A CASE STUDY OF ORGANOPHOSPHATE CONTAMINATION IN A SEMICONDUCTOR CLEANROOM: ASSESSMENT OF ANALYTICAL METHODS

MARK CAMENZIND, Ph.D.; ANURAG KUMAR, Ph.D.; LATIF AHMED, Ph.D.

Balazs Analytical Laboratory, 252 Humboldt Court, Sunnyvale, CA 94089-1315

I. ABSTRACT

Construction materials and polymers used in cleanrooms are major sources of organic contaminants. In cleanrooms that are used for critical processes in the semiconductor, disk drive, optical and aerospace industries, these materials can outgas organic compounds and cause significant yield losses. Organophosphates outgassing from HEPA (High Efficiency Particulate Air) filter potting compounds have been documented as especially problematic for silicon semiconductor processing.[1-3] In this paper, we compare methods for assessing organophosphate contamination, including air sampling, wafer exposure tests and outgassing test methods. An example of an organophosphate contamination problem from HEPA filters that affected the yield of silicon wafers is used to explore application of various outgassing methods. Outgassing methods compared include:

1. ASTM E-595-vacuum outgassing
2. Static headspace GC-MS (Gas Chromatography-Mass Spectrometry) tests at 100°C
3. Dynamic headspace GC-MS "screening tests" at 100°C
4. Room temperature GC-MS "engineering test" methods.

The method 3 is recommended for assessing outgassing of organophosphates and other airborne molecular contaminants from cleanroom material.

II. INTRODUCTION

Great emphasis is placed on controlling particulate contamination in modern cleanrooms since the effects of these contaminations on clean manufacturing processes are well understood. In contrast, the origins of airborne molecular compounds in the cleanroom air and their effects on clean-manufacturing processes are not yet well understood. With reducing line widths of semiconductor devices, AMC (airborne molecular contamination) is posing an increasing challenge. Most cleanroom air is dirtier than outside air for many airborne molecular contaminants, especially organics, acids, bases and dopants.[4-6] Some of the molecular compounds can cause disastrous yield losses or degradation of electrical, mechanical, optical or other properties. The mass arrival rates of molecular contaminants at the wafer surfaces are orders of magnitude higher than particle arrival rates.[4] HEPA and ULPA (Ultra Low Penetration Air) filters which remove particles, do not remove many molecular compounds and can even contribute to molecular contamination in the cleanroom[1,2,7]. Many contaminants come from outgassing of materials used in the cleanroom.[8] These contaminants need to be better controlled.

Organophosphates have been identified as one of the most detrimental contaminants in cleanrooms used for semiconductor fabrication.[1,2] If organophosphates are present in cleanroom air, adsorb onto wafers, and are not removed prior to thermal processing, the phosphorus can diffuse into the silicon and change the dopant levels and electrical properties of the surface.[2] Nearly all semiconductor fab's specify that no organophosphates be used in construction materials since they can n-dope silicon wafers. Sematech has forecasted molecular contaminant limits for dopants at 0.1 pptM (parts-per-trillion-molar) in air for early processing steps.[9] Organophosphates outgassing from HEPA or ULPA filter potting compounds have upset processing at several semiconductor facilities.[1,2,7] The "potting" compounds are used to seal in the edges of the pleated filter media to the filter housing. Organophosphates are common flame retardants or plasticizers in urethane polymers used as foams and sealants, e.g., in HEPA filters, or other applications. Several labs have developed methods for identifying organic contaminants, including organophosphates, in cleanroom air and on wafers.[5,6,8,10-12]

This paper presents a case study of organophosphate contamination at a major semiconductor fab which was experiencing up to 15% yield loss. Air and wafer sampling was carried out to assess the types and levels of contaminants in cleanroom air. Since the problem started shortly after HEPA filter had been replaced, outgassing from HEPA filters was suspected. Outgassing tests of HEPA filter components were initiated to confirm the source of the contamination. The problem with this company also gave us the opportunity to determine the usefulness of four representative methods for assessing outgassing from construction materials used in the fab.

III. EXPERIMENTAL METHODS

III A. Air Sampling

The air was sampled for several hours at critical locations in the cleanroom using air sampling tubes and pumps.[4,11] The sampling tubes contained appropriate adsorbents to trap and concentrate organic compounds. These sampling tubes were analyzed by TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry).

