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## Upcoming Events

### Technoday Asia

Singapore  
April 18

### SPCC

### Surface Preparation and Cleaning Conference

Austin, TX  
April 25-26

**Dr. Scott Anderson  
will present**

### ESTECH

Bloomington, IL  
April 30-May 01  
Tabletop #21

### Nanotech 2007

Santa Clara, CA  
May 20-24

### Semicon West

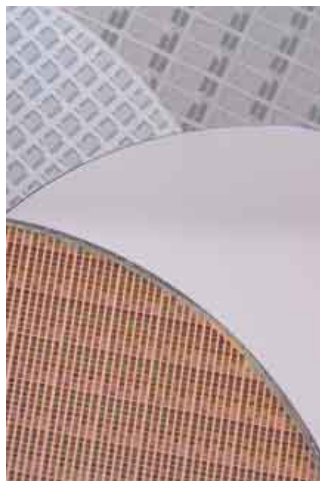
San Francisco, CA  
July 16-20  
Booth# 630

**Fall 2006 Edition of  
Analytical Insight**

## Urea in Air: Sampling and Analysis Techniques

Urea is a problematic contaminant in fabs, first because it is a reactive amine, and secondly because it can decompose to ammonia. Amines generally, and ammonia in particular, are critical impurities in photolithography.

The ITRS specifies control of airborne molecular contamination, including amines and ammonia. In addition to techniques for measuring urea in water, Balazs has developed airborne urea sampling techniques to further reduce cleanroom contamination.



[Read Full Article](#)

## Don't Forget the Edge! Significance of VPD ICP-MS Edge Exclusion



solution over the surface.

In order to preserve the integrity of the sample, it is critical that no collection solution is lost over the edge of

VPD ICP-MS (Vapor Phase Decomposition followed by ICP-MS analysis) is a technique used to measure trace metal surface contamination over the entire wafer surface. 'Scanning' of the wafer involves the maneuvering of a known volume of collection

## Quick Notes

### RoHS Analysis Boosted by New Equipment

Balazs has added XRF capabilities to its strong portfolio of RoHS services. The XRF provides the basic screening tool identifying the presence of restricted...

[Read Note](#)

### Understanding Incorrect Advanced Precursor Analyses

Traditional techniques to identify contaminants in advanced precursors (i.e. hafnium compounds) can lead to incorrect COA reporting. The April issue of *Semiconductor International* highlights...

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[Read Note](#)

## Do You Know???

the wafer. Therefore, common laboratory practice involves an 'edge exclusion' of 5mm to ensure none of the collection fluid is lost. Recent studies completed by Balazs, however, indicate that excluding the edge causes a significant underreporting of trace metal contamination.

[Read Full Article](#)

### **Trivia- Win \$50**

Balazs is giving away a \$50 gift certificate for submitting the correct answers to each of the trivia questions in this issue. Answers must be submitted before April 20, 2007. A random drawing of all qualified entries will determine the winner.

Enjoy the challenge!

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# Airborne Urea Sampling and Analysis



By Dr. Dan Cowles, Dr. Mary Havlicek, Lynn Vanatta, Piyamit Chitrathorn

## Introduction

Balazs™ Analytical Services developed a method for capture and analysis of airborne urea. Urea is a problematic contaminant in fabs, first because it is a reactive amine, and secondly because it can decompose to ammonia. Amines generally, and ammonia in particular, are critical impurities for photolithography. Although a method is already in place at Balazs to quantify urea in water, a sampling method for airborne urea provides further control and quantification of this semi-volatile contaminant for the fabs.

