Using GD-OES to Characterize Challenging Thin-Films and Advanced Materials

BALAZS™ ANALYTICAL SERVICES

By Dr. Fuhe Li

Introduction

This article summarizes the use and advantages of using Glow Discharge Optical Emission Spectroscopy (GD-OES) as part of an overall analysis program for advanced materials (i.e. hafnium and zirconium precursors) and any other thin-films. Other equipment and techniques such as Laser Ablation IC-PMS and SIMS provide complimentary data to provide a comprehensive analytical report of a sample (Table 1).

Technique	Elements Detected	Profiling Mode	Analysis Area	Detection Limit
GD-OES	Periodic Table Including H, O, C, N and Cl	Survey Simultaneous up to 46 elements	4 mm	ppm
LA-ICP-MS	Periodic Table Except for He, H, F, N, Ar, and O	Survey Simultaneous up to 85 elements	5 μm	ppm - ppb
SIMS	Periodic Table H to U	Sequential 1-5 elements per film thickness	75 μm	ppm - ppb

Table 1: Summary of equipment/techniques used in material analysis

GD-OES provides fast, simultaneous analysis of all elements of interest including carbon, nitrogen, oxygen, hydrogen and chlorine. It is an ideal tool for thin film characterization, contamination identification and depth profiling. Accommodating fragile samples using an RF plasma source operating in pulse mode, use of GD-OES is ideal for semiconductor and other high-tech industries.

Thank you to Horiba Jobin Yvon for providing the majority of the pictures and graphs used in this article.

Principles of Function

The basic principle of operation relies on an applied voltage from an anode to the sample (acting as the cathode) in an argon-rich environment. Electron interactions with the argon gas create positively charged argon ions that are drawn to the sample surface. Upon collision at the sample surface (sputtering), atoms are released from the sample. These atoms become excited and de-excited upon collision with argon, ultimately leading to photon emission. The photons, or the 'glow', are measured via optical emission spectrometry to identify elemental make-up of the surface. Figures 2 and 3 summarize the aspects of a typical sputter spot on a sample surface.

