MICRO
CONTAMINATION IDENTIFICATION, ANALYSIS, AND CONTROL

How clean is your cleanroom air?

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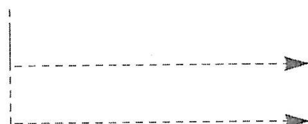

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Both nonparticulate and particulate contamination in the cleanroom can be identified and evaluated using three new air-sampling methods.

Semiconductor manufacturers have long been aware of the importance of a clean environment for maintaining high production yields. As chip geometries and complexity have increased, cleanroom technology has kept pace, dropping from Class 1000 through Class 100 to Class 10 and Class 1 as ever-increasing amounts of HEPA and ULPA filtration and the gowning of personnel have enabled significant reductions in airborne particle levels. Certainly everyone recognizes that particle control is a necessary requirement for IC production, but is it the sole criterion for determining the ultimate cleanliness of a cleanroom? Is a virtually particle-free manufacturing environment insurance that other contaminants won't cause yield problems for future IC technologies? These questions are being asked more frequently, especially in conjunction with the recognition that wafer haze can be caused by organic compounds or ammonia salts from cleanroom air. Also, it has been known for some time that aluminum corrosion in a package can be caused by vaporous contaminants from the fab that contain chloro or fluoro atoms.

To address these and other problems, various researchers have begun to monitor cleanroom air for such materials as ammonia and acidic fumes, organic compounds, metals, and dopants. Cleanroom specifications do not cover these materials, and there are very few data available regarding their concentrations in clean air and their effect on wafers. Consequently, in 1993 we started a program to develop analytical methods that could be used to obtain accurate measurements of the full range of contaminants in a cleanroom. The focus was on cleanroom air sampling, with particular attention to inorganic and organic vapors, and on improving available techniques for measuring and evaluating particles, their composition, and their sources. The methods that resulted from this effort were based on three sample-collecting devices: an inorganic scrubbing unit, an organic adsorption unit, and a new type of particle impinger. Each works independently and uses a pump to draw air into its collection chamber. Descriptions of the three devices are presented here, along with a discussion of some of the data that have been obtained using them.

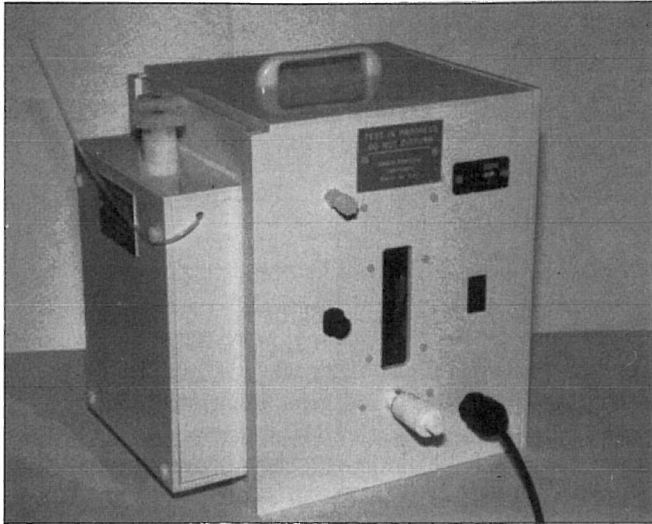

Figure 1: The inorganic scrubbing unit for cleanroom air sampling.

Element	Limit (ng/L)
Aluminum	0.003
Boron	0.02
Calcium	0.1
Copper	0.003
Iron	0.02
Nickel	0.002
Potassium	0.2
Sodium	0.002
Tin	0.001
Zinc	0.002
Ammonium	0.02
Fluoride	0.3
Chloride	0.01
Sulfate	0.02

Table I: Typical detection limits for metals and other contaminants when sampling with the inorganic scrubbing unit.

Element	Concentration (μg/m³)					
	Location 1		Location 2		Location 3	
	Feb.	May	Feb.	May	Feb.	May
Ammonium	61	7.9	12	4.4	3	2.9
Fluoride	28	1.4	10	1.1	2.9	1.6
Chloride	0.14	<0.01	0.045	<0.01	0.14	0.16
Nitrite	33	3.3	9	1.4	6.9	3.7
Phosphate	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Bromide	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Nitrate	3.1	0.67	0.94	0.4	1.6	0.82
Sulfate	0.14	0.04	0.16	<0.02	0.51	0.25

Table II: Nonmetallic contaminant results from Class 100 cleanroom evaluations using the inorganic scrubbing unit. Sampling was performed before and after airflow adjustments were made in the fab.