Urea is a ubiquitous environmental contaminant that enters fabs through the water supply (1). Unfortunately, urea is only partially removed in the production of ultra-pure water (UPW). For example, samples of water were collected from various stages of a DIW production facility and analyzed for urea. Table 1 displays the urea results. Purification reduces the urea concentration from about 40 ppbw in incoming city water to around 3 ppbw in the final delivery DIW. Historically, semiconductor DIW samples analyzed by Balazs have contained up to 20 ppbw urea (1).

| Sample # | Description                        | Bottle# | Urea (ppb) |
|----------|------------------------------------|---------|------------|
| 1        | City water                         | S011    | 41         |
| 2        | Post carbon bed                    | A017    | 8.5        |
| 3        | Post RO                            | A002    | 8.9        |
| 4        | Post storage tank after deaeration | S025    | 3          |
| 5        | Post 1st UV                        | S012    | 2.7        |
| 6        | Post Cation and Anion beds         | S032    | 2.9        |
| 7        | Post 2nd UV, before mixed ion beds | A019    | 3.2        |
| 8        | Post mixed beds                    | A027    | 3          |
| 9        | Water leaving TIME to Fabs         | S016    | 2.7        |
| Blank    | Distilled water blank (Sparkletts) | S014    | <0.5       |

Table 1: Urea Concentrations in UPW Purification Process.

Wafers-in-process can be exposed to urea directly in any fabrication step utilizing UPW. In addition, urea in UPW can potentially migrate to the cleanroom air supply via the humidity-control mechanism. Fab humidity control typically involves steam generation from DIW, which, as demonstrated above, often contains low-ppb concentrations of urea.

Finally, urea can conceivably enter the cleanroom from outside as a particle or vapor in the make-up air. Airborne urea itself, or its decomposition byproduct, ammonia, can negatively impact photolithography processes, for example by neutralizing photoresist acids.

Therefore, although a method has already been established by Balazs for direct quantification of urea in water, there is additionally a need to measure urea in air.

## Method

Urea is a solid at room temperature, however it possesses a sublimation-pressure sufficient to form ppb-level concentrations in air. The sublimation-pressure is known to vary sharply with temperature.

In our experimental apparatus, humidified clean-dry-air (CDA), or alternatively UHP nitrogen, flows through a cartridge filled with urea crystals (>99.5%). The CDA flow-rate through the cartridge ranges from 0.3 to 3 LPM. Relative humidity in the CDA exiting the cartridge is controlled at around 50 %. A fraction (or sometimes all) of the CDA exiting the cartridge is sampled using a conventional Balazs impinger train. The sample flow-rate to the impingers varies from 500-900 cc/min and the impinger is loaded with an aqueous solution which has been previously verified to be free of urea (i.e. urea <DL of IC-MS).

Analysis for urea was performed on a Dionex DX600 ion chromatograph with a Finnigan MSQ mass spectrometer. The instrument was calibrated by analyzing (in replicate) multiple urea standards that spanned the concentration range of interest. At the 95% confidence level, the uncertainty in the reported results is  $\pm 2$  ppbw.

## Results

### Capture Efficiency Test

The most important aspect of ensuring method success was to check the capture efficiency of urea in air with the Balazs sampling system. Different experimental setups were made to check this capture efficiency in a variety of conditions. Urea capture efficiency was measured for three carrier gases: UHP nitrogen, clean-dry-air (CDA), and CDA humidified to 50% R.H. In the initial tests, three impingers were arranged in series. However, after breakthrough of urea beyond the first impinger was found to be undetectable, a single impinger was used. Capture efficiencies are shown in Figure 1 below.

