

Eliminating siloxane impurities from silane process gas using next-generation purification

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Silane and other process gases used for thin-film formation in semiconductor fabrication must be purified in order to eliminate contaminants that can lead to yield-inhibiting defects. One of the most difficult contaminants to control is moisture in silane gas, which can cause

con dioxide nuclei formation, which can be followed by nuclei condensing and particle formation. The clustering of siloxane molecules can also lead to particle formation.

In order to achieve gas purity at the low to single-digit parts-per-trillion level, an alternative purification approach is required. The Gaskleen PPT reactive filter technology developed jointly by the Sematech Center of Excellence at the University of Arizona (Tucson)

and Pall (Port Washington, NY) is one such approach. Because the reactive sites are located on the stainless-steel filter medium, this next-generation filter is a true integrated purifier/filter (see Figure 1).¹ The chemistry is an integral composite of intercalate reactive metal compounds in reduced form. These compounds become an integral part of the existing fibrous filter matrix, thus creating a true point-of-use purification surface. The use of a high-surface-area stainless-steel filter medium as the support structure for the reactive sites

Parts-per-trillion-level purification of process gases can be obtained with a new purification technology and confirmed through APIMS measurements.

particle generation in tubing and chambers and can adversely affect the quality of thin films, which have become increasingly thinner with each process generation.

Filtration is a standard practice for maintaining the particulate cleanliness of process gases. In the case of anhydrous silane, particles are expunged by classical methods, ensuring removal of those particles generated upstream in the gas delivery lines. However, if moisture contaminates the gas, particles will form downstream of the filter because of sili-

ULTRAPURE GAS DELIVERY

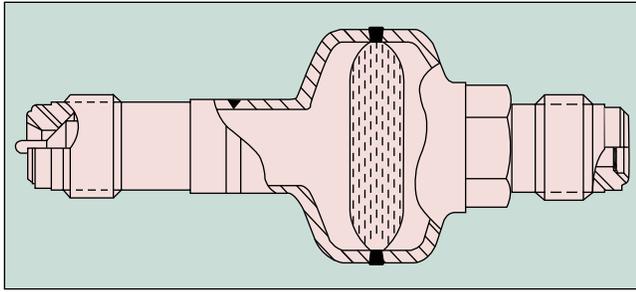


Figure 1: Schematic of the next-generation purifier.

facilitates the removal of homogenous impurities by ensuring contact of the impurity with the reactive sites.

The reactive filter is well suited for the purification of specialty hydride gases. The filter's efficacy in purifying silane gas is demonstrated by a quantitative reduction in siloxane peaks in the atmospheric pressure ionization mass spectroscopy (APIMS) spectrum of silane. The use of high-purity silane gas is essential to reduce silicon dioxide film thickness to the extent that 256-Mb and 1-Gb DRAM processes can be successfully developed. The recent introduction of a modified APIMS that can measure impurities in silane permits confirmation of the required purity levels.²⁻⁴ In conjunction with the modified APIMS for silane purity analysis, laser particle counters can be used to examine particle levels in the gas.

Experimental Data

A study that tested filters in nitrogen and silane, without purification, demonstrated that particles were found downstream of the filters validated for their performance in nitro-

gen.⁵ This study utilized a newly designed particle counter with 0.1- μm resolution, which could be used in situ with silane. A PTFE membrane filter used in nitrogen yielded <1 particle $>0.1 \mu\text{m}$ per 100 ml of gas. When the gas was switched to silane, the filter yielded 22,000 particles $>0.1 \mu\text{m}$ per 100 ml. The gas was switched upstream of the filter without disturbing any connections to the filter. An interesting observation was that without a filter, 1200 particles per 100 ml of silane gas were measured.

It is hypothesized that the increase in particles found downstream of the filter occurred because of increased collisions of siloxane molecules, formed from moisture in the gas reacting with silane, downstream of the filter membrane. The enhanced formation is caused by the increased turbulence of gas flow through the filter. Clustering of these molecules creates measurable-sized particles. Purification of the silane gas can eliminate this contamination by removing the moisture and siloxane before it can react with the silane. Figure 2 shows 0.1–0.2- μm particle counts on wafers detected with a surface scanner from KLA-Tencor (San Jose). The counts depicted in the figure were taken before and after the silane purification began. The wafers that were analyzed came from a low-pressure CVD process in a DRAM line at a major semiconductor manufacturer. As the figure illustrates, the particle counts on the wafer dramatically dropped with purification. These data corroborate the study's particle data and the hypothesis that particles were generated by the reaction of silane and moisture.

