

Using a cryogenic aerosol process to clean copper, low-k materials without damage

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For several years, the semiconductor industry has been using cryokinetic cleaning with a solid aerosol derived from argon and nitrogen to remove particle defects from the wafer surface

Tests demonstrate that an aerosol cleaning technology using argon and nitrogen is compatible with copper and low-k processes and effective at removing associated particle defects.

during aluminum metallization and interconnect processing.¹⁻³ The cryokinetic cleaning technology is a completely dry, gas-phase, nonreactive process that does not damage sensitive films and has a minimal environmental impact. In contrast, traditional particle removal methods involve potentially damaging megasonic energy and

reactive liquid chemicals that can change film properties and require extensive waste treatment.

IC manufacturers have found the argon/nitrogen aerosol process easy to implement in the production line. The process has been implemented in copper/low-k dielectric processing on 200- and 300-mm production lines. After describing the cryokinetic aerosol process and

briefly discussing its successful use with aluminum/TEOS and high-density plasma deposition processes, this article focuses on the suitability of the cleaning technique in copper and low-k applications. Various tests have demonstrated that the technique is highly efficient at removing defects that remain after copper chemical-mechanical

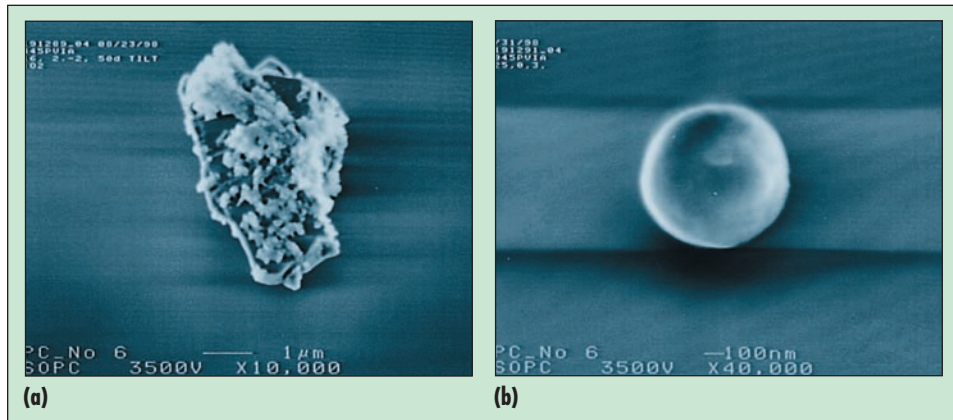


Figure 1: Micrographs showing typical defects remaining on the wafer surface after aluminum/TEOS via patterning. These defects were composed of (a) silicon dioxide and (b) aluminum.

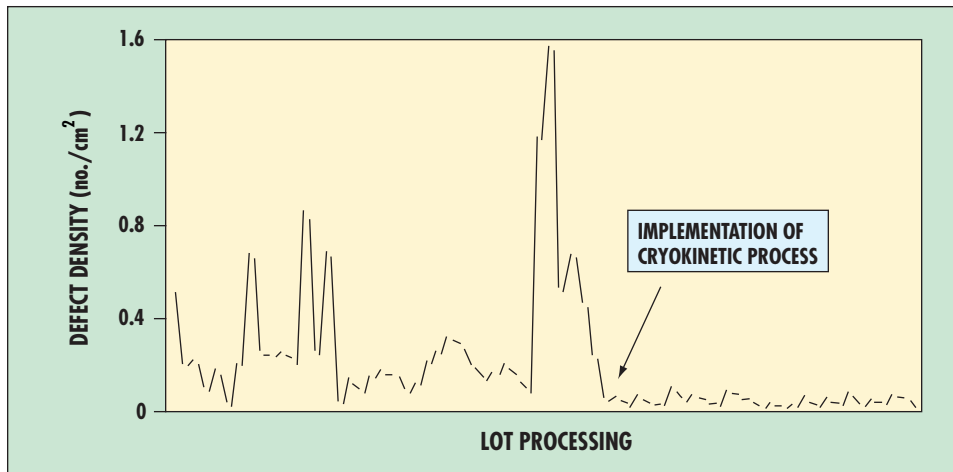


Figure 2: Trend chart showing the significant reduction of in-line TiN barrier defect density at the second via level after implementation of the cryokinetic aerosol cleaning process.³

polishing (CMP) without affecting the properties of low-k dielectric materials.