The range of compounds that could be detected by this method includes hydrocarbons and other semivolatile compounds with volatilities in the range of C6 to C28 n-alkanes (approx. bp 100-450°C), including: organophosphates such as trimethyl phosphate (TMP); triethyl phosphate (TEP); tributyl phosphate (TBP); and tris(chloropropyl) phosphate (TCPP). Detection limits for selected organophosphates in air are below 0.05 ppbM by GC-MS. For the air sampling and all other GC-MS studies in this paper, the amounts of individual compounds are semiquantitatively estimated by using a n-decane external standard.

III B. Wafer sampling

A clean, baked out wafer was exposed to the cleanroom air for 24 hours. This wafer was then thermally desorbed in a purged chamber, and desorbed organic compounds were collected onto air sampling tubes. The air sampling tubes were analyzed by TD-GC-MS as described above (III.A). The range of compounds that can be recovered by this method

includes hydrocarbons and other semivolatile compounds with boiling points in the range of C7 to C28 (approx. bp 100-450°C), including organophosphates and plasticizers (DOP). The detection limit is ~25 ng of individual component/wafer (≈ 0.1 ng/cm^2) for 125-150 mm wafers. For an organophosphate such as TCPP, this corresponds to ≈ 10^{11} Phosphorus-atoms / cm^2. Lower detection limits are possible for specific compounds.

III C. Outgassing Methods

III C 1. Vacuum outgassing by ASTM E595-93

The sample was outgassed under vacuum at 125°C for 24 hours. Following measurements were made:

- The total mass loss (TML).
- Amounts of Collected Volatile Condensable Material (CVCM) on a 25°C plate.
- The Water Vapor Regained (WVR) when the sample was re-equilibrated in 50% RH air, for 24 hrs.

ASTM E-595-93 is a common method used to assess outgassing. For 100-300 µg sample the detection limits for CVCM and TML are ~0.01%.

III C 2. 100°C Outgassing GC-MS Methods

Static Headspace

A 0.7 g piece of the potting compound from the suspect HEPA filter was heated in a sealed container for 24 hours. A 1-mL portion of the gas phase was then analyzed by GC-MS. The detection limits may depend on the volatility of the compounds studied.

Dynamic Headspace

A 0.2 g portion of the HEPA filter potting compound was placed in a stainless steel tube (8.9 cm long x 6.4 mm O.D. x 5 mm I.D.) with 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

continuously sweeping the tube with nitrogen. The outgassing organic compounds were cryofocused on a cold trap. After cryofocusing all the outgassing compounds, the cold trap was rapidly heated to desorb compounds into the GC-MS for analysis.

The range of compounds that could be detected by this method includes hydrocarbons and other semivolatile compounds with volatilities in the range of C6 to C28 n-alkanes (approx. bp 100-450°C). For a 0.2 g sample, typical detection limits are <1 ppmw (parts per million by weight, μg/g). Lower detection limits for specific compounds are possible.

III C 3. "Engineering Test". Room temperature (RT) dynamic headspace GC-MS outgassing method.

A 6"-long piece (15.2 cm x 1.9 cm x 0.7 cm) of the potting compound was removed from the suspect, one-year-old, HEPA filter. This sample was placed inside a glass tube and clean 40% RH (relative humidity; this is typical of many semiconductor fab's) air was passed through the glass tube at 200 mL/minute and at room temperature for 1/2 hr to equilibrate. An air sampling tube was then connected and outgassing compounds were collected onto this tube for 1 hour. The sampling tube was analyzed by TD-GC-MS method described in III.A. This "engineering test" has been previously described[13].

