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Glow Discharge Mass Spectrometry (GDMS) Services

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GDMS is a robust analytical technique for direct determination of elemental compositions of solid samples. GDMS combines a glow discharge source with a high-resolution magnetic sector mass spectrometer, providing excellent sensitivity and mass resolution. It remains among the most sensitive analytical techniques for full survey elemental analysis – lithium through uranium (excluding atmospheric gasses) – of homogeneous samples and is also highly effective for depth specific distribution evaluations of analytes in films and coatings in the micrometer range.

The overwhelming majority of commercially available GDMS instruments utilize a direct current (DC) source. Argon is typically used as the discharge gas. Samples analyzed using DC current are introduced to the glow discharge cell and behave as the cathode. During discharge the cathode/sample surface is bombarded with positive ions from the plasma. Consequently, the cathode not only releases secondary electrons, but also atoms. These atomized species from the sample surface diffuse into the plasma and are ionized. This separation of atomization and ionization results in glow discharge being near matrix independent. Subsequently, ions are extracted from the plasma and accelerated into the high mass resolution magnetic sector analyzer and are analyzed using a combination of analog and digital detectors. Ion beam intensities of all analyte elements are evaluated in reference to a matrix element or normalized to multiple matrix elements. These are called ion beam ratios. To convert the measured ion beam ratios of elements to mass fractions, relative sensitivity factors (RSFs) are used.

There are 2 geometries samples can be analyzed in. Flat and axial. The flat geometry allows for surface analysis, depth profiling, and analyzing thick films. The sampling orifice is ~10mm in diameter. The axial geometry is ideal for conductive pins 20mm long and 2mm wide, powders, and small chunks attached to a holding electrode. While the axial geometry lacks spatial resolution, it provides better options for analyzing non-conductive samples.

Ideally, samples to be analyzed by commercial GDMS instruments should be electrically conductive. However, there are three principal methods which can be applied to analyze non-conductive solid samples. The first method is to use a well-characterized conductive host matrix that the sample can be easily pressed into, such as indium, silver, carbon powder etc., as a binder. The second method is using a solid conductive sample holding electrode for introducing the sample into the glow discharge source, such as tantalum. The third technique is to use a solid conductive mask with appropriate sampling orifices over the analyzed sample surface which is then acting as a cathode to sustain the plasma during analysis and the sample is sputtered via the sampling windows.

Pulsed Source GDMS

Pulsed source GDMS utilizes a DC source that is able to pulse on and off for very short durations, anywhere from 10–100µs. Combined with fast plasma gas flow rates of 300–400mL/min, it is capable of very rapid full survey of solid samples. Pulsing the source has a couple of advantages over continuous DC sources. First, it slows the sputter rate of materials which is especially important for samples that are thermally sensitive and might otherwise overheat or for thick films which require depth-resolved data. Secondly, by controlling the atomization, and subsequently, ionization of analytes, it allows for even surface removal during the sputtering process and reduces the level of polyatomic interferences.

Strengths

- Full survey technique.
- ppm to sub-ppb determination limits (Example on table 1).
- Nearly matrix independent.
- Depth specific measurements through thick layers.
- Robust - applicable to a wide variety of samples.
- Long-term stability - does not require daily standardization.
- No chemical preparation.
- Does not require large sample size.

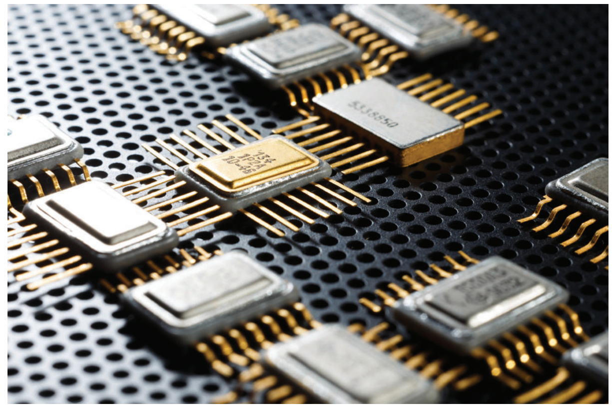
Limitations

- Polymers and organic samples.
- Liquids.
- Sample dimensions.
- Analytical area.
- Vacuum stability.
- Not fully quantitative due to lack of matrix-specific standards.

Ideal Applications

The direct sampling and full survey capability makes GDMS an ideal technique for the following types of general applications:

- Ultra-high purity metals and alloys.
- Manufactured carbons, graphites, and carbides.
- Semiconductors.
- Rare earth oxide concentrates.
- Oxide and ceramics.
- Depth specific distribution analysis of coatings and films.