Argon/Nitrogen Cryogenic Aerosol Cleaning

Introduced by FSI International (Chaska, MN) in 1996, the cryokinetic process uses an aerosol formed from a cryogenically cooled mixture of argon and nitrogen. A 3:1 mixture of these gases first flows into a coil immersed in a dewar of liquid nitrogen, where it is cooled and partially liquified at a temperature of ~100 K and a pressure of ~75 psia. This mixture of gas and liquid then flows through a vacuum-jacketed line into the cleaning system’s single-wafer chamber. The aerosol is formed when the mixture is dispensed from several small holes in the wall of a tube extending across the wafer surface. As the mixture flows into the vacuum chamber, the liquid portion breaks up into a fine mist, which quickly solidifies owing to evaporative cooling in the vacuum environment. The resulting submicron aerosol crystals can reach speeds of up to 100 m/sec.⁴ When a heated wafer is scanned under the aerosol-dispensing tube, the crystals dislodge sur-

face particles, which become entrained in the cold gas stream by viscous and thermophoretic forces.^{5,6} Gas flow in the chamber is carefully engineered and controlled to eliminate recirculation zones so that once the particles are detached and entrained, they are carried into the exhaust.

Because of the low pressure in the vacuum chamber, the solid aerosol crystals pass directly back into the gas phase without becoming liquid. Only inert gas and solid crystals contact the wafer surface; therefore, the cleaning process leaves no watermarks and does not chemically alter the materials on the wafer. Several studies have shown that the process also does not cause roughening, surface damage, or surface charging.¹

It also has been demonstrated that the cleaning process is particularly useful in cleaning the surface of interlevel dielectrics after via patterning in aluminum/TEOS interconnect processing.³ In one study, high levels of defects on the surface of the dielectric layer were causing electrical defects (shorts and opens) in

the next metal layer. These defects included oxide flakes and metal particles (see Figure 1). After implementation of the cryokinetic clean, in-line defectivity measurements

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improved dramatically, as illustrated in Figure 2, and final electrical yields improved by as much as 4%.

In another study, the cleaning process was used after metal patterning. Patterns of 0.28- μ m lines with 0.32- μ m spaces and 0.32- μ m lines with 0.28- μ m spaces were processed through metal etch and resist ash prior to cleaning with a

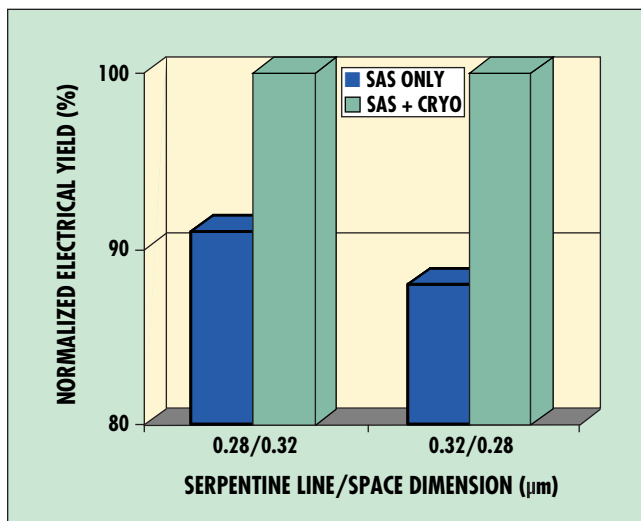


Figure 3: Comparative normalized electrical yields for serpentine comb aluminum/TEOS structures processed using a semiaqueous solvent (SAS) clean alone and the SAS clean followed by the cryogenic aerosol clean.

semiaqueous solvent (SAS) process only or the SAS chemistry followed by the aerosol process. Figure 3 shows the electrical yield improvement on serpentine comb structures that was realized with the cryogenic aerosol process. A normalized improvement of 10% was seen after aerosol cleaning.