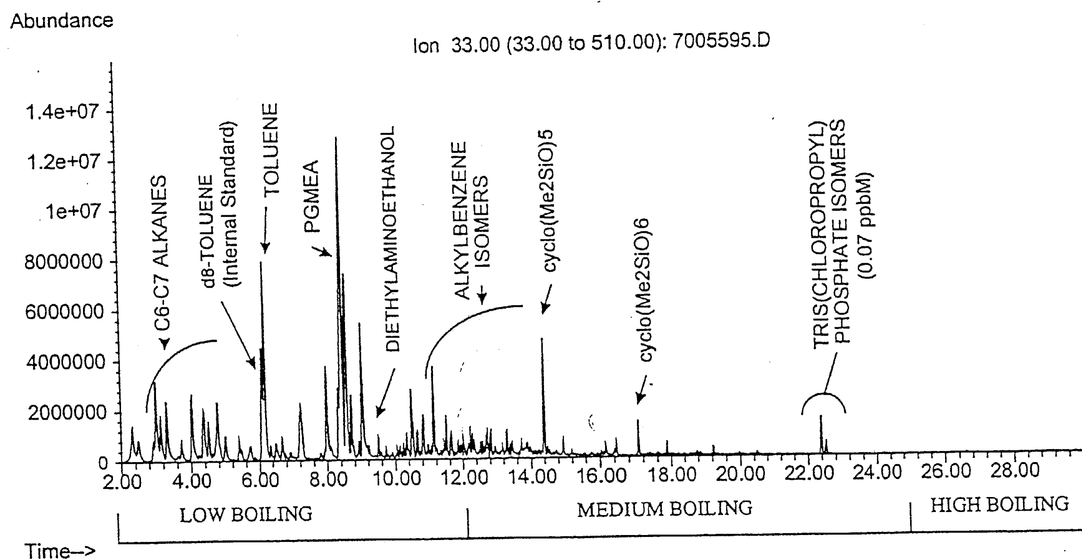
IV. RESULTS AND DISCUSSION

IV A. Air and Wafer Analysis

The air sampling method detected 0.07 ppbM (parts per billion molar) TCPP for the cleanroom site that was having yield problems **(Figure 1)**.

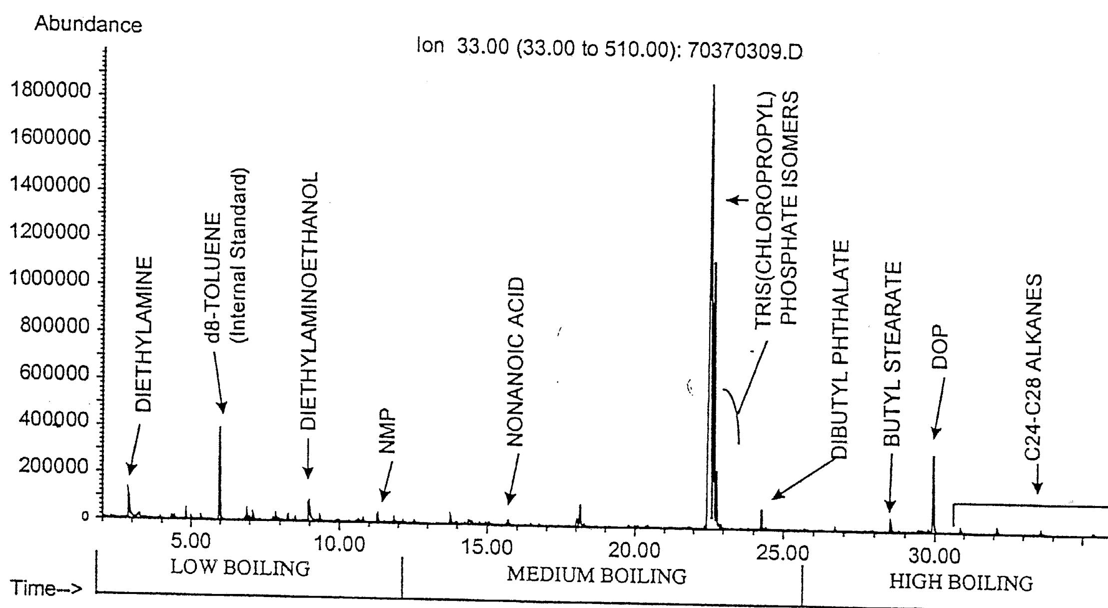
The wafer sampling method found 13 ng of TCPP/cm^2 desorbing from the wafer **(Figure 2)**. This corresponds to ~3E13 P atoms /cm^2 (~1/100th of a monolayer of P) adsorbed on the wafer surface

FIGURE 1: TRIS(CHLOROPROPYL) PHOSPHATE (TCPP) IN CLEANROOM AIR BY TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry). Air was analyzed for organics at a fab that was discarding Si wafers due to anomalous n-doping. GC-MS detected 0.07 ppbM (0.9 ng/L) tris(chloropropyl) phosphate (TCPP).



