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What's driving the new momentum behind cryogenic aerosols

OVERVIEW Whether the particle defects are random or due to process excursions, their removal from wafer surfaces is becoming more difficult without damaging or altering the material properties of surrounding structures. Smaller device geometries mean more fragile features, lower material-loss budgets, and overall smaller killer-defect sizes. Cryogenic aerosols are now proving to be an effective technique for removal of particles without damaging small device features, material loss, charging, changes to film characteristics, or generating chemical effluents. The net result is increased manufacturing yield.

The *2003 International Technology Roadmap for Semiconductors* (ITRS) paints a challenging picture for wafer surface preparation and yield enhancement teams [1]. Material loss budgets for the 65nm node and beyond are limited to <1Å. Smaller device geometries are limiting the use of megasonics and other energy sources in wafer cleaning and surface preparation due to the risk of damage. Incorporating new materials requires cleaning particles from hydrophobic surfaces. Many surfaces are also now becoming sensitive to water and other aqueous-based chemicals. All these challenges must be faced at a time when the killer defect size is smaller than ever.

Many IC manufacturers have limited the use of megasonics over the past two process nodes due to damage to sensitive structures, especially when the gate structure is exposed. To compensate, a significant amount of material often is etched to maintain particle removal efficiencies. While this material loss was acceptable in the past, process nodes beginning at the 90nm generation will no longer have this luxury. To fully understand the issue, it is important to note that 10–15 cleans can take place after the formation of the gate structure. If each cleaning step etched 3Å of material, a significant amount of the gate structure would be modified.

New materials, especially in the interconnect area, are also changing the wafer-cleaning landscape. In the pursuit of lower effective *k* value (dielectric constant), device manufacturers are beginning to implement carbon-doped oxides in interconnect layers. The hydrophobic nature of these compounds reduces the particle removal efficiency for conventional aqueous-based cleans. In addition, watermark-free drying after the aqueous clean also presents a challenge.

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To meet these challenges, a number of advanced IC manufacturers have turned to cryogenic aerosol, which has been used in fabs for nearly a decade to control device defectivity and enhance overall final yield [2–5]. The inert nature of cryogenic aerosol and the ability to control aerosol aggressiveness make it a viable technique to remove particles from most surfaces. Cryogenic aerosol treatment has thus been easily inserted into the process flow without concern for structure damage, film etching, material changes, watermarks, added particles, or electrical charging [6].

This article elaborates on four aspects of the cryogenic aerosol process. First, we demonstrate that the process does not alter the properties of exposed materials (e.g., porous low-*k* dielectrics). Second, we show the ability of cryogenic aerosol to clean substrates with fragile structures (e.g., sub-100nm polysilicon line structures and low-*k* damascene structures). Third, we discuss the cryogenic aerosol particle-removal efficiency when compared to conventional wet techniques, especially for hydrophobic surfaces. Finally, we demonstrate decreased defectivity and increased final yields when inserting cryogenic aerosols to control defects in 180nm and 130nm process flows.

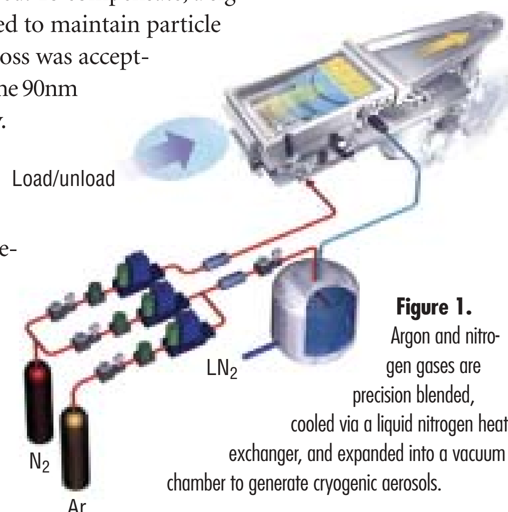

Figure 1. Argon and nitrogen gases are precision blended, cooled via a liquid nitrogen heat exchanger, and expanded into a vacuum chamber to generate cryogenic aerosols.

