c) after being cleaned with the ammonium fluoride–based chemistry.

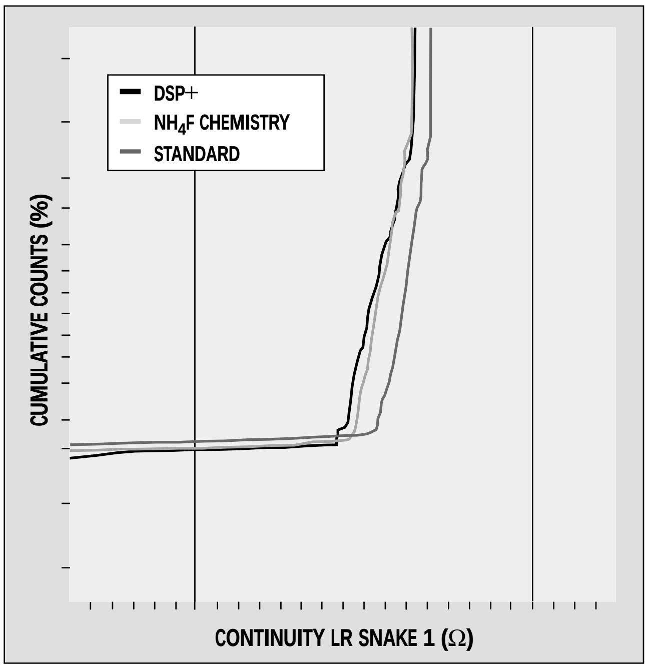


Figure 8: Electrical tests of devices presented in Figure 7. Snake continuity measurements demonstrate that the use of the DSP mixture produces structures with lower resistivity than the process of record.

demonstrated that the use of the DSP mixture produces structures with lower resistivity than the hydroxylamine-based process of record (POR). While the DSP mixture seemed to perform slightly better than the proprietary ammonium fluoride–based chemistry, the results were not yet statistically significant. However, the process throughput of the DSP mixture was greater than that of the proprietary ammonium fluoride–based chemistry.

Electrical (resistivity) data from subsequent, more comprehensive electrical tests on contacts/vias 1, 2, and 6 and metal 6 structures cleaned with the DSP mixture are typically comparable to or better than those from similar structures cleaned with the POR hydroxylamine-based chemistries (within 3σ error). The results of many electrical tests indicate that dispensing the DSP mixture on a spin-processing system offers tighter process control than does the POR compound.

A device's electrical characteristics are a product not only of the efficiency of the cleaning chemistry but also of the effect of the chemistry on the underlying materials, since any loss of critical dimension affects a device's electrical properties. While it is thought that sulfuric acid/peroxide/HF mixtures, even if diluted, damage metal surfaces, an analysis of device layers' etch characteristics and supporting electrical data demonstrate that the use of the DSP mixture in a spin processor is safe. Table I summarizes the etch characteristics of selected layers after being cleaned with the DSP mixture.

Conclusion

In response to rapid technological changes in the semiconductor industry, a cleaning application has been developed that uses a dilute, entirely inorganic mixture of mineral acids and peroxide in combination with spin-processing technology to remove postash polymer residue from wafer surfaces. The DSP mixture is an effective alternative to residue strippers containing conventional organic chemicals, which involve proprietary, supply, and waste-disposal overhead costs. The process window of the DSP mixture, when used in a spin processor, is two orders of magnitude larger than when used in a wet bench. Coupled with its short process time, its relatively low cost of ownership, and its enhanced electrical characteristics, the chemistry has the potential to replace conventional strippers in high-volume manufacturing.

As a result of process refinements to optimize the chemistry's throughput without jeopardizing performance, metal lines can be cleaned in 30 seconds and contact/via structures

Device Layer	Amount of Material Removed (Å)	Etch Time (sec)
TEOS	<2	120
HDP TEOS	<1.5	120
PVD Ti	<0.25	90
IMP Ti	<1.1	90
PVD TiN	<44	120
Al/Cu (0.5%)	<65	90

Table I: Summary of etch characteristics of selected device layers.

in less than 100 seconds. Experiments demonstrated that the chemistry can clean metal layers 1 through 6 and contact/via layers 1 through 6 successfully. It was determined during testing that using ozonated DI water has no significant effect on process performance. During these experiments, all processes were run at room temperature. Ongoing tests are being performed to determine the effectiveness of using the DSP mixture at higher temperatures. Moreover, the effect of the DSP mixture on die yield is under investigation.

References

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