Our study demonstrates that although the TCPP was present in extremely low concentrations in the fab air, the amount detected on the wafer was significant enough to cause up to 15% yield loss. The impact of the presence of phosphorus-containing airborne molecular contamination was also demonstrated at Eastman Kodak where 0.2 ppbM TCPP in air inverted the doping of a charge coupled device (CCD)[2]. In Japan, tris(chloroethyl) phosphate was reported as a major contaminant on wafer surfaces although it was detected only in small quantities in the cleanroom air.[7] Comparison of our air sampling and wafer sampling results also illustrates that the relative levels of contaminant in cleanroom air do not correspond with the amount adsorbed onto the wafer. Due to their large surface area, wafers can sample cleanroom air very quickly by diffusion. The trace levels of higher boiling compounds such as organophosphates in air adhere strongly to the wafer surface. The lower boiling compounds in air generally do not stick strongly to wafers.

FIGURE 2: ANALYSIS OF TCPP ON WAFER BY TD-GC-MS. (Thermal Desorption-Gas Chromatography-Mass Spectrometry). A 5" wafer was exposed to cleanroom air for 24 h. GC-MS analysis found Tris(chloropropyl) phosphate (TCPP), at level corresponding to 3E13 P atoms/cm². TCPP was causing loss of end wafers and some peripheral die due to n-doping.



IV-B. *Outgassing analysis*

Based on the detection of TCPP in air and on wafer, and knowing that the yield problem started after installation of new HEPA filters, a variety of components of HEPA filters were tested by dynamic headspace outgassing "screening test". This test determined that the major source of TCPP was the HEPA filter potting compound. This organophosphate contamination problem provided an excellent opportunity to compare different outgassing methods for assessing outgassing problems. Thus, the potting compound from the suspect HEPA filter was analyzed by four methods used for outgas testing.

ASTM-E-595-93 Vacuum Outgassing Test

The following results were obtained from the analysis of the potting compound from the suspect filter by ASTM-E-595-93 method.

Total Mass Loss = 8.42%

Collected Volatile Condensable Material = 0.04%

Water Vapor Recovered = 0.08%

If the TML and CVCM levels are low (<0.01%, 100 ppmw, parts per million by weight), the materials are more likely to be acceptable for cleanroom use, but even 0.01% CVCM of a highly detrimental compound could be disastrous to wafer processing. This test does not identify individual outgassing compounds. The identification and quantitation of individual compounds will provide very useful information for screening of materials to be used in cleanrooms.

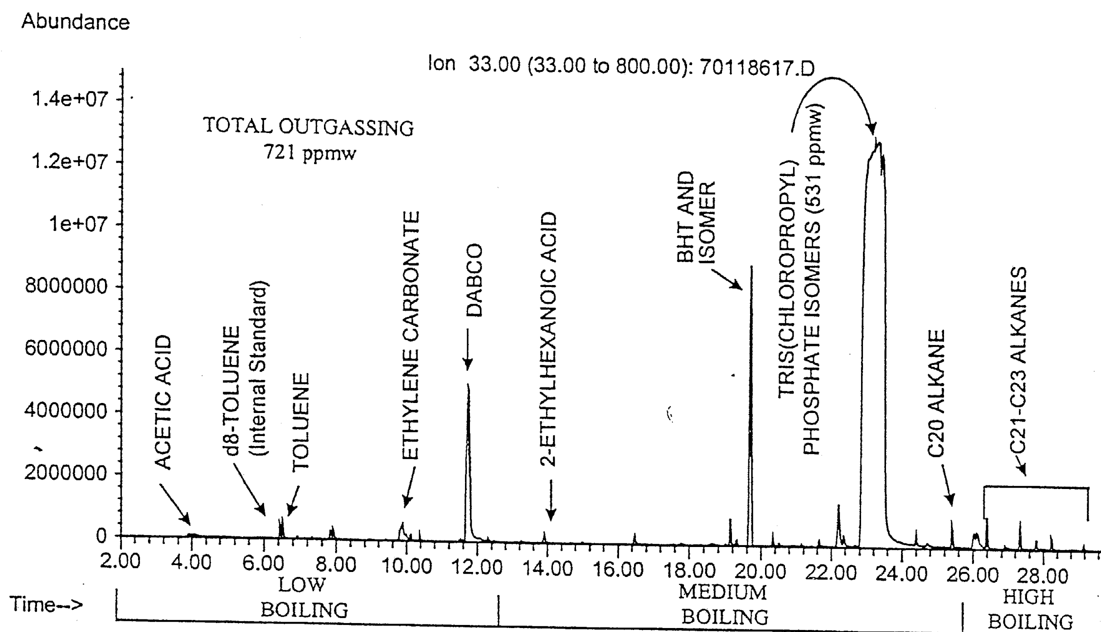
Static Headspace and Dynamic Headspace Outgassing Tests at 100°C