Detecting Inorganic Contaminants

The inorganic scrubbing unit, shown in Figure 1, contains a series of tubes that are filled with either ultrapure water or dilute acid. As cleanroom air is pulled through this system at a rate of 1 L/min, volatile anhydrides, such as ammonia and hydrogen fluoride, as well as other materials, such as aerosols and supersmall particles, are scrubbed out of the air and trapped in the liquid, which is analyzed later using ion chromatography or inductively coupled plasma–mass spectrometry (ICP-MS). For anhydrides of acids and bases, a sample sufficient for analysis is collected within 8 to 16 hours, while metallic contaminants require sampling times of 3 days. Table I lists detection limits for metals and nonmetals when these sampling times are used. It is rare for a cleanroom not to have some measurable quantities of the elements under these sampling conditions.

New cleanrooms had lower inorganic contaminant levels, but their concentrations were measurable.

Over the past two years, new, upgraded, and old cleanrooms have been evaluated using the scrubber, and differences in both the type and quantity of materials they contained were observed. In general, the new cleanrooms had considerably lower levels of inorganic contamination, but nevertheless their concentrations were measurable. In older operating cleanrooms, high levels of acidic and basic fumes were often found. Frequently, such levels could be reduced simply by adjusting airflow rates within the fab. For example, Table II gives the results for a U.S. fab that was evaluated for volatile acidic and basic anhydrides in February and again in May after airflow studies and ventilation adjustments had been made. Because these materials can cause haze formation and corrode aluminum metallization, reducing their concentration is important.

Results of another study, which identified the concentrations of metals and dopants in various locations within a single cleanroom, are presented in Table III. Of particular interest are the levels of magnesium, sodium, boron, and silicon. Magnesium is found in cleanroom materials and sodium has several sources, but the boron and silicon must have come from the HEPA filters.

Another interesting contamination problem that was studied involved high iron concentrations on wafers analyzed by vapor-phase decomposition ICP-MS. In an effort to trace the source, the fab's ultrapure water and process chemicals—both as received and at the wet station—were analyzed. The water and source chemicals proved to be iron-free, but the chemicals in the bath were high in iron. Air measurements taken above the chemical baths also revealed high iron levels, and the air immediately upstream of the HEPA filter proved to be higher

Element	Concentration (µg/m³)		
	Location 1	Location 2	Location 3
Sodium	0.001	0.007	<0.001
Magnesium	<0.001	0.001	<0.001
Aluminum	<0.002	<0.002	<0.002
Boron	0.056	0.022	0.024
Calcium	<0.07	<0.07	<0.07
Potassium	<0.1	<0.01	<0.1
Iron	<0.01	<0.01	<0.01
Nickel	<0.001	0.001	<0.001
Silicon	0.02	0.05	0.04
Copper	0.002	<0.002	<0.002

Table III: Metallic contaminant results from a Class 100 cleanroom evaluation using the inorganic scrubbing unit.

in iron than the filtered air. The source of this iron was ultimately traced to corrosion in the air-conditioning system.

Identifying Organic Contaminants

In the organic adsorption sampler, a routine-type sampling tube filled with activated carbon is used with an air-intake pump to collect organic compounds from cleanroom air (Figure 2). Using a sampling flow rate of 100 ml/min, enough material will be collected in 12 to 16 hours to permit analysis by gas chromatography–mass spectrometry (GC-MS). Because of the nature of the sample and the limits of the analytical techniques, the GC-MS results are semiquantitative at best. They are useful, however, for identifying organic contaminants.

Among the organic compounds that may be found in cleanrooms are aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, alcohols (especially isopropyl alcohol), N-methyl pyrrolidone (NMP), silicones from sealants, phthalates that outgas from plastic materials, creosols and amines from photoresist processing materials, and organic compounds from latex paint, cleaners, and other materials used in a cleanroom. Figure 3 is a typical spectrum of an organic sample collected in a cleanroom. Only major peaks are identified on the figure, but it can be clearly seen that numerous other organic compounds are present in cleanroom air.