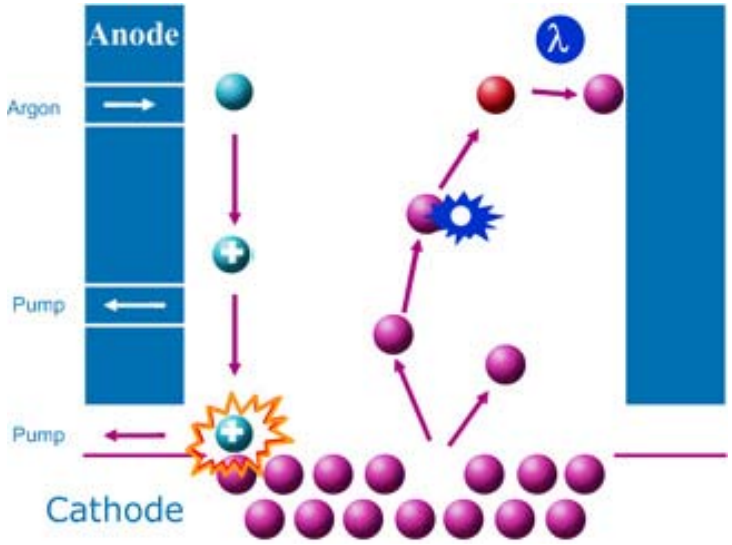


Figure 1: Example of glow discharge 'sputter' interaction

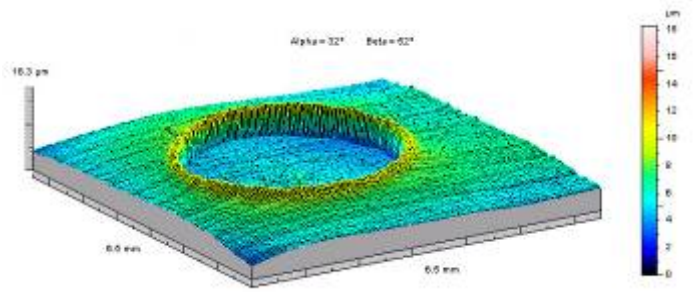


Figure 2: Typical glow discharge crater shape

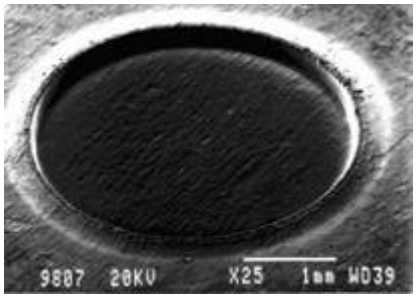
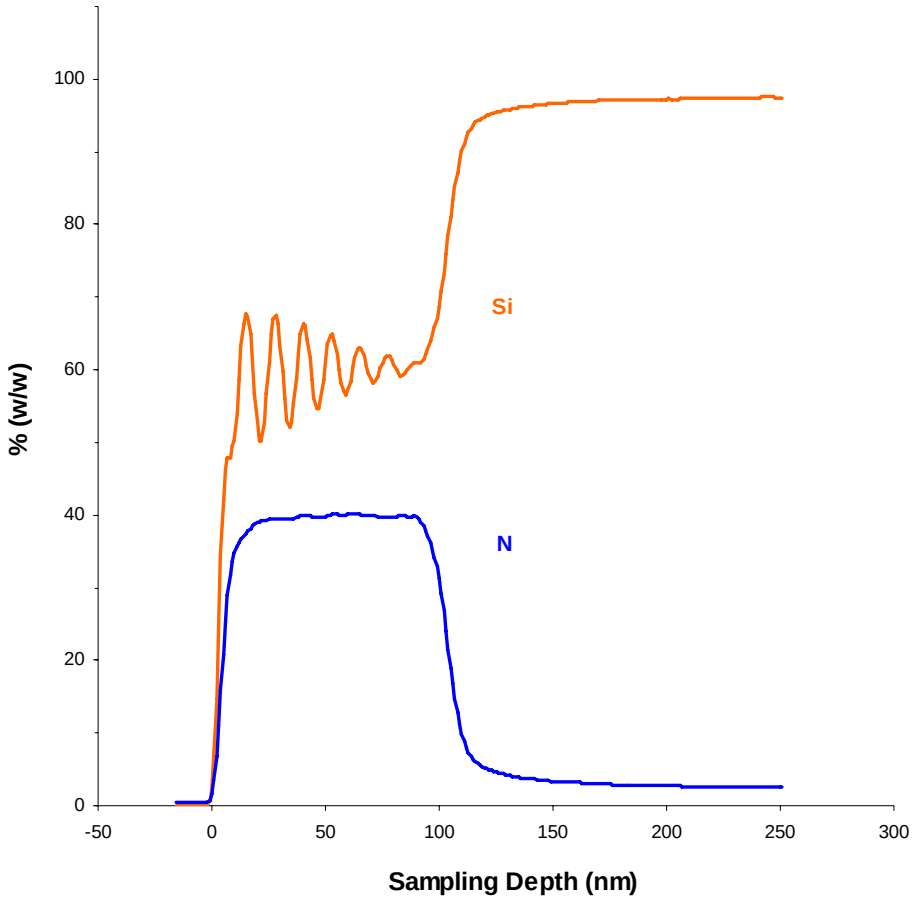


Figure 3: SEM image of a sputter spot

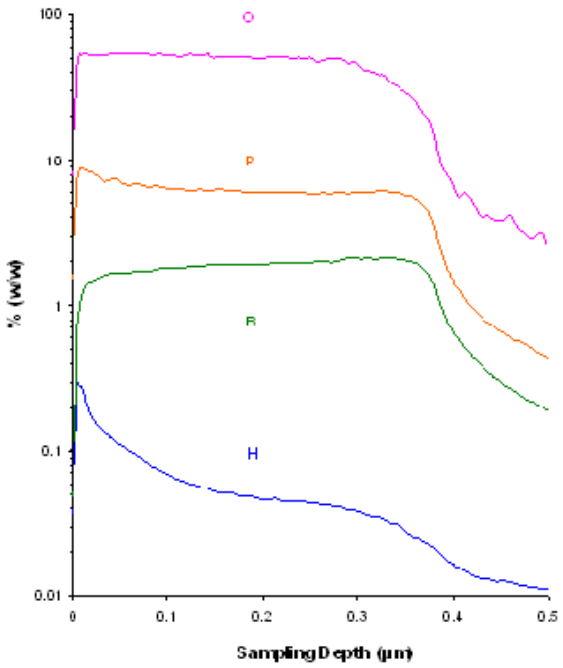
Examples of GD-OES Analyses for Various Films

The following pictures and graphs illustrate the range materials the GD-OES methods analyze. The results provide data to characterize a thin-film, identify contamination and provide high-resolution depth profiling.