Upgraded Metallurgical Grade Silicon for Photovoltaics							
X	ppm wt	X	ppm wt	X	ppm wt	X	ppm wt
Li	<0.001	Co	<0.005	Cd	<0.05	Tm	<0.005
Be	<0.001	Ni	<0.01	In	<0.01	Yb	<0.005
B	1.9	Cu	<0.01	Sn	<0.01	Lu	<0.005
F	<1	Zn	<0.05	Sb	<0.01	Hf	<0.01
Na	<0.01	Ga	<0.05	Te	<0.01	Ta	Source
Mg	<0.005	Ge	2.4	I	<0.01	W	<0.05
Al	<0.01	As	<0.05	Cs	<0.001	Re	<0.01
Si	Matrix	Se	<0.01	Ba	<0.01	Os	<0.01
P	11	Br	<0.01	La	<0.01	Ir	<0.01
S	<0.1	Rb	<0.01	Ce	<0.005	Pt	<0.01
Cl	<0.05	Sr	<0.01	Pr	<0.005	Au	<0.1
K	<0.05	Y	<0.01	Nd	<0.005	Hg	<0.01
Ca	<0.05	Zr	<0.01	Sm	<0.005	Tl	<0.01
Sc	<0.001	Nb	<0.01	Eu	<0.005	Pb	<0.01
Ti	<0.005	Mo	<0.05	Gd	<0.005	Bi	<0.01
V	<0.005	Ru	<0.01	Tb	<0.005	Th	<0.005
Cr	<0.01	Rh	<0.01	Dy	<0.005	U	<0.005
Fe	<0.05	Ag	<0.01	Er	<0.005		

< means that the species was not detected above the level listed

Table 1: Typical GDMS reporting limits on pure silicon samples.

Case Study 1: Developing a Generalized Oxide RSF Set

Oxide materials are used in a wide variety of applications, from ceramics to thermal and electrical insulators. Accurate analysis of the impurities present is of the utmost importance as many materials in use today (such as lithium-ion batteries, optical lenses, micro-LEDs, etc.) require ultra-high purity oxide materials.

Analysis of oxide materials using a tantalum holding electrode induces over-estimation of the alkali and alkali-earth elements. This is due to the generalized standard RSF set being developed using steel, aluminum, titanium, nickel, copper, and platinum alloys. Oxide matrices sputter differently than conductive metals due to the different bond strengths and mechanism of atomizing elements. Oxide materials generally have much stronger bond strengths than metal alloys and require back deposition of a secondary tantalum electrode material in order to create a thin conductive surface film on the oxide sample that will co-sputter the sample into the plasma.

We analyzed 4 different reference powders on 3 different GDMS instruments and on different days to create a generalized oxide RSF set. NMIJ CRM 8006a and NMIJ CRM 8007a are high purity aluminum oxide standards, NIST SRM 1413 is an aluminum rich silicon oxide (SiO_2) sand, and USGS BCR-2 is a basalt rock powder (54-wt% SiO_2). This new RSF set enabled us to analyze oxide materials more accurately than by just using the standard RSF set.

		Standard RSF		Oxide RSF	
X	GeoRem ppmw	ppmw	% of GeoRem	ppmw	% of GeoRem
Li	9.13	71	781%	12	128%
Be	2.17	0.80	37%	1.8	81%
O	Matrix	Matrix	-	Matrix	-
Na	Matrix	Matrix	-	Matrix	-
Mg	Matrix	Matrix	-	Matrix	-
Al	Matrix	Matrix	-	Matrix	-
Si	Matrix	Matrix	-	Matrix	-
S	318	125	39%	296	93%
K	Matrix	Matrix	-	Matrix	-
Ca	Matrix	Matrix	-	Matrix	-
Sc	33.53	26	78%	34	100%
Ti	Matrix	Matrix	-	Matrix	-
V	417.6	504	121%	419	100%
Mn	1522.6	2113	139%	1769	116%
Fe	Matrix	Matrix	-	Matrix	-
Co	37.33	35	94%	37	99%
Ni	12.57	10	78%	12	99%
Cu	19.66	19	96%	18	90%
Zn	129.5	97	75%	127	98%
Ga	22.07	32	144%	25	112%
Ge	1.46	2.7	183%	1.1	73%
As	0.86	1.3	146%	1.2	138%
Rb	46.02	35	76%	61	134%
Sr	337.4	355	105%	411	122%
Y	36.07	31	85%	41	113%
Zr	186.5	173	93%	172	92%
Sn	2.28	2.1	94%	2.2	97%
Sb	0.302	0.44	145%	0.27	88%
Ba	683.9	583	85%	632	92%
La	25.08	16	63%	24	95%
Ce	53.12	35	65%	48	91%
Pr	6.827	5.2	77%	6.4	94%
Nd	28.26	20	72%	28	99%
Sm	6.547	4.9	75%	6.5	99%
Eu	1.989	1.6	79%	1.9	96%
Gd	6.811	4.7	69%	6.7	98%
Tb	1.077	0.88	82%	1.2	107%
Dy	6.424	5.0	78%	6.2	96%
Ho	1.313	1.1	82%	1.3	99%
Er	3.67	3.0	81%	3.4	94%
Tm	0.5341	0.46	87%	0.59	111%
Yb	3.392	3.1	91%	3.3	98%

Table 2: Elemental concentrations calculated using the standard RSF and oxide RSF in BCR-2.