How cryogenic aerosols work

In the cryogenic aerosol process, argon and/or nitrogen gases are individually flow-controlled and mixed prior to entering a liquid nitrogen heat exchanger (see general system layout, Fig. 1). The temperature of the liquid nitrogen heat exchanger determines the percentage of argon/nitrogen gas that is liquefied. The process gas/liquid mixture flows to an injection nozzle and expands into the process chamber through an array of nozzle holes. Nozzle pressure is ~70psig and process chamber pressure is typically 50torr. The superheated liquid breaks apart as it enters the chamber and evaporative cooling causes the aerosols to solidify.

In the FSI ANTARES system, a 129-hole nozzle creates a continuous 300mm-wide stream of cryogenic aerosols [7]. Wafers as large as 300mm are linearly translated under the aerosol nozzle, resulting in full aerosol cleaning. Tests on heavily contaminated wafers confirm no streaking with respect to particle removal. In addition, full wafer scanning confirmed no local areas of structural damage.

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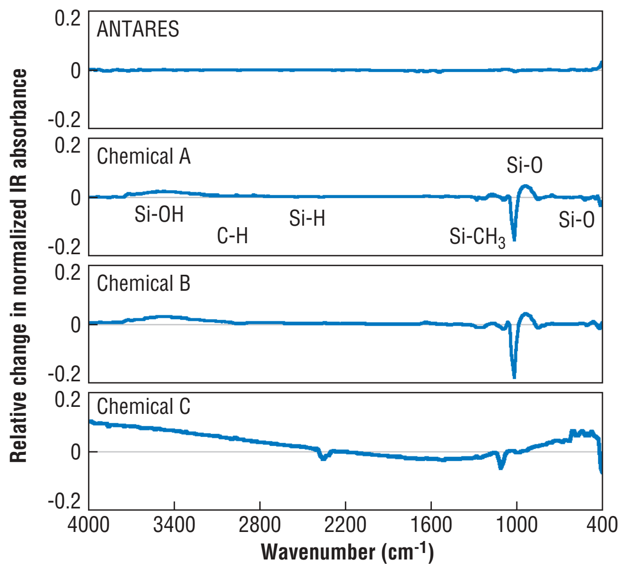

Figure 2. Post-pre FTIR difference spectra shows no change in porous-MSQ film properties for cryogenic aerosol, but significant change for standard BEOL chemistries A, B, and C [5].

The aerosol cleaning mechanism has been described in detail elsewhere [8]. Briefly, the aerosol collides with the particles on the surface and the resultant transfer of kinetic energy facilitates overcoming the adhesion energy between the particle and substrate. The suspended particles are entrained in the gas flow and removed from the process chamber via vacuum pump.

No change to exposed materials

The inert properties of argon and nitrogen provide many unique advantages when implementing cryogenic aerosols into the IC manufacturing process flow. Perhaps the best evidence of this came from a recent study where the cryogenic aerosol process was inserted into more than 30 different FEOL and BEOL steps in a 130nm logic-device flow. The net result was nearly a 13% increase in device yield and no indications of detrimental effects from the cryogenic aerosols [9].

More specific studies have shown no charging of surface features or changes to surface material properties. Charging studies have encompassed both blanket oxide films [6] and antenna arrays [10]. Neither of these studies identified any charging from the aerosol process.

Changes to material properties — such as film thickness, refractive index, and chemical bonding — have been investigated with Fourier transform infrared (FTIR) analysis. No measurable changes have been seen in film thickness or refractive index in materials such as SiLK and porous methylsilsesquioxane (p-MSQ) in these studies [11].

Figure 2 shows FTIR difference spectra for p-MSQ comparing changes to the film from exposure to cryogenic aerosols and several common liquid-chemistry cleaning processes. Before and after exposure, spectra were normalized to absorbance value and then subtracted. Chemicals A and B resulted in reduction in the Si-O peak, showing signs of silicon-oxide etching due to the fluoride-based chemistry. The increase in the Si-OH peak indicates water adsorption. Chemical C had less effect on the Si-O bonding, but did cause modifications to the Si-OH, C-H, Si-H, and $Si-CH_3$ bonds [5]. The cryogenic aerosol-exposed surface showed no changes to the chemical structure of the film.