The purifier's ability to deliver silane gas without siloxane impurities was demonstrated by another study on silane purification that used APIMS as the analytical method. The study was conducted from 1998 to 1999 at Tadahiro Ohmi's laboratory at Tohoku University in Sendai, Japan. The test setup, shown in Figure 3, consisted of a silane gas cylinder, moisture injection line, and argon carrier gas. The APIMS was modified to analyze silane by initially ionizing argon in the first chamber, then ionizing silane and its impurities in the second chamber.²⁻⁴ This eliminates interference by the argon, oxygen, nitrogen, hydrogen, and CH_4 because of their high ionization potential.

Figure 4 depicts the impurities found in the silane without purification and following 10-ppb water injection. Silane peaks are at a mass per charge of 31 and 63 (SiH_3^+ and SiH_4^+ , respectively). Moisture peaks are at a mass per charge of 49, 67, and 79 ($\text{H}_2\text{O-SiH}_3^+$, $2\text{H}_2\text{O-SiH}_3^+$, and $\text{H}_2\text{O-Si}_2\text{H}_3^+$, respectively). Siloxane peaks

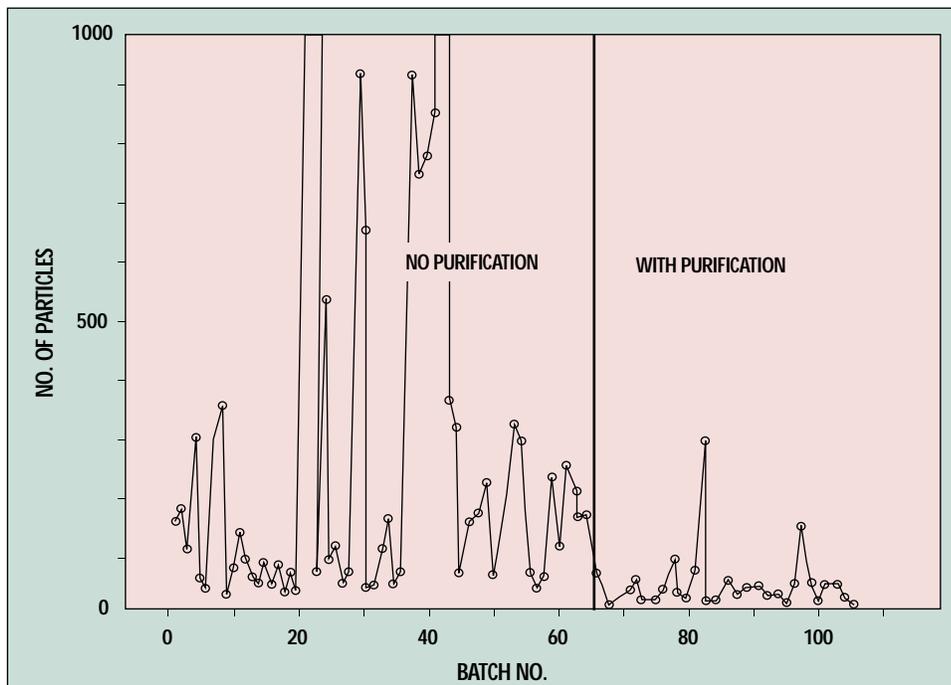


Figure 2: Wafer counts of 0.1–0.2- μm particles, with and without the purification of the silane gas.