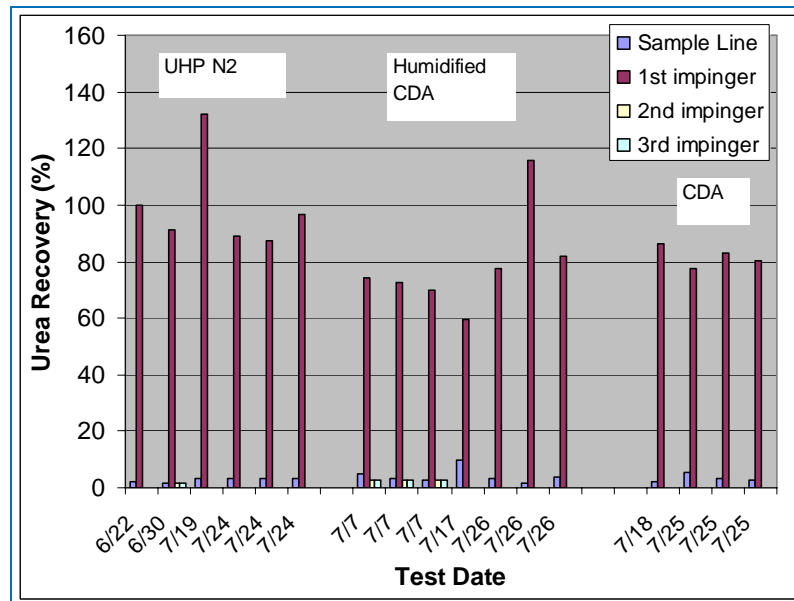


Figure 1: Urea Recovery Test Summary.

The calculated capture efficiency is typically 90-100% when UHP N<sub>2</sub> is used as the carrier gas, ~80% when CDA is the carrier, and 70-80% when 50% relative humidity CDA is used. Although we have not analyzed our CDA for moisture, CDA often contains >100 ppm H<sub>2</sub>O. We believe moisture adsorbed on the urea crystals can depress the sublimation-pressure, due to the strong attraction of urea for moisture.

### Conclusions

Balazs has shown that the urea capture efficiency in air with the Balazs impinger is 90-100% within experimental error. We are currently performing experiments in different fab settings and during different weather seasons to gauge the presence of urea in fab air.

### References

1. *Urea and TOC Detection - Are Your Current Systems Able to Meet Ever-Decreasing Detection Limits?*, S. Schoen, S. Anderson, and M. Haddix, Air Liquide Technoday 2006.

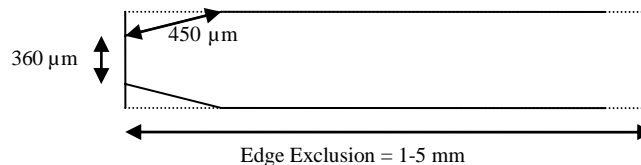
# Don't Forget the Edge!

## Significance of VPD ICP-MS Edge Exclusion

By Annie Watts and Carolyn Vercell

VPD ICP-MS (Vapor Phase Decomposition followed by ICP-MS analysis) is an analytical technique gaining momentum as an important method used to measure trace metal surface contamination on wafer surfaces. Historically, TXRF has been used to analyze surface metal contamination since many facilities have TXRF equipment available in-house, providing quick results. However, VPD offers distinct advantages, making it a more thorough technique. Compared to TXRF, VPD provides results for the entire mass spectrum including lithium and boron, offers lower detection limits and has the ability to analyze the entire wafer surface.

During VPD, the native or thermal oxide wafer surface is dissolved using HF vapors that react with the metal impurities in the oxide layer to form soluble fluorides. Then, a known volume of collection solution is placed on the wafer. The droplet is maneuvered over the wafer surface (scanning) to collect the metal impurities. After scanning, the collection solution is analyzed via ICP-MS resulting in data that represents the total surface metal contamination of the wafer surface.



Scanning the wafer surface involves several different patterns to ensure the entire wafer surface is covered and all metal impurities are collected. Common industry practice includes a 5mm edge exclusion, meaning that the collection solution does not come within 5mm of the wafer's edge.

Balazs has developed a technique to analyze the entire wafer surface and has recently conducted experiments to identify the significance of excluding the wafer edge and the results were, well, significant. The data (Table 1) shows four wafers from the same lot and process comparing a 5mm edge exclusion versus including a 0mm edge exclusion.