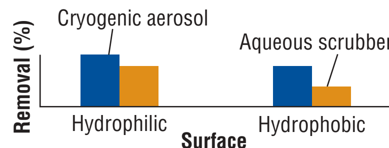

Figure 3. Particle-removal efficiency comparison of cryogenic aerosol vs. conventional aqueous-based scrub cleans. Particles were PSL spheres deposited on SiO_2 (hydrophilic) and SiN and SiOC (hydrophobic) planar surfaces [6].

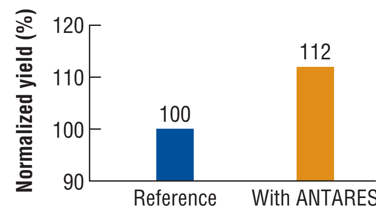

Figure 4. Normalized yield benefit obtained from inserting ANTARES into the process flow for 130nm logic devices.

Tunable for planar surfaces and delicate structures

It is desirable to tune the aggressiveness of the cryogenic aerosols, particularly for surfaces with delicate structures. The intensity of the aerosol's energy and size can be controlled most effectively by varying the argon-to-nitrogen ratio, process chamber pressure, and the pressure (temperature) of the liquid nitrogen heat exchanger [9].

There are two recipes with very different levels of aerosol aggressiveness. For planar surfaces, FSI's ArgonClean process is recommended, while the AspectClean recipe is aimed at surfaces with delicate structures. The ArgonClean process has an $Ar:N_2$ ratio of 3:1. It also has a relatively high ratio of process gas converted to liquid (30% by weight) by the liquid nitrogen heat exchanger. Though the liquid solidifies as it expands into the vacuum chamber, the resultant aerosol tends to be larger and more aggressive. The AspectClean process does not contain argon (only nitrogen), and has 15% (by weight) of the process gas converted to liquid. The resultant smaller aerosol does no damage to the many structures tested.

The AspectClean process was tested to be nondamaging on many structures. Several different polysilicon structures were successfully tested, with the smallest width and highest aspect ratio being 60×220nm. Test results also showed no damage on 130nm porous-MSQ lines, 110nm Black Diamond lines, 200nm SiLK lines, and 300nm-wide Al lines.

Tackling hydrophobic surfaces

Hydrophobic surfaces have always been particularly challenging due to their affinity to attach particles, which are then difficult to remove, and their susceptibility to watermark formation during drying. Porous low-*k* materials provide further challenges due to their hygroscopic properties.

In light of this, a cleaning study was performed that compared the cryogenic aerosol process to conventional aqueous-based scrub processes. Polystyrene latex (PSL) particles were deposited onto both hydrophilic (SiO_2) and hydrophobic surfaces (SiN and SiOC). As shown in Fig. 3, cleaning by cryogenic aerosols outperformed aqueous scrubbers, particularly for the hydrophobic surfaces [6].

Final device yields

The inert nondamaging properties of cryogenic aerosols, coupled with higher particle-removal efficiency, makes this a unique technique to control process excursions, reduce overall defectivity, and increase final device yield. Figure 4 shows one example of how cryogenic aerosol was used to control defectivity after the Al-line etch in 130nm logic devices. While the 12% yield improvement is atypical, it is routine to see 3%–4% yield improvements. Thus, IC manufacturers commonly recoup their full investment within 1–3 months.

Any IC manufacturing step containing particle defects can ben-

efit from cryogenic aerosols. In addition to replacing conventional scrubber techniques, these aerosols have been used to augment current cleans that are particularly troublesome or are not practical due to the sensitivity of the exposed materials. Typical insertion points are pre- or post-deposition (both FEOL and BEOL), post primary (or integrated) CMP clean, post-etch clean, and post in-line electrical probe cleans.

Conclusion

While the cryogenic aerosol cleaning technology has been available for IC manufacturing since 1996, its adoption has recently accelerated. This is due to new materials, such as low-*k* dielectrics, being introduced into the interconnect area that are incompatible with traditional scrubbing techniques. In addition, the cryogenic aerosol does not etch the surface, so it can also meet the new frontend cleaning requirements for 90nm and beyond.