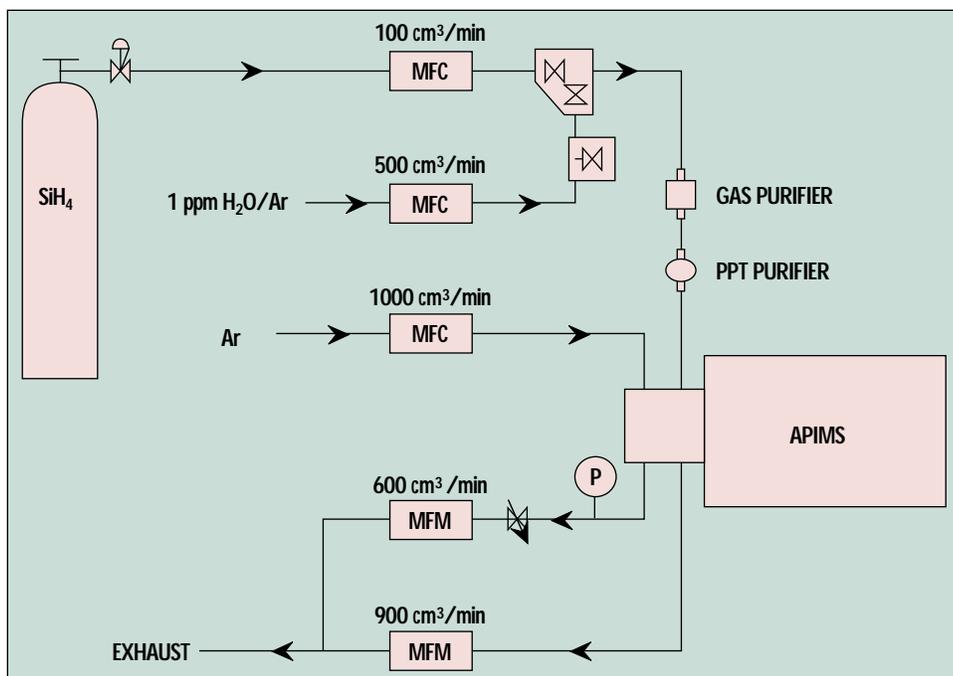


Figure 3: Schematic of the APIMS test setup.

are at a mass per charge of 77 and 109 ($\text{SiH}_3\text{OSiH}_2^+$ and $[\text{SiH}_3]_2\text{O-SiH}_3^+$, respectively), while disilane peaks are at 61 and 93 (Si_2H_5^+ and $\text{SiH}_4\text{-Si}_2\text{H}_5^+$, respectively).

When the silane gas with the 10-ppb water injection was passed through a purifier, the water and siloxane peaks were reduced. The purifier uses a chemically reactive resin-based material for parts-per-billion-level purification. A comparison of Figures 4 and 5 reveals decreases in the relative intensities of siloxane and water. When the same silane gas with 10-ppb moisture was further treated with the new purifier technology after the resin-based purifier, the siloxane and water peaks were essentially eliminated. These results suggest that additional purification of the gas helps reduce particle contamination and film defects to the levels needed for advanced devices. Figure 6 shows the benefits of the additional purification by illustrating the absence of the siloxane

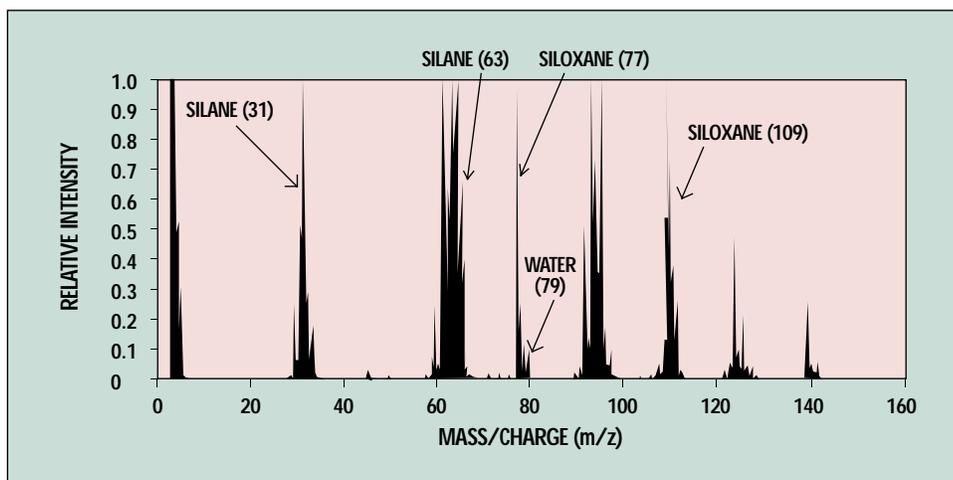


Figure 4: APIMS reading of silane impurities without purification.

and water relative ion intensity peaks.