In addition, it has been demonstrated that the cryogenic aerosol cleaning process effectively removes particles remaining after high-density plasma oxide deposition. Figure 4 compares the defect counts on three wafers that were cleaned using the cryokinetic process with those on a wafer cleaned using a traditional DI-water scrubber. Both pre- and post-cleaning counts are included, along with data on the percentage of defects removed. It is clear from this figure that the cryogenic process removes this type of particle more effectively than does a scrubber.

Copper/Low-k Dielectric Cleaning

The adoption of copper and low-dielectric-constant materials for IC interconnection layers has introduced a new set of potential particle defects and cleaning challenges. The efficiency of standard chemical cleaning techniques is often improved at the cost of an increased etching rate for both dielectric films and metal lines. While such overetching leads to lower line resistance and a reduction of shorts in traditional, subtractive-etch aluminum line patterning, it has the opposite effect in the damascene patterning methods used for copper. Overetching during the

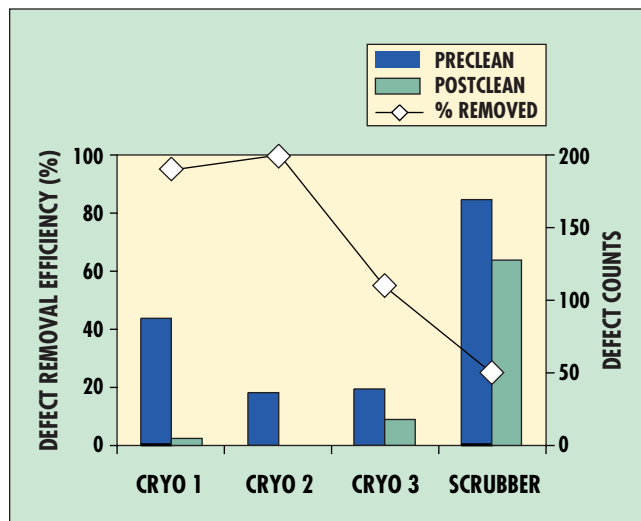


Figure 4: Data on the removal of >0.2-μm particles after high-density plasma silicon oxide deposition. Three wafers were processed using the cryogenic aerosol clean and one using a DI-water scrubber.

cleaning of damascene trench structures leads to wider features being filled with copper, lower resistance, and a higher occurrence of shorts.

The adoption of copper and low-k materials has introduced a new set of potential particle defects and cleaning challenges.

In addition, when exposed to cleaning chemicals, the new low-k materials appear to be more susceptible to changes in chemical and structural properties than the dielectrics commonly used with aluminum. These porous, less-dense materials tend to etch faster in traditional cleaning chemistries

Test Sample	Thickness (Å)	Refractive Index
Test 1: Blanket films from source 1		
Porous MSQ A after deposition	4125.4	1.257
Porous MSQ A after two aerosol cleaning passes	4124.4	1.257
Porous MSQ B after deposition	4127.0	1.258
Porous MSQ B after four aerosol cleaning passes	4125.6	1.258
Test 2: Blanket film from source 2		
Porous MSQ after deposition	5710.0	1.263
Porous MSQ after photoresist ashing	5314.0	1.281
Porous MSQ after ashing and chemical clean	4746.0	1.245

Table I: Ellipsometry measurements on porous MSQ films.

