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Defect/Yield Analysis

Investigating yield loss caused by airborne organophosphates

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A case study investigates air-sampling, witness wafer, and dynamic headspace outgassing methods for tracking yield-limiting organophosphate contaminants in cleanroom air.

Organophosphates are among the most detrimental contaminants in semiconductor cleanrooms.[1,2] The outgassing of these compounds from HEPA or ULPA filter polyurethane material (also known as potting compounds) has disrupted processing at several semiconductor facilities.[13] Potting compounds are used to seal the edges of the pleated filter media to HEPA and ULPA filter housings. If organophosphates are present in cleanroom air and not removed before thermal wafer processing, they can adsorb onto the wafers, and then the phosphorus they contain can diffuse into the silicon, changing dopant levels and affecting the electrical properties of the wafer surface.[2] To counteract the danger of n-doping in silicon wafers, nearly all semiconductor fabs specify that organophosphates may not be used in construction materials. Sematech has forecast that molecular organophosphate contaminant limits for dopants will be <0.010 ppbM (parts-per-billion-molar) in air for early processing steps.[4] Moreover, several labs have developed methods for identifying organic contaminants, including organophosphates, in cleanroom air and on wafers.[513]

This article presents a case study of organophosphate contamination at a major semiconductor fab that was experiencing a substantial yield loss. Air and witness wafer sampling was carried out to assess the types and levels of contaminants in the cleanroom air. Because the problem started shortly after HEPA filters had been replaced, outgassing from these filters was suspected. To confirm this hypothesis, tests were conducted to determine if volatile components from the filters were present. At the same time, the investigation provided an opportunity to determine whether dynamic headspace thermal desorption methods are useful for assessing outgassing from fab construction materials.

Quantifying Organophosphate Contamination in the Fab

Despite the problems, a surprising range of materials used in

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semiconductor fabs outgasses organophosphates--some materials at very high levels. Phosphates commonly found in cleanrooms, on wafers, or in outgassing products include trialkyl phosphates (methyl, ethyl, butyl, cresyl, chloroethyl, and chloropropyl) and triaryl phosphates such as triphenyl phosphate. Organophosphates are commonly used as flame retardants or plasticizers in cleanroom materials containing plastics, elastomers, and urethanes (especially ULPA and HEPA filter potting compounds). Existing fire codes make it impractical to ban flame retardants from the fab entirely. However, while all organophosphates should be excluded from semiconductor cleanrooms, the potential effects of alternative flame retardants has yet to be assessed.

The anomalous doping problems at the test site under discussion caused an overall yield loss of between 10 and 15%. Doping was especially severe for the last 3 wafers in each 25-wafer batch. Contamination occurred while bare silicon areas of the wafers were exposed to the air while awaiting processing. Die yields were lower on the wafer's flat end, which faced upwind for most of the exposure time. Die yields for wafer 25 in each batch varied from 0 to 90%, as illustrated by the red areas of the wafer maps presented in Figure 1. Longer exposure times resulted in lower yields. In addition, the peripheries of wafers 23 and 24 had lower die yields.

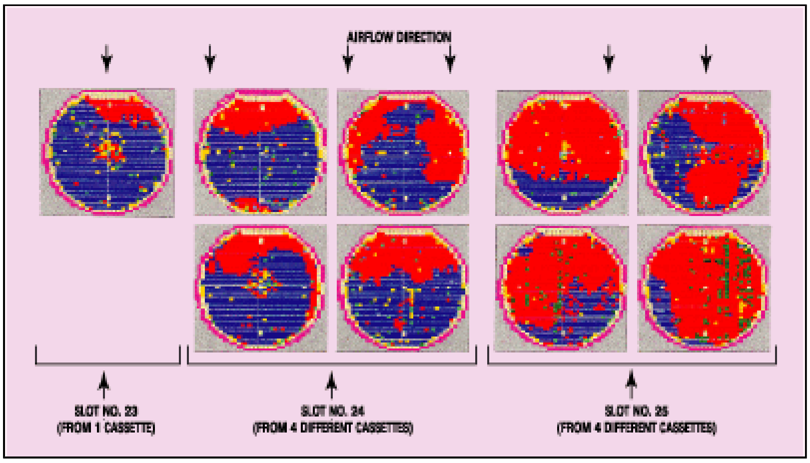

Figure 1: Wafer electrical test yield maps. The blue areas indicate die that passed and the red areas show failed die that had been n^+*-doped by phosphorus.*

A series of sampling methods and tests were performed to determine the organophosphate levels in the cleanroom and to track the source of the yield loss.