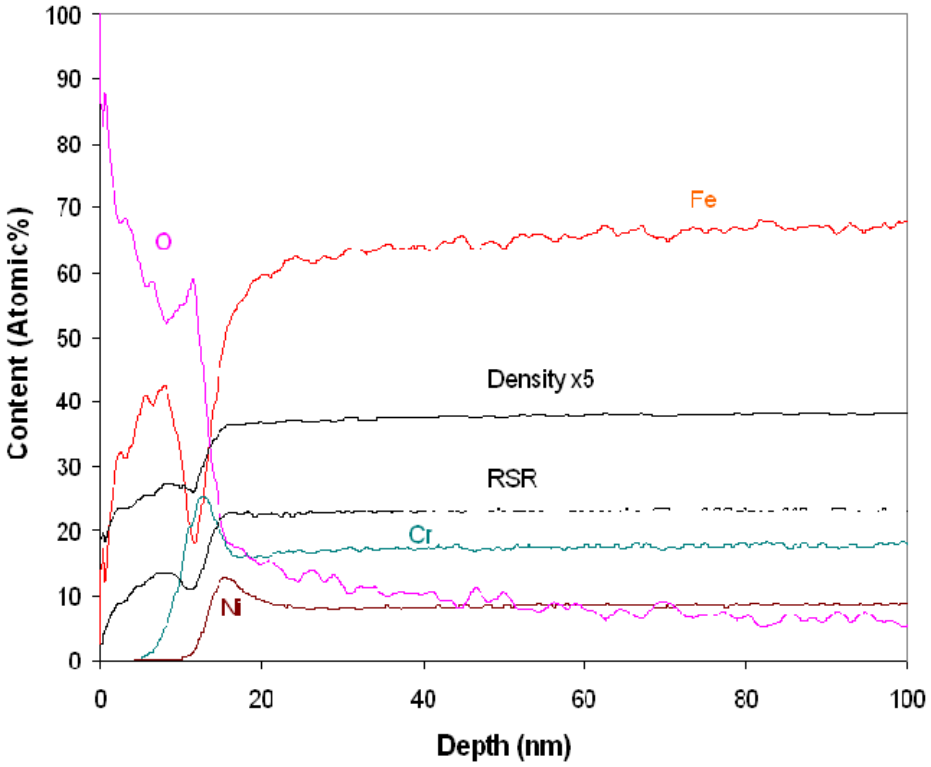
Si_3N_4 Films



BPSG Films



Thin Oxide on Stainless Steel



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