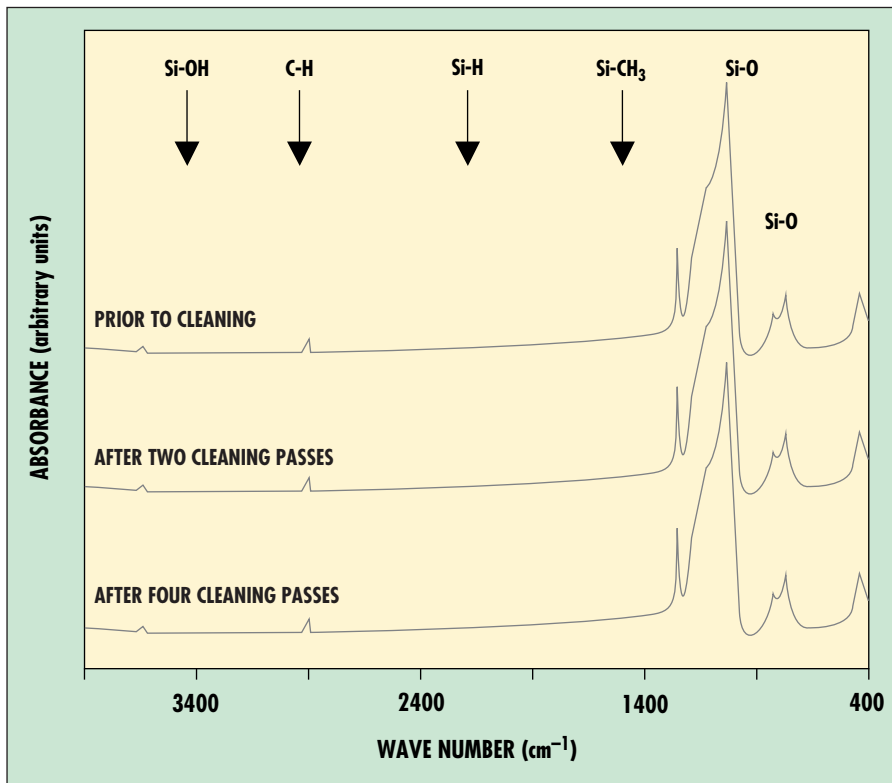


Figure 5: Comparative FTIR spectra for porous MSQ before and after cryogenic aerosol cleaning. The locations of important absorption peaks are indicated.

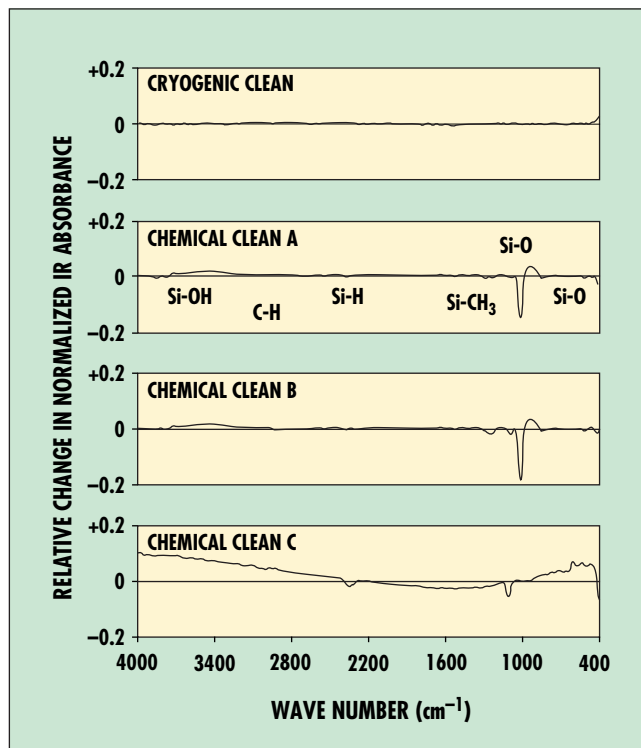


Figure 6: Comparative FTIR difference spectra for porous MSQ cleaned with the aerosol process or one of three liquid chemicals.⁹ After the spectra have been normalized, the preclean value is subtracted from the postclean value.