Air Analysis. The air was sampled for several hours at critical locations in the cleanroom using air-sampling tubes and pumps.[10,12,14] The sampling tubes contained appropriate adsorbents to trap and concentrate organic compounds and were then analyzed by thermal desorptiongas chromatography mass spectrometry (TD-GC-MS). For all the GC-MS tests performed in this study, the amounts of individual compounds were semiquantitatively estimated by using an n-decane external standard total ion count response factor. Air samples detected that the cleanroom site with yield problems had 0.07 ppbM tris (chloropropyl) phosphate (TCPP), as shown in Figure 2.

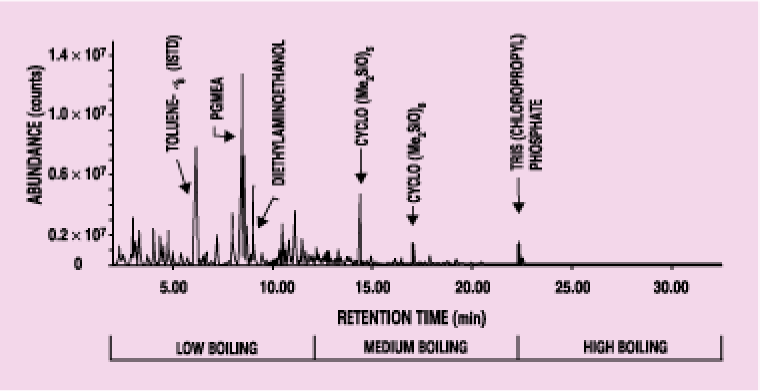

Figure 2: Results of an air-sampling test for organics in which 0.07 ppbv of organophospates were found in cleanroom air.

Witness Wafer Sampling. A clean, organic-free silicon wafer with a thermal oxide surface was exposed to cleanroom air for 24 hours. This wafer was then thermally desorbed in a purged chamber, and desorbed organic compounds were collected onto adsorbent-containing sampling tubes. The sampling tubes were analyzed by TD-GC-MS. This method has been described in detail in ASTM F198299.[15] Witness wafer sampling, the results of which are presented in Figure 3, indicated that 13 ng of TCPP per square centimeter desorbed from the wafer, which corresponds to phosphorous adsorption on the wafer surface of ~3 x 10^{13} atoms/cm^2 (~1/100th of a monolayer of phosphorus).

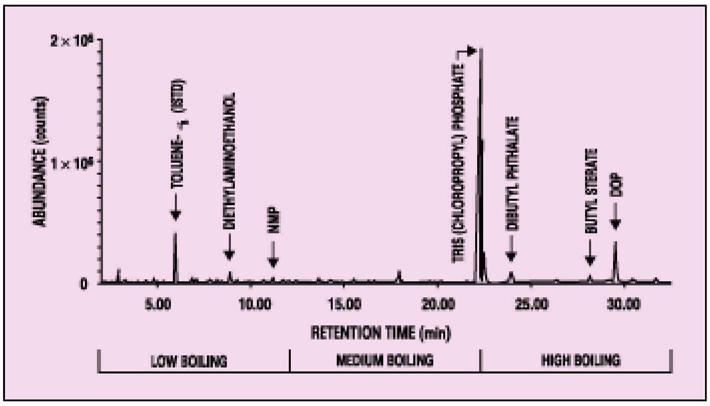

Figure 3: Results of TD-GC-MS wafer sampling for organics showing that the organophosphate TCPP, with 3 x 10^{13} atoms of phosphorus per square centimeter, is the dominant contaminant on the wafer.

The study demonstrated that even when TCPP is present in extremely low concentrations in the fab air, the amount detected on the wafer is significant enough to cause a substantial yield loss. The negative impact of phosphorus-containing airborne molecular contamination has also been demonstrated at Eastman Kodak (Rochester, NY), where

0.2 ppbM of TCPP in the air inverted the doping of a charge-coupled device.[2] A facility in Japan has reported that TCPP was a major contaminant on wafer surfaces, although only small quantities of the compound were detected in the cleanroom air.[3] A comparison of the air and wafer samples collected in this study also illustrates that the relative levels of contaminants in cleanroom air do not correspond to the relative amounts adsorbed onto the wafer. Because of their large surface area, wafers can sample cleanroom airborne molecular contaminants very quickly by adsorption. While trace levels of higher-boiling compounds, such as organophosphates in air, adhere strongly to the wafer surface, lower-boiling compounds in air generally do not stick strongly to wafers.

Figure 4 shows comparative data from a series of fabs in which organophosphorous compounds were thermally desorbed from witness wafers that had been exposed to cleanroom air for 24 hours. Phosphorus contamination levels on wafers exposed to most of the fabs were in the range of 0.020.2 x 10^{13} atoms/cm^2. Approximately 8% of the fabs had levels >0.2 x 10^{13} atoms/cm^2. The fab in this study experiencing the yield loss of up to 15% had approximately 3 x 10^{13} phosphorus atoms per square centimeter.

