Ultra-trace Elemental Analysis of Pure Metals and Quantitative Depth Profile Analysis in Coated Materials by Glow Discharge Mass Spectrometry

Dr. Myint Myint Sein,[1] Dr. Joachim Hinrichs[2] and Peter Glörfeld[3]

[1,3)] Institut für Materialprüfung Glörfeld GmbH, Frankenseiten 74-76, 47877 Willich, Germany
Tel. +49 (0) 2154 48273 20; Email: seinm@img-labor.de

[2)] Thermo Fisher Scientific, Hanna-Kunath-Str. 11, 28199 Bremen, Germany
Tel. +49 (0) 421 5493 345; Email: joachim.hinrichs@thermofisher.com

---

Keywords: Depth profile, elemental analysis, GD-MS, pure metals, ultra-trace

Abstract

Due to increasing demands on the physical and physico-chemical properties of materials in many areas of high-technology the use of pure metals and compounds is apparently increased. Optimization of certain properties, such as the efficiency of photovoltaics, conductivity, reduction of contact resistance, high-temperature resistance of super alloys and many other properties of materials can be achieved by direct use of high purity metals and/or doping with special trace metal additions.

In the production and application of high purity metals, alloys and compounds, a reliable method for the investigation and determination of contaminations is needed. This can be carried out by direct analysis using high resolution glow discharge mass spectrometry (GD-MS). This technique is commonly applied for the characterization of elements in quality control and production.

In our lab, the Thermo Scientific Element GD Plus GD-MS is used to detect trace impurities in a wide range of pure metals, alloys and materials. The contents of ultra-traces and matrix elements in the wide range from ppb to % level can well be analyzed.

Besides the bulk concentration information, the sputter process also yields vertical information, since material is eroded from sample surface down to the substrate material. Due to the high scan speed and widely adjustable sputter parameters, the Element GD Plus delivers excellent quantitative analyses of elemental depth profiling of conductive coating materials with thin (10s of nanometers) to

thick (many micrometers) layers. For complex alloys, galvanized steels, photovoltaic solar cell, corrosion-resistant thin film on stainless steel and other multilayer systems a depth profiling can be accomplished by GD-MS analysis.

The combination of trace impurity analysis and depth profiling in metals by means of GD-MS can provide a profound attribution with vital importance for the metal industry.

1. Introduction

Analytical methods with sufficient sensitivity are needed for the characterization in quality control and in the production of high-tech equipments and scientific instruments. It is important to use the high-purity materials in their producing since even a very low content of impurities can drastically change the properties and performance of such materials [1]. It is therefore important to dertermine trace element contents with high accuracy and efficiency, and it is essential to achieve low limits of detection for pure metals, alloys and metallic compounds at background levels. Trace impurities in most pure metals, alloys, materials like semiconductors and non-conductors can be determined by a high-resolution glow discharge mass spectrometer (GD-MS) which is typically applied for full scan analyses of all available trace elements. It allows fast and sensitive multielement analysis and does not require laborious sample treatment [2]. For metallic samples, the detection limits of traces are very low, down to sub-ppb level under optimum conditions with a few percent of precision [3, 4].

The advantage in GD-MS analysis is the materials to be analyzed are directly used as the cathode and discharge cells serve as the anode. Metals including metallic alloys, steel and high purity metals are possible by the direct analysis. By this means, the dilution factor encounters in wet chemical analysis such as dissolution and/or digestion processes are eliminated [3]. Consequently, increasing risks of sample contamination in the dissolution process and the loss of spatial information are decreased. In addition, minimum calibration and less sample preparation are needed for the measurements of each element. Solid samples in the form of wires, rods, pins, sheets, irregular pieces, chunks, flat wafers, targets or powders can be analyzed.

The Element GD Plus GD-MS features a fast flow glow discharge source that can be operated in continuous or in pulsed mode [5]. Continuous mode operation offers the advantage of high sputter rates to remove the contaminated surface layers quickly. The wide application set of calibration factors (Standard RSF = general Relative Sensitivity Factors) is based on continuous mode operation. The pulsed (or modulated) mode of the glow discharge source results in enhanced overall stability.

An efficient pulsed ionization results in lower sample consumption, lesser need of consumables and overall higher precision of analysis and reduced time for calibration [6].