and also undergo structural changes that alter their overall dielectric constant. Because the open spaces of porous low-k materials can hold on to chemicals and moisture, high-temperature vacuum baking may be required to recover their low-k properties. Finally, copper interconnect structures are vulnerable to photo-induced copper redeposition if exposed to a light source while in contact with aqueous cleaning solutions.^{7,8}

All these cleaning problems can be avoided by using the argon/nitrogen aerosol method for particle removal. The cryogenically cooled, inert gas does not degrade film thickness or affect the dielectric constant of low-k materials. Several tests have demonstrated this compatibility of the cryokinetic cleaning process with copper/low-k interconnects as well as its cleaning capability.

Process Compatibility Testing.

The first tests used in evaluating the compatibility of the cleaning process with low-k materials measured

changes in film thickness and refractive index using spectroscopic ellipsometry. The measurements were taken on ultra-low-k, porous methyl silsesquioxane (MSQ) films from two sources. As shown in Table I, neither two nor four passes of the cryogenic aerosol cleaning process changed the thickness and refractive index of MSQ blanket films. In contrast, both film thickness and refractive index were significantly affected by photoresist ashing and by a standard chemical cleaning

In the argon/nitrogen aerosol method for particle removal, the cryogenically cooled, inert gas does not degrade film thickness or alter the dielectric constant of low-k materials.

process. While cryokinetic cleaning will not be able to replace these methods for removing postetch residues, it can replace the chemical cleans used to remove particle defects.

Fourier transform infrared (FTIR) absorption spectroscopy also was used to evaluate the cleaning process. In this test, infrared light is passed through the wafer (and the low-k film)

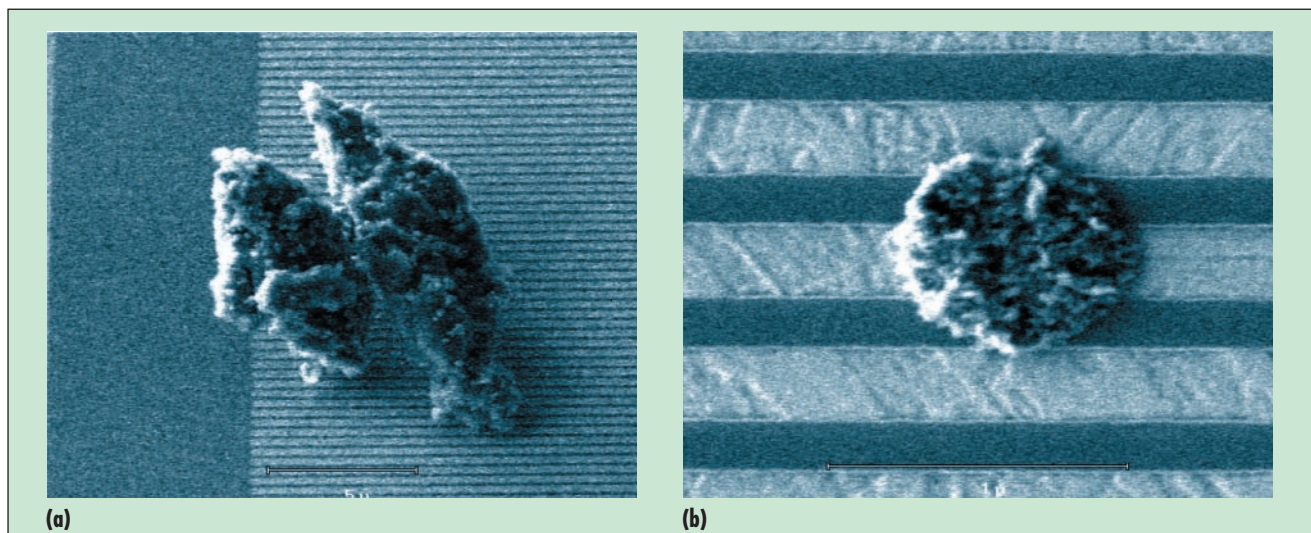


Figure 7: Micrographs showing typical defects that can be removed by cryogenic aerosol cleaning. The defect on the left is approximately 10 μm wide, while the one on the right is approximately 0.5 μm wide.