		Standard RSF		Oxide RSF	
X	GeoRem ppmw	ppmw	% of GeoRem	ppmw	% of GeoRem
Lu	0.5049	0.46	91%	0.51	101%
Hf	4.972	4.6	93%	5.2	104%
Re	0.0126	0.06	476%	0.01	95%
Tl	0.267	0.17	62%	0.29	107%
Pb	10.59	8.3	78%	12	109%
Bi	0.05	0.03	60%	0.03	68%
Th	5.828	2.4	41%	5.2	90%
U	1.683	1.0	61%	1.6	93%

Table 2: Continued

Case Study 2: Depth Profiling of Electroless Nickel Plated (ENP) Materials

ENP materials are widely used in the aerospace industry. ENP coatings are nominally in the 10 µm range. Ensuring the film does not have any substrate incursion and is homogenous at depth is of the utmost importance when dealing with such tight tolerances. In order to analyze such short distances, we need to control the sputter rate in such a way that it provides good signal, a flat crater, and depth resolution.

We analyzed CRM JK SUS NiP-1, an ENP standard from Swerea KIMAB (release date May 18, 2016). The NiP layer is 8.7 ± 0.5 µm thick on a steel substrate. We were able to create a sensitive depth profile on a low allow steel substrate and track the behavior of all major and minor elements in the NiP-1 layer (Figure 1a) and monitor the transition of all minor and trace elements into the substrate (Figure 1b). Interestingly, we were able to detect the substrate elements (Fe, Cr, Cu, Ti, Mn) leaching into the NiP layer prior to the expected transition.

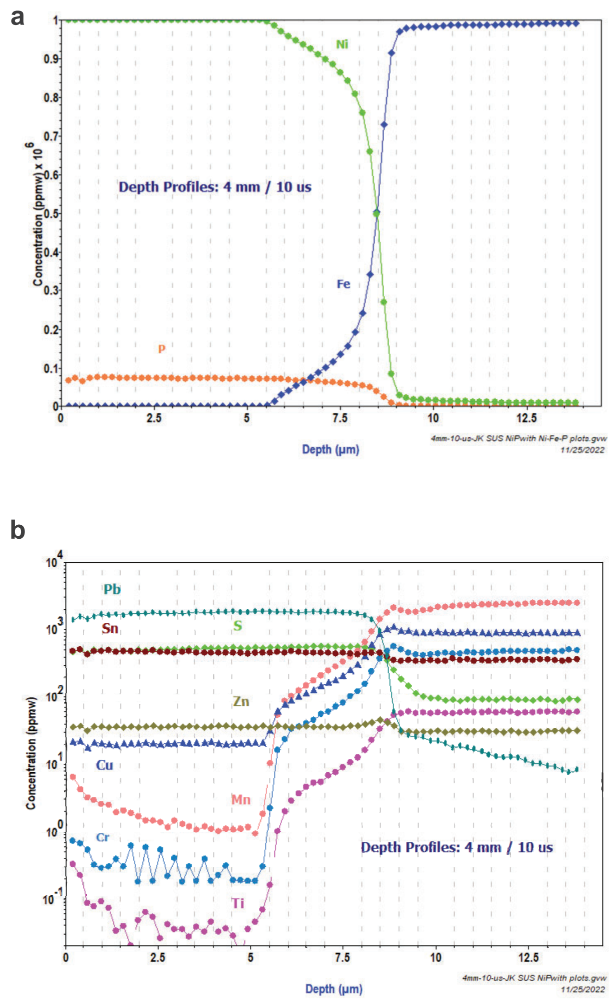


Figure 1: Quantitative depth profiles of a) Ni, P and Fe; and b) Pb, S, Sn, Zn, Cu, Mn, Cr and Ti.

GDMS at EAG

Eurofins EAG Materials Science is the industry leader for Glow Discharge Mass Spectrometry (GDMS) analytical services with the largest number and variety of GDMS instruments installed. Our depth and breadth of experience and dedication to innovative analytical methods is unrivaled.

EAG offers the best detection sensitivity along with accurate mass fraction determinations in bulk solids and thick coatings. EAG has over thirty (30) GDMS instruments worldwide and highly qualified scientists familiar with a wide range of applications from production, quality assurance, failure analysis, and R&D environments. EAG's GDMS instruments consist of a balanced mix of low-pressure type and fast flow type instruments, allowing us to cover the greatest range of applications.

Eurofins EAG Laboratories has been a trusted, long-standing partner in high technology industries. Over the past three decades, we have established a full suite of trace analysis services that feature advanced analytical tecniques, a comprehensive reference material database, high educated staff leveraging scientific expertise for problem solving, and a rigorous data security and IP confidentiality practice.