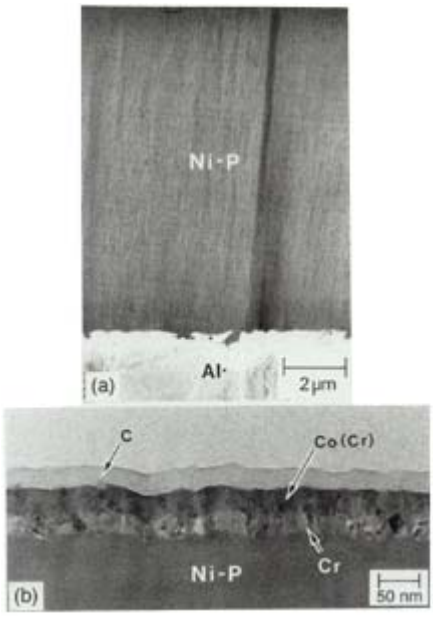
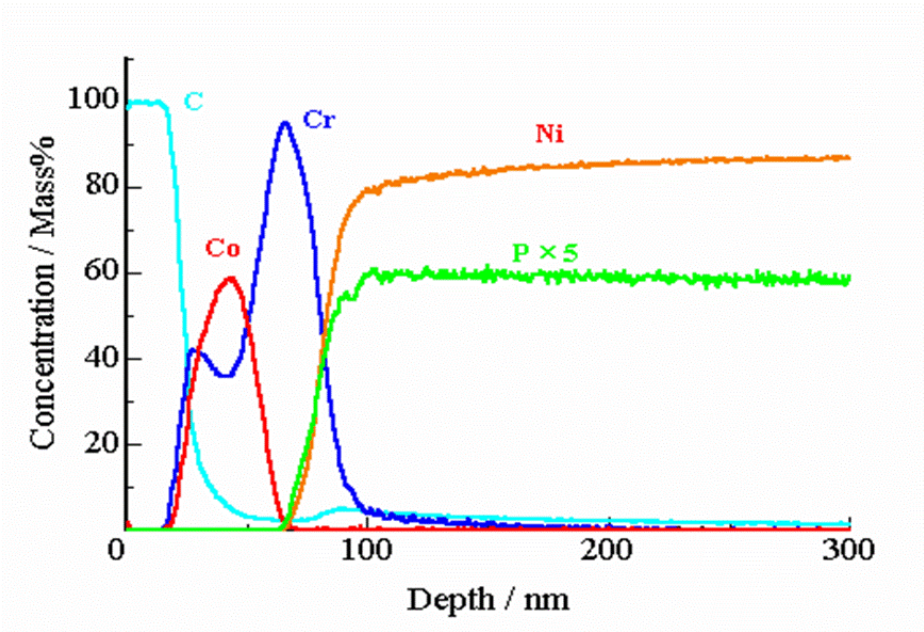
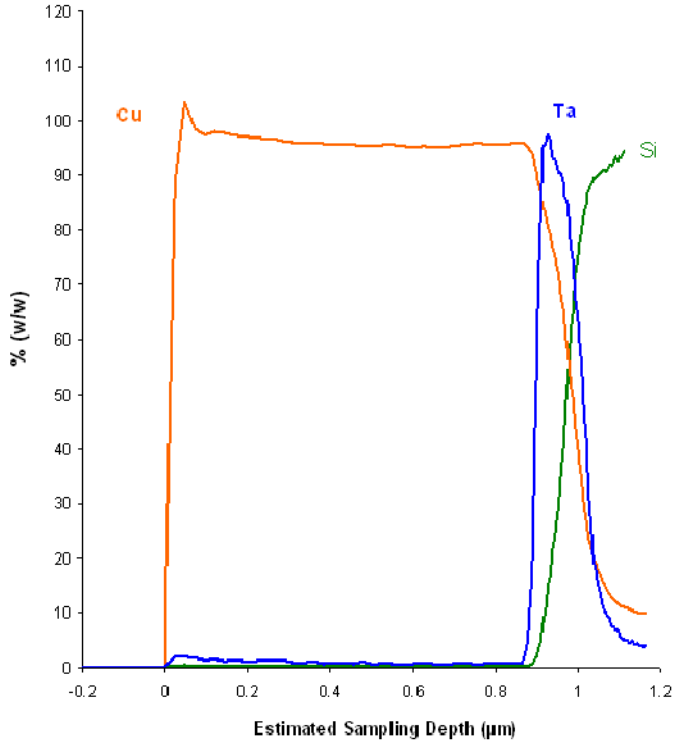
Hard Disk Analysis