and the absorption of that light is measured as a function of wavelength. Analysis of the absorption spectra will identify specific bonding structures in the low-k film, such as Si-O and Si-CH₃. Changes in these absorption peaks following exposure to a cleaning process indicate that there has been a change in the chemical structure of the film or a loss of film thickness. Si-OH bonding, which indicates the presence of moisture in the film, also is detectable by FTIR.

Figure 5 shows the FTIR spectra for a porous MSQ film before cleaning and after exposure to two and four passes through the cryogenic aerosol cleaning chamber. All three spectra are virtually identical, indicating that the cleaning process had no impact on the chemical structure of the film.

In contrast, the difference spectra plotted in Figure 6 show that while cryogenically cleaned films remain unchanged, some common liquid-chemistry cleaning processes have a measurable effect on the chemical structure of the film.⁹ The data in this figure were obtained by first normalizing each spectra according to the range of the absorbance value and then subtracting the normalized value taken at each wavelength before cleaning from the comparable value taken after cleaning. As the figure makes clear, chemicals A and B caused a reduction in the Si-O peak height, which is indicative of a fluoride-based chemistry etching silicon oxide, and a slight increase in the Si-OH peak, indicating water adsorption. Chemical C caused a broad increase in the Si-OH and C-H bonding regions and a decrease in Si-H bonding and possibly in Si-CH₃ bonding. However, it had much less effect on Si-O bonding than the other two chemistries.

Other films, including low-k fluorine-doped silica glass, very-low-k organic-doped silica glass, and ultra-low-k porous hydrogen silsesquioxane, also were evaluated with ellipsometry and FTIR, and the results indicated that no changes were caused by the aerosol cleaning process. Because the process is dry and carried out with inert gases, it does not damage copper or low-k films.

Particle Removal Testing. Typical defects on the wafer sur-

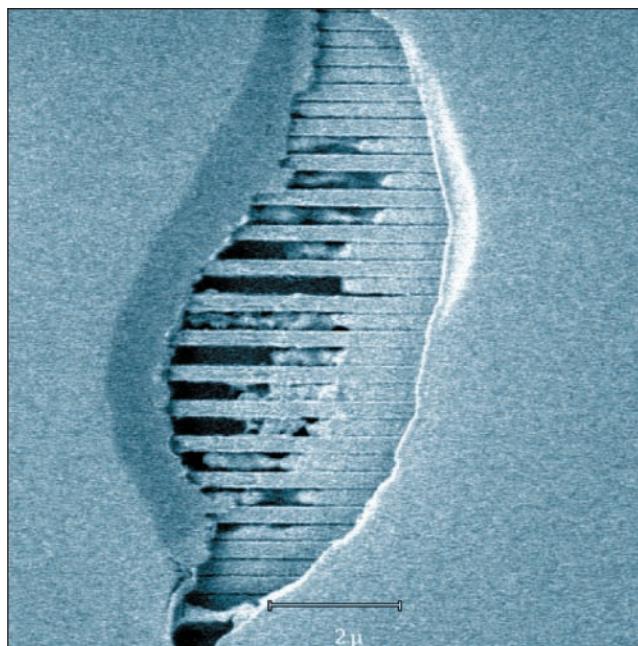


Figure 8: Micrograph showing a nonremovable defect caused by a ripout during CMP processing.

face before interlayer dielectric (ILD) deposition are shown in Figure 7. Generated during the copper dual-damascene processing sequence, these defects can range in size from several microns (Figure 7a) to only a few hundred nanometers (Figure 7b). Because they are loosely bound to or lying on the wafer surface, they are easily removed with cryogenic aerosol cleaning. The defect shown in Figure 8, which is called a ripout, is formed during CMP operations and cannot be removed through cryokinetic cleaning. However, by removing the underlying particles that lead to ripouts, the cleaning process can help prevent them from happening.