Figure 2: The organic adsorption sampler.

Maximizing Particle-Sampling Data

To improve on such commonly used measurement methods as particle monitors and witness wafers (wafers left exposed to air in a cleanroom and then examined by a surface scanner or scanning electron microscope [SEM]), a particle impinger was developed for cleanroom air sampling (Figure 4). This unit draws air through a nozzle and impinges the airborne particles onto a clean wafer. Figure 5 depicts a typical test wafer surface after 16 hours of air sampling at a rate of 30 L/min. Because of the air mass/flow relationship, particles are impinged at different distances from the center of the wafer, often creating visible rings. The impinger collects 30 times more particles than a witness wafer in the same amount of time and, because the greatest number of particles are at the center of the wafer, its sample surface can be evaluated more readily by such techniques as SEM, Auger electron spectrometry, electron spectroscopy for chemical analysis, and secondary ion mass spectroscopy. After physical and chemical evaluations of a wafer have been completed, it can be kept for later comparisons with subsequent test wafers for purposes of statistical quality control.

The particle impinger collects 30 times more particles than a witness wafer in the same amount of time.

Thus far, the primary use of this sampling unit has been for studies comparing particle contamination at different locations in a fab, and evaluating and identifying particles around a specific piece of equipment. Generally only the total number and sizes of the particles were determined by using a surface scanner. However, when elemental data were collected, the elements most frequently found were calcium, magnesium, zinc, silicon, and boron. Studies are continuing to obtain sufficient data to make more-definitive statements on the use of this unit.

Other Applications

Because the three sampling devices described above are basically collectors of contaminants found in a gas (air), any type of gaseous system could be evaluated using these systems if the sample inlets were adapted to the application. The scrubbing unit already has been adapted to measure metals in carrier gases, minienvironments, gas generators, and other gas-phase systems. For example, the results of a study measuring metal levels in oxygen downstream of a process tool are shown

1. HEPTANE
2. TOLUENE
3. BUTYL ACETATE
4. SILOXANE (Me_2SiO)
5. ETHYLBENZENE
6. M,p-XYLENE
7. o-XYLENE
8. 2-BUTOXYETHANOL
9. TRIMETHYLBENZENE
10. SILOXANE ($(Me_2SiO)_4$)
11. SILOXANE ($(Me_2SiO)_5$)
12. PLASTICIZER

0 4 8 12 16 20 24 28

TIME (min)

Figure 3: A typical spectrum of an organic sample from a cleanroom.

Figure 4: Particle impinger for air sampling.

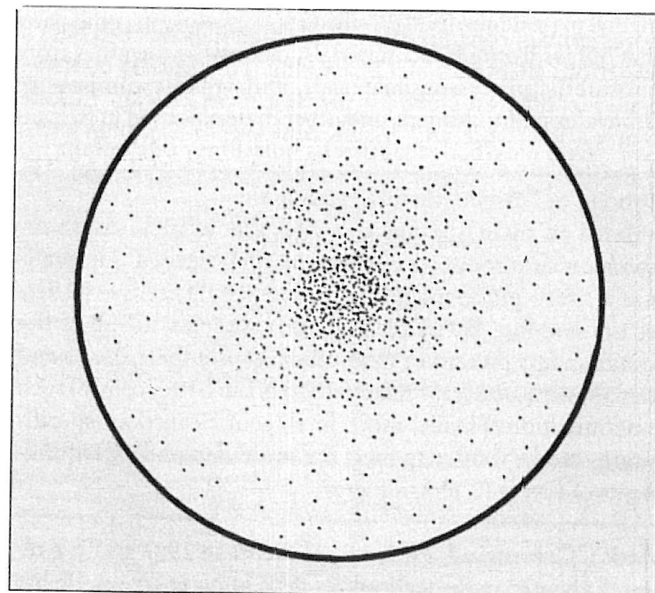

Figure 5: Particle distribution on test wafer taken from the particle impinger.