Conclusion

Semiconductor manufacturers continue to use conventional purification techniques for process gases with impurities in the low-parts-per-billion to high-parts-per-trillion range. However, the development of APIMS and the continuing demand for higher-purity gases in many applications has resulted in the need for purification to low-parts-per-trillion levels. A new purifier/filter's ability to achieve low-single-digit parts-per-trillion purity gas has enhanced the ability of APIMS to detect purity levels of <20 ppt for inert gases. In addition, purification to low-parts-per-trillion levels will ensure that film defects are reduced to the levels required for advanced devices and can be a significant aid in reducing the downtime of process equipment.

Acknowledgments

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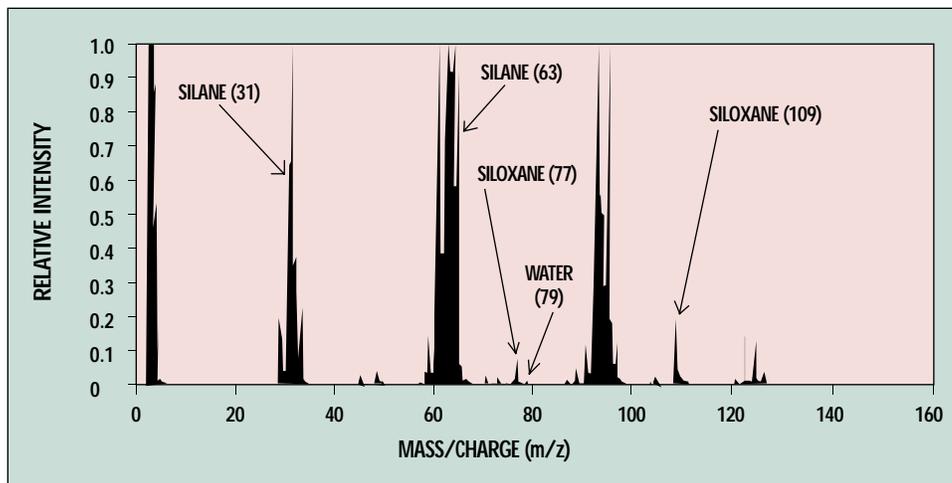


Figure 5: APIMS reading of silane impurities with resin-based purification.

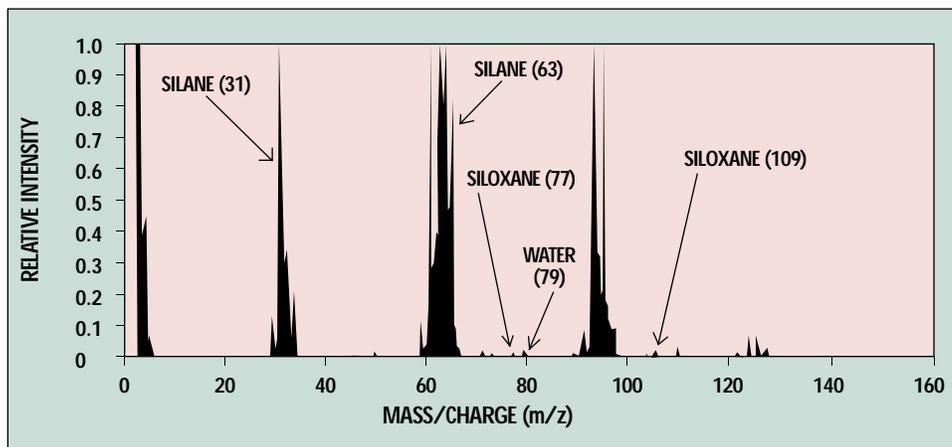


Figure 6: APIMS reading of silane impurities with resin-based purification plus purification with the new method.



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