Copper Film Consistency



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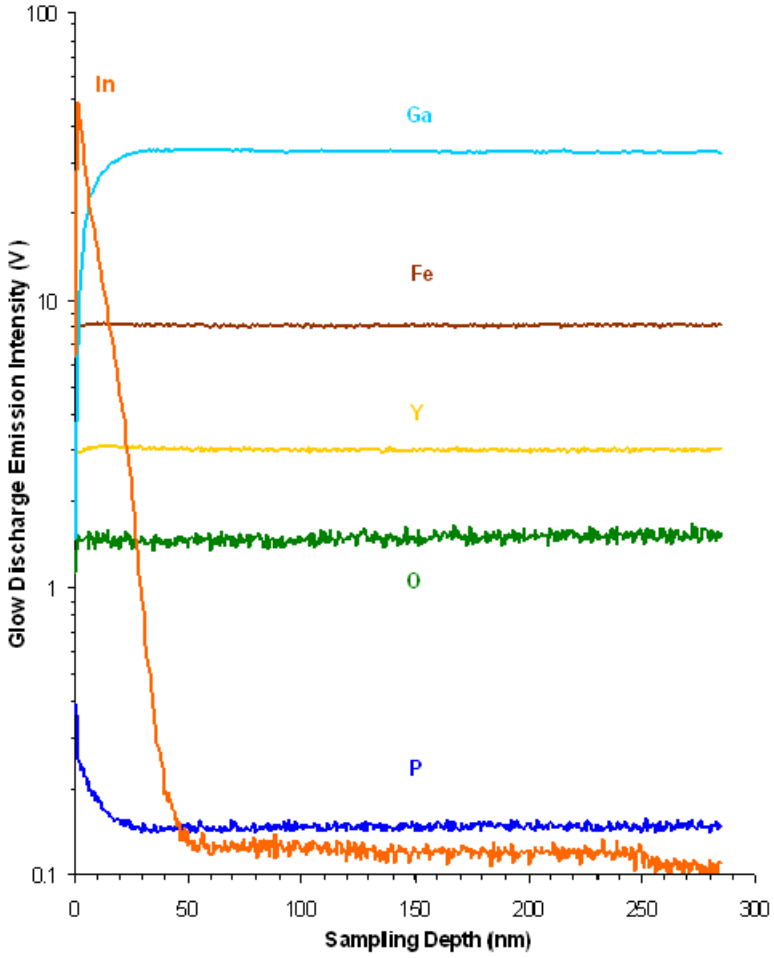
Solar Cell - InGaP Profile



Benefits of Using GD-OES in Conjunction With Other Techniques

- **Simultaneous depth profiling capability-** GD-OES can be used for elemental survey by simultaneously depth profiling more than 40 elements in a film or a material while maintaining a similar depth resolution to SIMS
- **Ultra-fast analysis**
- **No charge effect-** Use of an RF plasma source, instead of an ion or electron beam, for sputtering allows for conductive and insulating films to be analyzed without sample modification and the disruptive presence of charge effects.
- **Large sample spot (4mm)**- Provides a more representative sampling for heterogeneous materials.
- **Increased sensitivity and higher spectral resolution-** when compared with techniques such as Auger and ESCA

Read more about thin-film and depth profiling program

IEST Working Group and Recommended Practice Support from Balazs Analytical Services

Introduction to Standards Developing Organizations
Many industries look to external technical societies or standards developing organizations, such as the Institute of Environmental Sciences and Technology (IEST), in order to optimize their operations, drive technological growth, and ensure continued improvement for an entire industry segment. Groups like the IEST manage the technical Working Groups that generate the peer-created and peer-approved standards and solicit input from industry experts on an ongoing basis.

Balazs actively participates in many standards-developing organizations including IEST, SEMI (for semiconductor and photovoltaics), IDEMA (for disk drives), ASTM (Electronics, air, water, chemicals, materials tests) and ITRS (International Technology Roadmap for Semiconductors). As a participating member we contribute by:

- Providing expertise regarding current analytical capabilities
- Identifying gaps in current techniques and methods compared to proposed standards and leading edge technology requirements
- Suggesting new methods and techniques to eliminate roadblocks from advancing standards & technologies

Specific to the IEST
As stated on the IEST website, http://www.iest.org: "The Institute of Environmental Sciences and Technology (IEST), founded in 1953, is a multidisciplinary, international society whose members are internationally recognized for their contributions to the environmental sciences in the areas of contamination control in electronics manufacturing and pharmaceutical processes; design, test, and evaluation of commercial and military equipment; and product reliability issues associated with commercial and military systems.

Balazs currently supports the analytical needs embedded within current recommended practices often exceeding the reporting limits of the standards. The remainder of this document focuses on the individual working groups (WG) and recommended practices (RP) that Balazs supports to ensure clients are complying with the standards, especially within the CC = contamination control section. In many cases, Balazs also offers specialized tests beyond those specified yet in the standards to cover leading edge issues where the consensus process has not yet developed standards or RP's