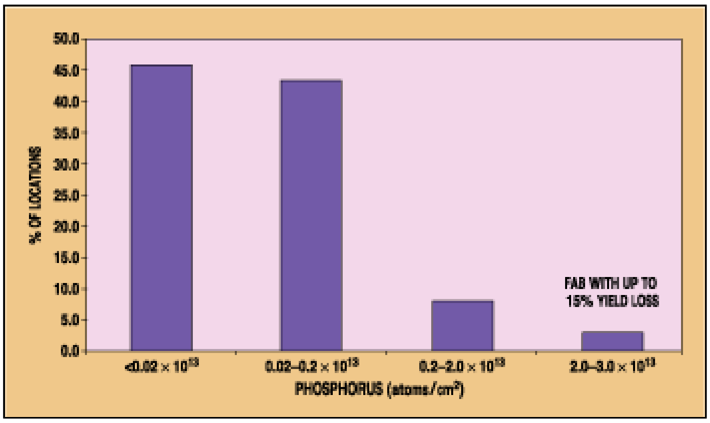

Figure 4: Comparison of typical levels of organophosphorous compounds desorbed from witness wafers in a series of fabs.

Organophosphate Outgassing from HEPA Filters

Based on the knowledge that high levels of TCPP had been detected on wafer surfaces and that the fab's yield loss began after new HEPA filters had been installed, two types of outgassing tests were performed to quantify the TCPP levels generated by the HEPA material.

The first test--a dynamic headspace 100°C outgassing GC-MS screening analysis--was performed on a variety of HEPA filter components. In this experiment, a 0.2-g portion of a polymeric sample was placed in a stainless-steel tube that was 8.9 cm long x 6.4 mm OD x 5 mm ID and had a retaining screen at one end. The sample was purged with an inert gas to remove air and then desorbed at 100°C for 30 minutes while the tube was continuously swept with helium.[16] The outgassing organic compounds were then cryofocused on a cold trap, after which the cold trap was rapidly heated to desorb compounds into the chromatograph for analysis. This test determined that the major source of TCPP was the HEPA filter potting compound, which outgassed 531 ppmw of TCPP, the highest peak in the GC-MS chromatogram shown in Figure 5.

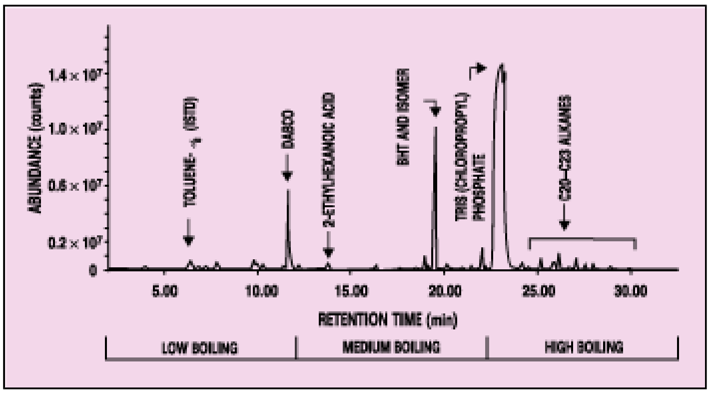

Figure 5: Results of the dynamic headspace 100°C outgassing GC-MS screening test on the HEPA potting compound, which outgassed 531 ppmw of TCPP.

Although this type of high-temperature screening test can sensitively detect outgassing compounds, it can be argued that most cleanroom materials are never used at 100°C. However, while testing at actual use temperature is more realistic than high-temperature testing, standard outgassing systems at room temperature are often inadequately sensitive. Hence, in this study an off-line, room-temperature engineering test was developed that ensures adequate sensitivity by using very large sample sizes and by collecting outgassing materials for long periods.

In this second test--a dynamic headspace room-temperature (RT) outgassing GC-MS engineering test--a 15.2 x 1.9 x 0.7-cm polymeric sample was removed from the 1-year-old suspect HEPA filter and placed in a glass tube, after which organic-free clean air with a humidity level of 40% (which is typical in semiconductor fabs) was passed through the tube at a rate of 200 ml/min. The glass tube was connected to an adsorbent-containing sampling tube, in which outgassing compounds were collected for 1 hour. Finally, the sampling tube was analyzed by TD-GC-MS. This test demonstrated that the polymeric sample from the HEPA filter outgassed ~0.5 ppbw of TCPP per hour, as illustrated in Figure 6. Accordingly, it was estimated that a 1-year-old HEPA filter would outgas ~20 mg of TCPP in a 24-hour period.

