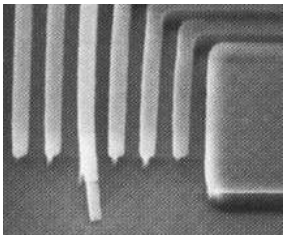
BALAZS™ nanoAnalysis

Bases in Air and Ultra High Purity Gases

Monitoring Bases Prevents Hazing and Deep UV Lithography Defects

Basic compounds such as amines, ammonia and amides are commonly used in cleanrooms for semiconductor processing, yet these same compounds can have disastrous effects on processing if their levels are not controlled. Amines and amides can negatively affect deep UV (DUV) lithography and increase linewidth. Amines can also react with acid vapors creating haze on wafers or optics.



DUV photoresist T-topping

Hazing of lithography optics is detrimental to performance

Sources of Bases

- Ammonia comes from SC-1 (APM), wafer cleaning solutions, fab cleaning solutions, CMP processes, TiN, SiN, HMDS hydrolysis in the lithography area, outside air, people and other sources such as coolant additives
- Amines and amides (e.g. NMP, N-methylpyrrolidinone) are commonly used in photoresist strippers and these can contaminate lithography
- Other sources of amines include air humidifiers for corrosion control, epoxies and cleaners
- Other amide sources include polyamides, polyimide solvents, epoxies, paints and coatings
- Urea comes from fertilizers, livestock or snow removal chemicals that wind up in the city water and can then end up in DI water; when used in humidifiers, it can get into the air and ultimately breakdown into ammonia

Due to the problems of bases in cleanroom air, SEMI has developed a classification of cleanroom air for molecular contaminants, including a category MB for molecular bases (SEMI F21-1102). Measuring ammonia, amines, amides and urea in cleanroom air will provide a missing piece of the cleanroom puzzle.

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AIR LIQUIDE ELECTRONICS

Methods of Choice

Amines and Ammonium: Balazs™ NanoAnalysis uses bubblers with solutions to trap bases, then ion chromatography (IC) to detect volatile amines and ammonia as well as the salts that form from reaction with acids. Sample pre-concentration coupled with IC capability has become the analytical method of choice to measure extremely low level ionic contaminants in liquids, down to parts per trillion levels.

Amides: Thermal desorption gas chromatography - mass spectrometry (TD GC-MS) is the tool used to detect these volatile, neutral compounds in air.

Urea: IC-MS provides a selective and sensitive method to analyze solutions from bubblers used to trap urea from air, or to test for urea presence in water.

Sampling and Analysis

Ammonium and Amine air samples are collected with an Air Sampling Module designed by Balazs™ where the air is scrubbed by an absorber solution placed in specially prepared tubes for air samples, or gas samples. Samples are collected for a predetermined amount of time, typically 24 hours. The aqueous solutions are then analyzed using IC. Using our current method, we analyze the most problematic amines and ammonia in cleanroom air. The method detection limits for these amines are shown in Table 1. Results from the analysis of cleanroom air and gases can be used to improve device yields, reliability and performance.

Amide air samples are collected onto adsorbent tubes, typically for 6 hours for ambient air and 24 hours for gases. These tubes are thermally desorbed onto a GC-MS, compared with library spectra and quantitated against an external standard. The method detection limits for amides are shown in Table 1. When testing for urea in air, samples are collected into sample modules with a urea-free aqueous solution. Samples are analyzed by IC-MS. The method detection limit is shown is Table 1. These same methods can also be applied to the analysis of these basic contaminants in UHP gases like N_2, He, clean dry air (CDA and XCDA) and purge gases that are used for steppers or inspection tools (see Table 1 below).

Table 1. Method detection limits for bases in air

	Detection Limit in Air (pptv = pptM)	Detection Limit in Gases (pptv = pptM)
Amines		
Aminoethoxyethanol	20	10
Ammonium	50	20
Cyclohexylamine	20	10
Diethanolamine	20	10
Diethylaminoethanol	20	10
Ethanolamine	30	10
Ethylamine	40	10
Methoxypropylamine	20	10
Methylamine	60	20
Morpholine	20	10
Triethylamine	20	10
Trimethylamine	20	10
Amides e.g. NMP	200	50
Urea $(NH_2)_2C=0$	100	100

Notes

- pptv = parts per trillion by volume (1 volume of compound in 10^{12} volumes of air)
- pptM = parts per trillion by moles (1 mole of compound in 10^{12} moles of air)