IEST Recommended Practices Supported by Balazs

- **RP-CC-003.3:** Analysis of new and used garments. Balazs also does analysis for the laundry water, packaging, residues, end of life cuff studies, since the cuff of the garment is closest to the products. Balazs reports ionic, organic, NVR contaminants ng/cm^2 , extractable particles, or per IEST 1246D. Similar tests can be applied to other disposables including hairnets, facemasks, etc.
- **RP-CC-004.3:** Analysis of new and used wipes. Balazs offers wipe tests for surface contamination for organics, inorganics, particle, contamination assessment, to assess cleaning residues, and to assess cleanup post fires, floods, spills, maintenance etc. Dirty surfaces can be wiped clean, but no wipe is perfect, so clean surfaces can be wiped dirty and this needs to be evaluated carefully; especially for high end optics.
- **RP-CC-005.3:** Gloves; new and end of use: Balazs tests for ionics, metals, organics, outgassing, and offers smudge tests and contact transfer assessment. Some gloves can have very high levels of Zn, Ca, Cl, nitrate, plasticizers etc, and this needs to be controlled for many applications. **RP-CC-006.3:** Testing cleanrooms. Many companies test for particle counts, and Balazs works with users to ID particles, document cleanliness of surfaces, AMC levels etc.
- **RP–CC-008.2**: Gas-Phase Adsorber Cell Balazs tests upstream and downstream of AMC filters to assess removal efficiency as a function of time for acids, bases, organics, SOx, metals, dopants, refractories, , and when to replace filters

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- **RP-CC-012.2:** Cleanroom design, materials selection, outgassing & leach tests, AMC & SMC monitoring, materials compatibility tests.
- **RP-CC-016.2:** Non-volatile residue to sub-monolayers, and semi-volatile organic compounds to 0.001 ML (0.1 ng/cm^2) using witness wafers and SEMI MF1982-1103 TD-GC-MS methods, that also meet ITRS requirements. FTIR, Raman, SEM/EDS and other methods can be used for residue ID.
- **RP-CC-025:** Swabs; new, & used to evaluate surfaces for baselining fab surfaces and cleanups, and small parts, areas, o-ring groves, etc
- **RP–CC026.2:** Cleanroom operations. Any changes in cleanroom air flows, exhausts, tools, processes, workflow can perturb parameters and lead to contamination problems. Cross contamination via people, processes and substrate movement must be assessed. Incoming materials must be cleaned, QC'd to avoid bringing contaminants into the cleanroom.
- **RP–CC027.2:** Personnel in cleanrooms. Personnel can contaminate cleanrooms with particles, vapors like silicones and ammonia, biologically active organisms. Procedures are needed to avoid cross contamination by personnel via garments, gloves, packaging, boxes, equipment, etc.
- **RP-CC28.1:** Minienvironments. Balazs uses witness wafers for Surface Molecular Acids (SMA), Surface Molecular Bases (SMB), Surface Molecular Organics/Condensables (SMOrgs), Surface Molecular Dopants (SMD), Surface Molecular Metals (SMM). Additionally, we leach boxes and minienvironments, other surfaces for acids and bases, organics, test outgassing, identify particles added to substrates and tests AMC Parameters for minienvironments, glove boxes, storage areas, stockers, etc
- **RP-CC031.2:** Balazs measures outgassing performance criteria for cleanroom materials, measured in ppmw. We can also test and report in ng/cm^2/day, do proximity outgassing onto surfaces/wafers per SEMI MF1982-1103, SEMI E108. For Disk drives, we can test to IDEMA standards, including whole running disk drive. We test whole running devices for outgassing including lasers, motors, actuators, etc.

IEST Working Group Participation

- **WG–CC032:** Packaging Materials for Cleanrooms. Balazs offers outgassing, extractables, contact transfer, compatibility, trace metals, organics, ionics testing. We can also assess parts contamination due to heat sealing bags, contact with gel based shipped or membrane boxes.
- **WG–CC035:** Design Considerations for Airborne Molecular Contamination Filtration Systems in Cleanrooms. Methods for baseline AMC analysis testing before and after filters and baseline witness wafers post filters. Comparison with ITRS, other standards. We apply similar test methods for optics, lasers, disk drives and other AMC sensitive industries
- **WG-CC040:** Cleaning of Equipment Surfaces in the Cleanroom & Controlled Environments. Balazs validates cleaning for residues using IC, GC-MS, NVR, FTIR, wipes, extracts, outgassing, ICP-MS, SEM/EDX, particle counts.

- **WG-CC041:** Recovery from Disruption to Cleanrooms and Other Controlled Environments (due to fires, floods, spills, leaks, power outage, HVAC failures) using AMC and SMC tests, witness wafers, swabs, and wipes. Reported per IEST 1246D, or ng/cm^2, using IC, GC-MS, FTIR, EDX, ICP-MS, etc. Contingency planning and baselining prior to failures.