Under static headspace outgassing conditions at 100°C for 24 hours, the GC-MS analysis found only 0.2 ppmw of TCPP outgassing from the potting compound of the suspect filter. The dynamic headspace outgassing at 100°C for one half hour detected 531 ppmw TCPP (by GC-MS) from the same potting compound. The TCPP peak dominated the GC-MS chromatogram (**Figure 3**).

To assess the sensitivity of the dynamic headspace outgassing method, we analyzed the potting compound used in another brand of HEPA filter. Only 0.2 ppmw TEP (Triethyl Phosphate) was detected outgassing from the potting compound of this reference filter.

In general, the static headspace test is useful for detecting low boilers such as volatile solvents. Since the higher boilers, e.g. compounds with bp >250°C, have very low vapor pressures, very little will equilibrate into the 1 mL of headspace sampled in a static headspace. For this reason, the static headspace outgassing method is dramatically less sensitive for higher boiling compounds. Under static headspace conditions, higher boilers can also condense and carryover within the instrumentation. This method is not effective for analyzing reactive compounds that outgas and may polymerize in the hot vials during the long sampling times. These reactive compounds that go undetected can react on substrate surfaces and lead to failures.

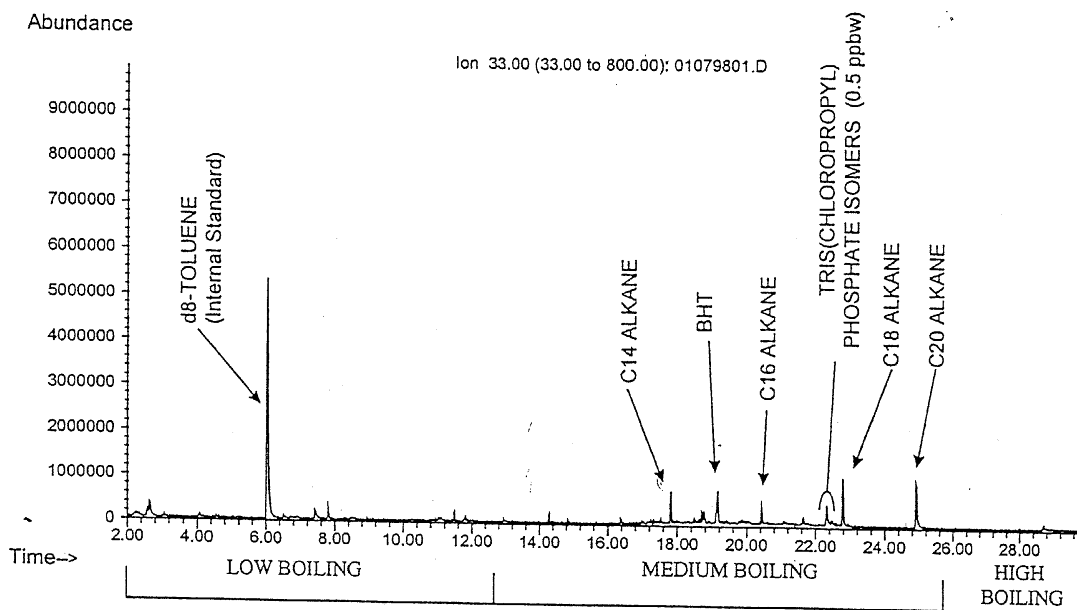
FIGURE 3: HEPA FILTER POTTING COMPOUND: DYNAMIC HEADSPACE OUTGASSING OF TCPP AT 100°C FOR 30 MINUTES ("SCREENING TEST"). GC-MS detected outgassng of 531 ppmw TCPP.