The attributes of the cryogenic aerosol process are unique when compared to many other particle-removal processes available today. Nearly all of the other options are aqueous-based, requiring some form of etching (or material loss) to initiate particle detachment. While trying to minimize material loss, some of these processes incorporate megasonics or a scrubbing technology to maintain or enhance particle-removal efficiency. Often this "energy" ends up damaging delicate device features. To eliminate damage, the energy source is diminished, often resulting in poor removal efficiency.

Meanwhile, cryogenic aerosol has demonstrated unique capabilities as a next-generation "scrubbing" technology. Many other scrubber technologies — including brush scrub, high-pressure scrub, megasonic scrub, soft scrub, and nanoscrub systems — have been extended to new process nodes while attempting to avoid damage to smaller device features. With these scrub processes, the initial device damage has been in the form of broken lines and surface scratches. More recently, however, the damage has taken other forms, including material loss, modification of exposed surface materials, and charging. As scrub processes evolve to address these concerns, the overall cleaning performance of the technologies has been sacrificed. Further degradation in cleaning performance has been seen as hydrophobic surfaces appeared.

While the scrubber processes have evolved, the advantages of cryogenic aerosol cleans have became more apparent. The cryogenic aerosol process, independent of device node, has shown that it does not suffer from charging, material loss, or surface modification. By properly turning the aerosol, damage can be controlled with minimal sacrifice to cleaning performance, even on hydrophobic surfaces. ■

Acknowledgments

SiLK is a trademark of Dow Chemical Co. Black Diamond is a trademark of Applied Materials Inc. ANTARES is a registered trademark of FSI International. AspectClean and ArgonClean are trademarks of FSI International.

References

1. *The International Technology Roadmap for Semiconductors,* 2003, Front End Processes, Table 70, p. 18.
2. J.J. Wu, D. Syverson, T. Wagener, J. Weygand, "Wafer Cleaning with Cryogenic Argon Aerosols," *Semiconductor Int'l,* Vol. 19, No. 9, pp. 113–118, 1996.
3. J.F Weygand, N. Narayanswami, D.J. Syverson, "Cleaning Silicon Wafers with an Argon/Nitrogen Cryogenic Aerosol Process," *MICRO,* Vol. 15, No. 4, pp. 47–54, 1997.
4. J.W. Butterbaugh, S. Loper, G. Thomes, "Enhancing Yield through Argon/Nitrogen Cryokinetic Aerosol Cleaning after Via Processing," *MICRO,* Vol. 17, No. 6, pp. 33–43, 1999.
5. J.W. Butterbaugh, "Using a Cryogenic Aerosol Process to Clean Copper, Low-*k* Materials Without Damage," *MICRO,* Vol. 20, No. 2, pp. 23–28, 2002.
6. H. Iwamoto, et al, "Environmental Friendly Cleaning Technology for Next Generation Device," *5th Surface Cont. Control Seminar, Semicon Japan,* Dec. 4, 2003.
7. T.J. Wagener, K.L. Siefering, P.A. Kunkel, J.F. Weygand, G.P. Thomes, "Rotatable and Translatable Spray Nozzle," US Patent Number 5,942,037.
8. N. Narayanswami, "A Theoretical Analysis of Wafer Cleaning Using a Cryogenic Aerosol," *J. Electrochem. Soc.,* Vol. 146, No. 2, pp. 767–774, 1999.
9. T.J. Wagener, K. Kawaguchi, "Improved Yields for the Nanotechnology Era Using Cryogenic Aerosols," *Proc. IEEE/Semi Advanced Semiconductor Manufacturing Conference and Workshop,* May 2004.
10. W. Lukaszek, "Quantifying Wafer Charging During Via Etch," *1st Int'l Symposium on Plasma Process-Induced Damage,* May 13–14, 1996, Santa Clara, CA.
11. P.G. Clark, J.W. Butterbaugh, G.P. Thomes, J.F. Weygand, T.J. Wagener, D.S. Becker, "Compatibility of a Cryogenic Aerosol Process on SiLK and Porous MSQ," *2003 IEEE International Symposium on Semiconductor Manufacturing,* Sept. 30–Oct. 2, 2003, pp 479–482.