| Element   | Detection Limit          | Control Solution         | NO Edge Exclusion        | NO Edge Exclusion        | 5 mm Edge Exclusion      | 5 mm Edge Exclusion      |
|-----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
|           | (atoms/cm <sup>2</sup> ) | (atoms/cm <sup>2</sup> ) | (atoms/cm <sup>2</sup> ) | (atoms/cm <sup>2</sup> ) | (atoms/cm <sup>2</sup> ) | (atoms/cm <sup>2</sup> ) |
| Aluminum  | 6.89E+ 08                | < DL                     | 1.34E+ 10                | 9.85E+ 09                | 1.89E+ 09                | 1.70E+ 09                |
| Calcium   | 4.64E+ 08                | < DL                     | 1.28E+ 09                | 4.50E+ 09                | < DL                     | < DL                     |
| Iron      | 3.33E+ 08                | < DL                     | 1.30E+ 10                | 5.02E+ 09                | 3.62E+ 09                | 3.74E+ 09                |
| Potassium | 4.75E+ 08                | < DL                     | 2.54E+ 09                | 8.17E+ 09                | < DL                     | < DL                     |
| Sodium    | 8.08E+ 08                | < DL                     | 9.48E+ 09                | 1.96E+ 10                | 9.17E+ 08                | < DL                     |
| Zinc      | 1.42E+ 08                | < DL                     | 3.12E+ 09                | < DL                     | < DL                     | < DL                     |

Table 1: Surface metal contamination data via VPD ICP-MS

As high technology processes have metal specifications less than 1E10 atoms/cm<sup>2</sup> one can see from the data that the contamination on the edge of the wafer is near or above this limit. Contamination levels above or close to the specification for metals such as sodium, potassium, aluminum, iron, and zinc can be detrimental to IC device operation.

## Don't Forget the Edge!

### Significance of VPD ICP-MS Edge Exclusion

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Most contamination on the edge of a wafer comes from the wafer boat and handlers within the fab that come into contact with the edge of the wafer. Regardless, this contamination is capable of migrating to other locations on the wafer as processing continues and may lead to device defects.

VPD analysis at Balazs is offered with no edge exclusion. Collecting this additional data provides an accurate report of total surface metal contamination while offering insight into contamination sources within the fab. By knowing and understanding the kind of contamination in the edge exclusion, contamination becomes better understood and easier to control. To ensure a complete contamination picture it is important for one to know how their lab is performing VPD.

## Note: RoHS Analysis Boosted by New Equipment

Balazs has added XRF capabilities to its strong portfolio of RoHS services. The XRF provides the basic screening tool identifying the presence of restricted substances. Discovery of restricted substances highlights the necessity of subjecting samples to more extensive methods to quantify and speciate the restricted compounds.

"The addition of XRF equipment allows Balazs to offer customers a complete RoHS compliance program," says Dr. Hugh Gotts, Director of Research and Development. "From low-cost screening capabilities to approved wet chemical analyses, Balazs offers certification of compliance for customer samples." Balazs' comprehensive testing program is available for parts, materials, packaging, and entire assemblies.



## Note: Industry Discovering Incorrect Advanced Precursor Analyses

Traditional techniques to identify contaminants in advanced precursors (i.e. hafnium compounds) can lead to incorrect COA reporting. The April issue of *Semiconductor International* highlights the reasons for reporting errors in an article written by Dr. Phil Clancy and Dr. Scott Anderson.



[Read the article now](#)

## Note: Balazs Offers Technoday Seminar in Singapore and Taiwan

# Technoday 2007

For the first time, Balazs will host Technoday in Singapore and Taiwan later this month. Technoday is a technical forum for engineers of all disciplines to meet and exchange ideas about process problems, contamination issues and material characterization challenges. This event is free to attend and will increase your knowledge regarding the leading edge research surrounding analytical support for the semiconductor industry.

[View invitation and itinerary now](#)

## Note: Stepper Warranty Validation AMC and Refractory Compounds

Stepper manufacturers require certain, periodic analyses in order to maintain full warranty coverage of the tool. Balazs conducts these analyses and provides analytical reports to illustrate due diligence to tool manufacturers. To maintain warranty coverage, the following analyses are typical (each manufacturer may have slightly different requirements):



Representation of haze build-up occurring on a photomask

- ✓ Airborne Molecular Contamination (AMC) in cleanroom air and the tool environment
- ✓ Analysis of refractory compounds
- ✓ Contamination in process and purge gases
- ✓ Mask and reticle contamination analysis
- ✓ Immersion fluid analysis

Additionally, if any analyses fail to meet the defined specifications, Balazs will conduct further evaluation to identify the root cause(s) of the problem to bring the environment back into compliance. Specifically, these tests involve further AMC analysis, organic outgassing studies, material compatibility studies and haze analysis for optics, mirrors and lenses.