By using dynamic headspace sampling, 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. The dynamic headspace outgassing from the reference filter potting compound clearly demonstrates that extremely low levels of organophosphates can be detected by dynamic headspace GC-MS method.

The dynamic headspace may not capture all of the low boiling compounds since they may not be effectively trapped on the adsorbents used. Some very high boiling or reactive compounds may be irreversibly adsorbed onto the sampling tube adsorbent, or may react or decompose during the analysis. For this reason recovery studies are essential for critical compounds.

FIGURE 4: HEPA FILTER POTTING COMPOUND: DYNAMIC HEADSPACE-ROOM TEMPERATURE OUTGASSING FOR 1 HOUR ("ENGINEERING TEST" METHOD). GC-MS found 0.5 ppbw tris(chloropropyl) phosphate (TCPP). 1 year old filter.



IV C. Contamination Control

The anomalous doping problems at the test site discussed in this paper caused 10% to 15% overall yield loss. Doping was especially severe for the last 3 wafers in each 25-wafer batch. Contamination occurred while wafers sat under air awaiting processing in the lithography area with a bare silicon area exposed. Wafer die yields for the last wafer, #25, varied between 0-90%, and were worse for longer air exposures. The previous two wafers also had reduced yields for the die on the periphery. Since the AMC problem was related to newly installed HEPA filters at this facility, the HEPA filters could have been removed, but this would be expensive and disruptive. As a compromise, carbon filters were added to the recirculation air system. The carbon filters strongly adsorb most higher boiling organic compounds. This reduced the organophosphate in air by about 6X and increased yield ≈15%. The n-doping problem was no longer limiting the yield.

A surprising number of materials still used in semiconductor fab's outgas organophosphates, some at very high levels. Organophosphates are commonly used as flame retardants in cleanroom materials containing plastics, elastomers and urethanes (especially ULPA and HEPA filter potting compounds). Some phosphates commonly found in cleanrooms, on wafers, or outgassing include trialkyl phosphates (methyl, ethyl, butyl, cresyl, chloroethyl, chloropropyl) and triaryl phosphates such as triphenyl phosphate. Ideally, all organophosphates would be excluded from semiconductor cleanrooms, but potential effects of alternative flame retardants also need to be assessed. Completely eliminating flame retardants is often impractical due to fire codes.

The manufacturing processes in cleanrooms are not only affected by organophosphate contaminants, but several other organic compounds have been shown to be detrimental to these processes. Some of these compounds may not be volatile enough to be detected under conditions of the engineering test. The dynamic headspace method at 100°C maybe a more practical and sensitive test for assessing the possible sources of such contaminants.

The ideal screening program would eliminate any sources of contamination in the fab. In our experience, the 100°C dynamic headspace screening test appears to detect most organic compounds that would negatively impact production of silicon based semiconductors. Some contaminants may get by undetected using the engineering test. In the real world, contaminants do get into the fab. For existing fabs, the on-wafer test for organics seems very sensitive to organo-phosphates and DOP (a plasticizer).

V. CONCLUSIONS

The air sampling tests are useful for establishing baselines for organophosphates and other organic contaminants in the cleanroom air and making sure that no detrimental compounds are present. The levels of organic compounds in the air however, may not be in direct correlation with organic compounds sticking to the wafer surface. Therefore, wafer sampling tests should

be carried out to establish the levels of specific organic contaminants that may adversely affect the wafer processing.

The 100°C dynamic headspace GC-MS screening methods is recommended as a first line of defense for assessing organic outgassing of prospective cleanroom materials. This method has adequate sensitivity (<1 ppmw) to detect the types of higher boiling organic compounds (e.g. phosphates, silicones, phthalates) that are most likely to affect processing of sensitive substrates. These methods are quicker, easier, and more sensitive than the "engineering test" method.

Molecular contamination can be greatly reduced by implementing a screening program for outgassing. Some yields may improve and some processes may allow longer hold times between processes without re-cleaning. It is conceivable that some cleaning steps might be eliminated altogether if AMC is controlled. The resulting reduced scrap, cycle times, cost of equipment and process footprints would give the biggest return on investment.

VI. REFERENCES

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