Testing has shown that cryogenic aerosol cleaning is very effective at removing many types of defects, such as those shown

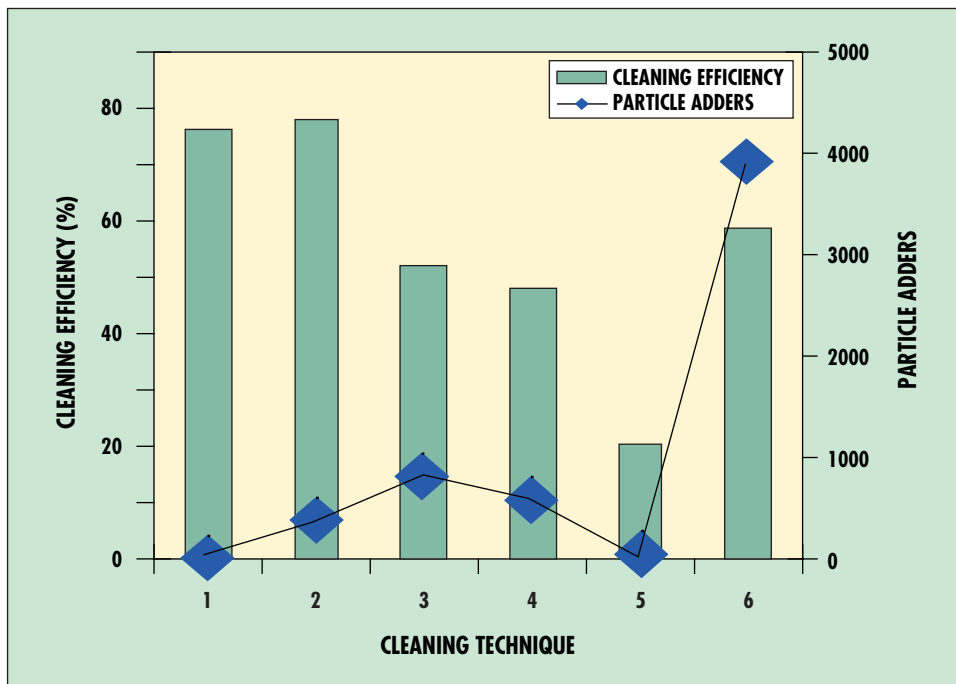


Figure 9: Comparative cleaning efficiency data for various pre-ILD cleans. Clean 1 is the cryogenic aerosol process; the other techniques are various standard wet cleans and brush cleans.⁹

in Figure 7, and can significantly improve electrical yields in an integrated copper/low-k dual-damascene process. A comparison of the technology's cleaning efficiency with that of other pre-ILD cleans is shown in Figure 9.⁹ Details of the wet cleans cannot be disclosed, but they included solvent processes with megasonics as well as scrubber techniques. It is evident from the figure that cryokinetic cleaning matches the removal efficiency of the best wet clean, but with fewer particle additions. Moreover, as previously discussed, it achieves this cleaning efficiency without etching and without causing changes to the low-k dielectric films. Based on these results, the cleaning technique already has been implemented in copper/low-k processes on both 200- and 300-mm wafers.

Conclusion

The introduction of copper and low-k dielectric materials has increased the challenges involved in removing particle defects from the wafer surface during interconnect processing. Standard liquid cleaning chemicals can attack low-k films and lead to other problems, such as photo-induced copper redeposition. Use of a cryogenic aerosol cleaning process prevents these problems. The process has been shown to be non-damaging to both dielectric films and copper and to achieve particle removal efficiencies equal to or better than traditional wet cleans.

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