# Technoday 2007

Singapore, Royal Plaza on Scotts, April 18, 2007

Sponsored by  
**SOXAL, Mr. Siewwah Woo**

Technoday is a technical forum for engineers of all disciplines to meet and to exchange new ideas about **process problems, contamination issues** and **material characterization** challenges. Presented annually in the United States, Balazs Analytical Services is proud to introduce Technoday to Asia in 2007.

## About the Speakers

**Scott Anderson, Ph.D.** is the Director of Operations for Air Liquide – Balazs Analytical Services. Including stints at IBM and Texas Instruments, Scott's post-academic research efforts have focused on analytical method development and solving contamination problems within the semiconductor industry. He received his BS in chemistry from North Carolina State University and his Ph.D. in analytical chemistry from the University of Texas at Austin.

**Victor Chia, Ph.D.** is the Director of Surface Contamination Technologies at Air Liquide – Balazs Analytical Services. Victor has served the semiconductor industry for over 20 years and is an expert in SIMS and surface metal analyses. He received his Ph.D. in Analytical Chemistry from the University of California, Santa Barbara and was a post-doctoral fellow at Lawrence Berkeley Laboratory.

**Hugh Gotts, Ph.D.** is the Director of Research and Development at Air Liquide – Balazs Analytical Services. Hugh has served the semiconductor industry for 25 years and is an expert in vibrational and surface organic analyses. Previously, Hugh worked for Philips Semiconductors and Analytical Services Group. He received his Ph.D. in Physical Chemistry from the University of California, Santa Cruz.

**Ravi Laxman, Ph.D.** is the Director of Advanced Materials ALOHA™ at Air Liquide Electronics US. Ravi has served the semiconductor industry for over 15 years and is an expert in material selection for FEOL and BEOL CVD and ALD processes. Previously, Ravi worked for ATMI as the Director for Advanced Materials, Novellus Systems as a Sr. Technologist and in R&D at Air Products and Chemicals. He received his Ph.D. in Organometallic Chemistry from the University of Missouri.

## Agenda

- 7:30 - 8:00 Registration and Refreshments
- 8:00 - 8:15 Welcome and Introduction
- 8:15 - 10:00 **“Contamination Characterization and Analysis Decision Tree”**  
*Victor Chia*
- 10:00 - 10:15 **Break**
- 10:15 - 10:45 **“Applications of SARIS™ for Materials Characterization”**  
*Scott Anderson*
- 10:45 - 11:10 **“PPQ Analysis of UPW for Semiconductor Fabs”**  
*Hugh Gotts*
- 11:10 - 11:30 **“Characterization of Advanced Semiconductor Compounds”**  
*Scott Anderson*
- 11:30 - 12:00 **“Alignment Between the ITRS Roadmap and Balazs Detection Limit”**  
*Hugh Gotts*
- 12:00 - 1:00 **Catered Lunch**
- 1:00 - 1:45 **“CVD and ALD precursors for 65nm and 45nm technology for advanced BEOL and FEOL processing”**  
*Ravi Laxman*
- 1:45 - 3:15 **“Fab Optima™: The Ultimate Program for Airborne Quality”**  
*Victor Chia*
- 3:15 - 3:30 **Break**
- 3:30 - 4:00 **“Contamination in Lithography Systems”**  
*Scott Anderson*
- 4:00 - 4:45 **“Tool Optima™: A Process for Achieving Contamination-Free Tools”**  
*Victor Chia*
- 4:45 - 5:00 Closing Remarks- *Louise Massoni, GM, Balazs Analytical Services*

**FREE** registration for this introduction of Technoday to Singapore

You may register by visiting [www.balazs.com](http://www.balazs.com), sending an email to [info@balazs.com](mailto:info@balazs.com) or by contacting your local sponsor:

**Singapore:** Ms. Ann Wong [Ann.Wong@AirLiquide.com](mailto:Ann.Wong@AirLiquide.com)

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