Element	Concentration (ng/L)
Aluminum	0.027
Barium	0.070
Calcium	0.42
Chromium	0.0021
Copper	0.0040
Iron	0.016
Magnesium	0.18
Manganese	0.0011
Molybdenum	0.0023
Nickel	0.0011
Sodium	4.2
Strontium	0.0016
Titanium	0.0001
Zinc	0.0034

Table IV: Metallic contaminant results of a study evaluating gaseous oxygen downstream of a process tool. The inorganic scrubbing tool was used for gas sampling.

in Table IV. Although these concentrations are small in terms of nanograms per liter, the number and type of elements found are of concern. Contrary to what was expected, these data suggest that the interaction of the gas and the equipment it is used in can contribute to metallic contamination even though the source gas is essentially metal-free.

The air-sampling system has also been used to study the relationship between air contamination and hard-disk corrosion. The corrosion was found to be dependent on the concentration of nitric oxides in the ambient air.

Conclusion

By using the three new sampling units and several analytical procedures, it is possible to conduct a cleanroom evaluation that encompasses all types of contamination. Studies already performed using the devices have revealed that cleanrooms contain considerable volatile materials that can have a deleterious effect on wafer processing. The primary contaminants identified are created in the cleanroom itself and include volatile acidic, basic, and organic compounds. Except in terms of particulate contamination, ambient cleanroom air was found to be "dirtier" than the source air.

Based on these findings, it is clear that more in-depth research on cleanroom air contamination is needed. Air quality as it affects processes, products, and people needs to be better understood. By increasing their understanding of the contaminants present in cleanroom air and their effects and sources, semiconductor manufacturers can better control such contamination. Finally, more-intelligent cleanroom specifications can be written to meet the more-demanding requirements of future IC technologies.

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Mark J. Camenzind, PhD, joined Balazs in 1987 and is a research chemist in the technology development group. He has been developing analytical services for trace organic analysis of chemicals on wafers and in cleanroom air or minienvironments. Techniques used include total oxidizable carbon, gas chromatography, gas chromatography–mass spectrometry, and thermal desorption–mass spectrometry. Camenzind earned a BS in organic chemistry at Massachusetts Institute of Technology and a PhD in inorganic chemistry from the University of California, Berkeley. He is a member of ACS, AVS, the Institute of Environmental Sciences, and the American Society for Mass Spectrometry. He also serves on ASTM and SEMI committees.

Hongjian Liang, special projects supervisor, joined Balazs in October 1988. She specializes in the area of analytical chemical instrumentation used to measure inorganic materials. She developed methods for the determination of trace metals in chemicals using ICP-MS. She received an MS in analytical chemistry from Zhongshan University in China in 1985.

János Fucskó, PhD, research chemist, joined Balazs in May 1990. He has studied the analysis of boron in BPSG and published on its anomalous behavior in the presence of HF. He has also developed methods for the determination of trace metals in native oxide and dielectric oxide films using ICP-MS and other thin-film analyses. Previously, he worked at the Hungarian Academy of Sciences in the Electroanalytical Research Group at the Institute of General and Analytical Chemistry, Technical University of Budapest for 9 years, where he was engaged in analytical chemical automation, flow injection analysis, electroanalytical sensors and monitors, and the application of solution equilibria and kinetics in method developments for wet chemical analysis. He received a PhD in analytical chemistry from the Technical University of Budapest in 1989. Fucskó is a member of the Society for Applied Spectroscopy, ACS, and IEEE. He has seven publications.

Marjorie K. Balazs is the founder and president of Balazs Analytical Laboratory in Sunnyvale, CA, and Austin, TX. She has worked in the semiconductor industry since 1968. Prior to that, she spent 10 years at Stanford Research Institute and taught for 6 years at the University of San Francisco. She received an MS in chemistry from USF and an MA in chemical education from Stanford University. She is a member of ECS, ASTM, ACS, and SEMI/Sematech, where she is also on the board of directors. Outstanding honors include an award from President Reagan in 1986 as an outstanding woman entrepreneur; a 1992 City of San Jose Small Business Award; and the 1993 SEMI Award for North America, recognizing her contribution in yield enhancement to the semiconductor industry over the past 25 years. (Balazs and the other authors can be reached at 408/745-0600.) ■