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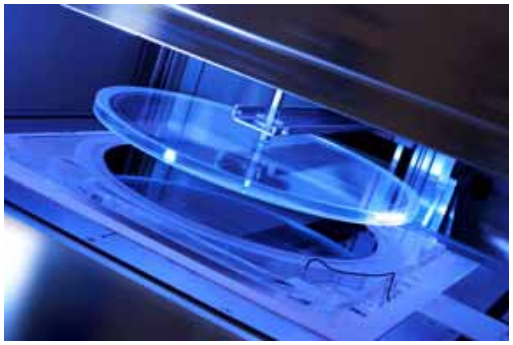
- **WG-CC042:** Liquid Particle Counters. Many companies count particles, and Balazs identifies particles by SEM/EDX, FTIR, Raman and other methods to help find particle sources for water, solvents, chemicals, extracts, gases.
- **WG-CC043:** SMC, Surface Molecular Contamination organics, ions, metals, dopants, NVR using IC, ICP-MS, GC-MS, FTIR, Raman on wafers, optics, any surface in critical environments, for SEMI, Disk, FPD, PV, Laser, optoelectronics, aerospace, medical, instrumentation, optics, coating and related industries.
- **WG–CC201:** Forum on Nanotechnologies. Due to their huge surface areas & small particle sizes, nanotechnologies can in some case be very sensitive to molecular contamination. Balazs can ID both composition, catalysts, additives and impurities in nanomaterials including particles, fibers, nanorods, films.



- **WG–CC901:** IEST-STD-CC1246D: Product Cleanliness Levels and Contamination Control Program See 1246D below.

Additional IEST Involvement

- **STD-CC1246D:** Method for specifying product cleanliness levels & contamination control program requirements. The emphasis is on contaminants that can impact product performance. Balazs tests surface cleanliness levels & can report contamination levels per this standard for particles and molecular contaminants on surfaces in various wt/area units .
- **WG–CC902 and MIL-HDBK-406:** Contamination Control Technology: Cleaning Materials for Precision Pre-Cleaning and Use In Cleanrooms and Clean Work Stations. Balazs tests environments, cleaning solutions, baths at end of life, residues on parts or coupons, packaging issues.
- **MIL-HDBK-407:** Contamination Control Technology: Precision Cleaning Methods and Procedures. Balazs bridges contamination control from %, to ppm, to ppb and ppt levels and from bulk composition to a millionth of a monolayer from the molder or machine shop to the end users reactor or systems

In addition to the above standards, many problems encountered by high tech facilities are not covered in any standard and often requires proper design of experiments to relate contamination issues or process problems to your key electrical, optical, pharmacological, mechanical, magnetic, chemical or other important properties, or media like water, gases, vacuum systems, plasmas, interfaces. Balazs will help you ID the contaminants, control the contaminants and set specification limits for your unique processes. We are here to help!

Quick Notes: Spring 2008

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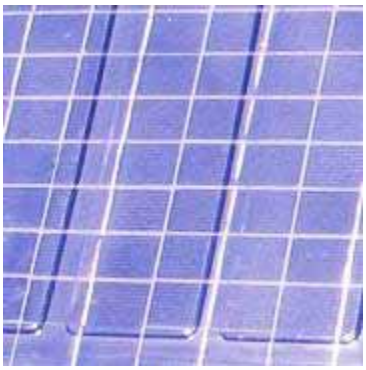
Note: Chlorine, Bromine and Total Halogen Content – Additional RoHS Capability

Balazs continues to support RoHS and similar industry programs by developing new methods to meet the requirements. Most recently, Balazs has developed a method to measure the concentrations of halides in base materials. The method is based on **IEC 61189-2 Test 2C12: Total Halogen Content in Base Materials**. The method reporting limit is 100ppm compared to the acceptable limits of 900ppm for chlorine and bromine individually and 1,500ppm for total halogen content.