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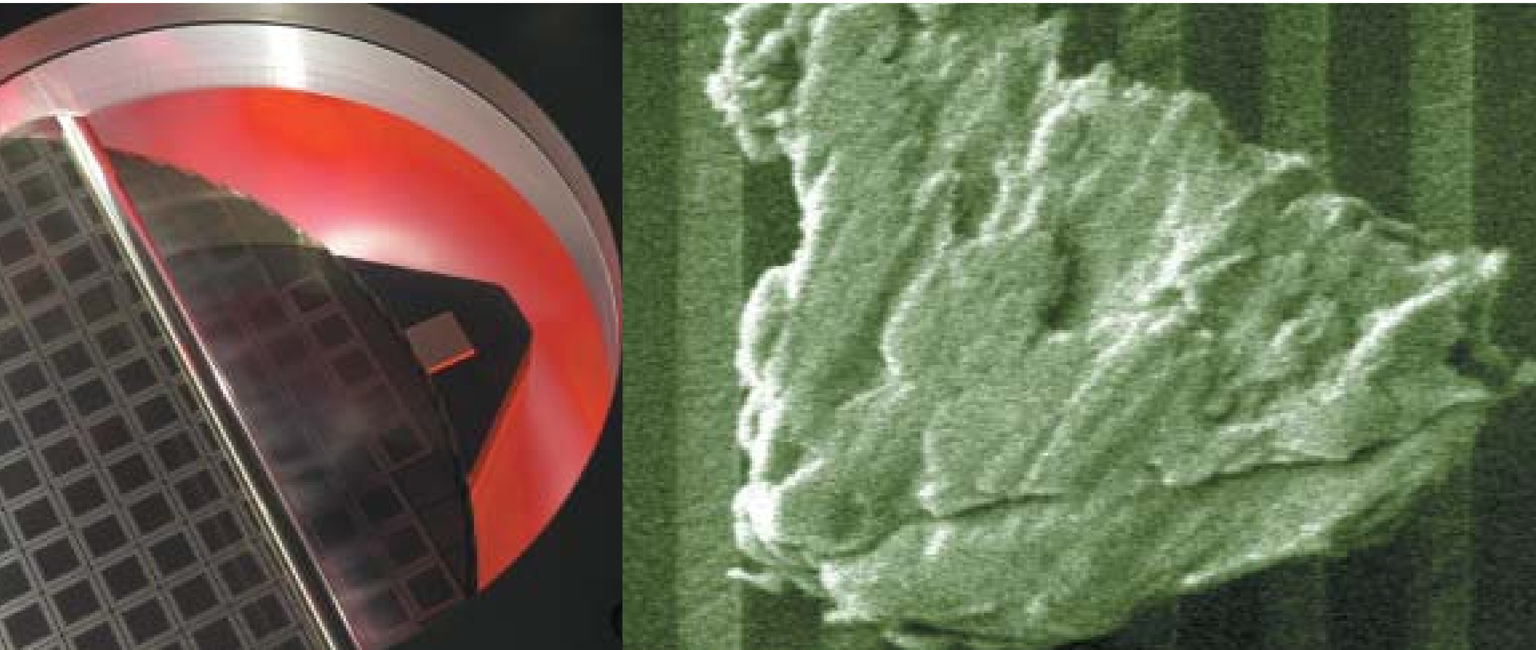
Blow Away Your Yield Expectations.



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The ANTARES system aggressively removes wafer surface defects using an all-dry, non-chemical cryogenic aerosol stream of frozen argon/nitrogen gas. High-velocity CryoKinetic force blows away particles as small as 60nm in diameter — without compromising device features. And it's accomplished with no damage, no etching, no watermarks or film property changes. Hard to believe? It's proven daily on real material in real manufacturing.

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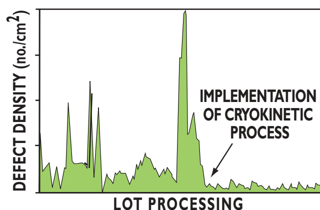
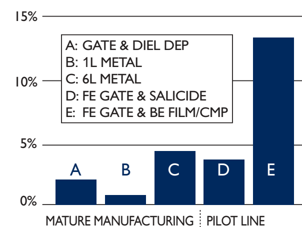


Significant reduction of in-line TiN barrier defect density after ANTARES CX aerosol process implemention



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