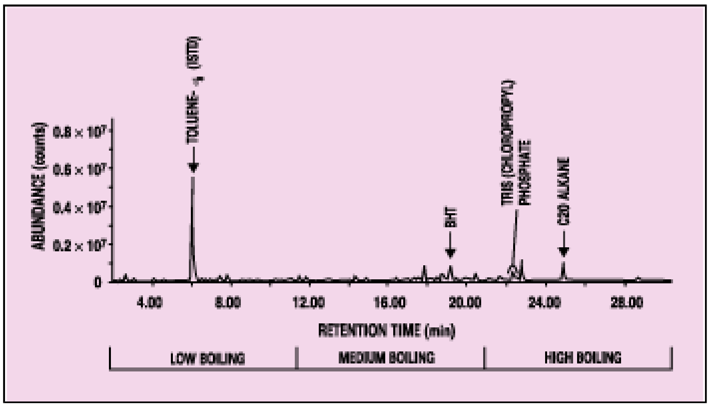

Figure 6: Results of the dynamic headspace room-temperature outgassing GC-MS engineering test on the HEPA potting compound, which outgassed 0.5 ppbw of TCPP per hour.

When dynamic headspace sampling is used, outgassed compounds, including reactive compounds, are swept out of the sampling vessel onto an adsorbent as soon as they are outgassed. This continuous sweeping removes the trace amounts of higher-boiling compounds for concentration and analysis and minimizes the chance that reactive compounds will polymerize and go undetected. However, the dynamic headspace method may not capture all low-boiling compounds, since they may not be effectively trapped on the adsorbents. And some very-high-boiling or reactive compounds may be irreversibly adsorbed onto the sampling tube adsorbent, or they may react or decompose during analysis.

An ideal screening program would eliminate any sources of contamination outgassing in the fab, and the dynamic headspace 100° C screening test appears to detect most organic compounds that can have a negative impact on the production of silicon-based semiconductors. Conversely, some contaminants may slip by undetected using the dynamic headspace RT engineering test. In the real world, contaminants do get into the fab. Moreover, the manufacturing processes in cleanrooms are affected not only by organophosphate contaminants, but also by several other organic compounds. Some of these compounds may not be volatile enough to be detected by the engineering test. The dynamic headspace 100°C screening test may be a more practical and sensitive test for rapidly assessing all possible sources of such contaminants. For existing fabs, the witness wafer test for organics seems very sensitive to organophosphates and the plasticizer dioctylphthalate (DOP).

After it was determined that airborne molecular contamination at the facility under investigation was related to newly installed HEPA filters, one option was to remove the filters in question—an expensive and disruptive solution. Instead, a compromise was reached by adding carbon filters to the recirculation air system. The carbon filters strongly adsorb higher-boiling organic compounds, which reduced organophosphates levels in the air by about six times and led to a yield increase of up to 15%. As a result of this retrofit, die yields were no longer decreased by n-doping problems.

Conclusion

Implementing methods to track and control organophosphates in semiconductor facilities has become increasingly important because of expanding new fab construction and the need to retrofit existing fabs. Appropriate methods include air-sampling, witness wafer, and dynamic headspace outgassing tests. These methods can detect hydrocarbons and other semivolatile compounds with volatilities in the range of C7 to C28 n-alkanes and approximate boiling points of 100°-450°C, including such organophosphates as TCPP, trimethyl phosphate, triethyl phosphate, and tributyl phosphate and such plasticizers as dioctyl phthalate.

Air-sampling tests are useful for establishing baselines for organophosphates and other organic contaminants in cleanroom air and ensuring that no detrimental compounds are present. The levels of organic compounds in the air, however, may not directly correlate to the levels of organic compounds that adhere to the wafer surface. Therefore, witness wafer tests should be carried out to establish the levels of specific organic contaminants that may adversely affect wafer processing.

The dynamic headspace 100°C outgassing GC-MS screening method is recommended as a first line of defense for assessing the organic outgassing of prospective cleanroom materials. This method is adequately sensitive (<1 ppmw) for detecting higher-boiling organic compounds such as phosphates, silicones, and phthalates that are most likely to affect the processing of sensitive substrates. This method is quicker, easier, and more sensitive than the dynamic headspace room-temperature outgassing GC-MS engineering method.

Molecular contamination can be greatly reduced by implementing a screening program for outgassing, leading to improved yields and longer hold times between processes without recleaning. Conceivably, it may be possible to eliminate some cleaning steps altogether if airborne molecular contamination is controlled, resulting in reduced scrap, shorter cycle times, lower equipment costs, smaller tool footprint, and, accordingly, increased return on investment.

Acknowledgments

This article is an updated and expanded version of a paper that was presented at the 17th Annual Semiconductor Pure Water and Chemical Conference held in Santa Clara, CA, in March 1998. The paper appeared in the conference proceedings. The authors wish to thank Marjorie Balazs for her helpful suggestions during the study.

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