Note: Advanced Materials Laboratory Supports Photovoltaics Processing

Using three of the most advanced depth profiling techniques available today, SIMS, GD_OES, and SARIS™ LA-ICP-MS, Balazs actively supports the photovoltaic industry by characterizing III-V materials, CIGS, a-Si, p-Si, c-Si, anti-reflecting coatings, metals, dielectrics, adhesive, polymers, industrial multilayer coatings and solder bumps. Combined with expertise in our water, chemical, gas, air and thin-film analyses, Balazs is able to provide analytical services to support:



- Quality control of substrate/starting materials
- Clean manufacturing
- Manufacturing process control
- Material selection

Photovoltaic manufacturers can count on Balazs to perform and educate manufacturers on new and pertinent analytical methods for photovoltaic manufacturing.

Read more about Balazs' support of Optoelectronics

Note: Supporting Standards – Continued ASTM Participation

Ms. Lynn Vanatta of Balazs currently serves as both the Definitions Advisor and the Recoding Secretary for the Water Committee (D19) of ASTM International. ASTM is one the world's largest volunteer standards-development organizations, creating trusted standards for use by various industries.

Participation in committees such as ASTM is important to the continued evolution of manufacturing beneficial products and services worldwide. Inputs from experts like Lynn are beneficial to electronics and semiconductor segments, to ensure that standards incorporate the needs and concerns of those industries.

Lynn leads and contributes to four task groups, each responsible for one standard:

- Electronic-Grade Water
- Measurement Uncertainty
- Definitions
- Precision and Bias

The standards are living documents that continue to evolve in conjunction with industry roadmaps like the ITRS and other 'forward-looking' documents. Direct participation in standards development is just one way Balazs shows its dedication to our customers' best interests. To read more about the ASTM Committee D19 please visit their website using the following link:

More About ASTM Committee D19

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Quick Notes- Spring 2008

Note: Advances in Real-Time Airborne Molecular Contamination Monitoring

The semiconductor industry is moving toward data on demand to monitor the levels of cleanroom contaminants. No single (or simple combination of) instrument(s) is available today that is sufficiently sensitive, absolutely selective and reliable to meet the requirements and provide the required online monitoring of all desired airborne molecular contamination (AMC) present in semiconductor fabs. However, on-line monitors are rapidly improving, and we present here a review of the monitoring requirements and the tools that can address these requirements.

Drs. Dan Cowles, Hugh Gotts, and Scott Anderson authored this article published in the inaugural issue of FEO Magazine. FEO is dedicated to content related to support and issues experienced by mainstream fabs. This practical information source is the first of its kind available to the industry. To view the article, click on the link below and enter your email address or register for free:

Read Article in FEO Magazine

Note: Updated AMC and UPW Guidelines Available

Updates to the Airborne Molecular Contamination (AMC) Guidelines and Ultrapure Water (UPW) Guidelines are complete. The guidelines incorporate industry oversight recommendations, methods used and identification of critical areas of concern. The new guidelines are re-formatted, making information easier to locate and reference. Balazs makes these guidelines available to the industry free of charge. Download your copy now!

Download AMC Guidelines

Download UPW Guidelines

Note: Upcoming ESTECH Presentation

Dr. Mark Camenzind will be **presenting a talk** on haze at ESTECH in Bloomfield, Illinois on May 6. The talk titled, ***Analysis of Contamination in Air & Gases that Degrade Steppers, Lasers, Masks, Inspection Tools & Other Optics,*** will review some analytical methods for key contaminants specified for control in the ITRS, especially for stepper purge gases and cleanroom air, and demonstrate that analyses are now possible to meet all the ITRS requirements with "no red brick walls" through 2015. Real-time analyses can be useful for cleanroom air, but UHP lens purge gases have some specifications below the reliable quantitation limits for some online analyzers, so that grab sampling methods are still required, e.g. for SO_2. Improved bubblers with high recovery for ionic compounds are described. Some tests can be performed for gaseous impurities to the required limits using pragmatic gas sampling cylinders and off-line analysis methods.

Note: Balazs' Steve O'Neil Presenting at the Green Technology Seminar

Are you looking to understand the acronyms of Green Technology *(RoHS, WEEE, Cr(VI), PBDE, PBB)* that are driving change throughout the Electronics Industry? Then please attend this day of information sharing at the TechMart on May 7th in Santa Clara, CA.

In addition to Steve O'Neil's presentation, the event sponsored by JJI Technologies will be featuring speakers from ADaM Solutions, AER Worldwide, JJI Technologies, Papros, Inc., and Thermo Fisher Scientific. This seminar will cover subjects that directly impact companies involved in the design, manufacture, distribution or sale of electronics.

Read more and sign up