One of the advantages of using glow discharge sources is the possibility for depth profiling and thin layer analysis which is of very important for the production, the development of new materials and coatings [2,7,8].

2. Analysis and Detection

2.1. Principle and Instrumentation of Glow discharge - Mass Spectrometer (GD-MS)

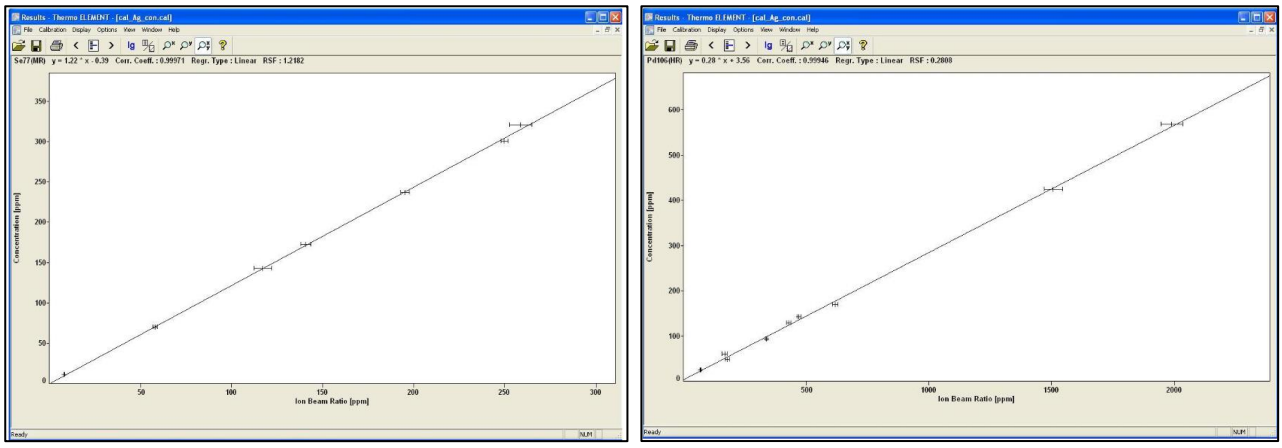
This work involved a Thermo Scientific ELEMENT GD Plus glow discharge mass spectrometer GD-MS for all analyses (**Figure 1**). Metal and non-metal samples are discharged directly or after a suitable treatment. The samples are analyzed using either continuous dc mode or pulsed mode. Pre-sputter time is necessary to get rid of the surface impurities. The discharge area is usually 8 mm in diameter. The anode, the cone and the anode tube are made up of stainless steel. Inert gas (typically argon) is used as a discharge gas.

In a glow discharge source, electrical power is supplied between the sample (cathode) and the anode by a power supply typically operated in direct current (0 mA – 300 mA) at a high voltage (0.5 – 2 kV). Inert gas argon is introduced into the discharge cell. When the discharge under the vacuum pressure (10 - 10^3 Pa), a glow discharge (plasma) is established due to a potential difference between the cathode and the anode. The accelerated ions are then separated with a magnet field according to their m/z ratios and are measured by a mass spectrometer. In the MS detector, the most abundant isotope of the element of interest is preferentially chosen for data analysis [3, 9]. Duration of an analysis is typically 5-15 min including pre-sputter time and data acquisition.

Data evaluation was attained by using relative sensitivity factors (RSF's) which were supplied with the instrument to calculate semi-quantitative results with limited accuracy [4,10,11]. For quantitative evaluation, certified reference materials (CRMs) with similar matrix composition are used whilst the differences in RSF's of elements must be considered.

In GD-MS analysis, a single point or multipoint calibration of the reference material can be used for calibration, and the analysis results are attributed according to this calibration [12]. The calibration is performed by plotting certified concentration vs. the measured Ion Beam Ratio (IBR), i.e., the raw elemental ratio relative to the matrix element. The slope of the regression curve is representing the Relative Sensitivity Factor (RSF) of the matrix matched calibration. Since the calibration is commonly forced through zero, no intercept is expected and thus R^2 values for this regression type are not available [12]. **Figures 2 a and b** show the linearity of the calibration of Se and Pd in Ag.

Figure 1: Element GD Plus Glow discharge-Mass Spectrometer (GD-MS), Thermo Scientific



(a) **(b)**

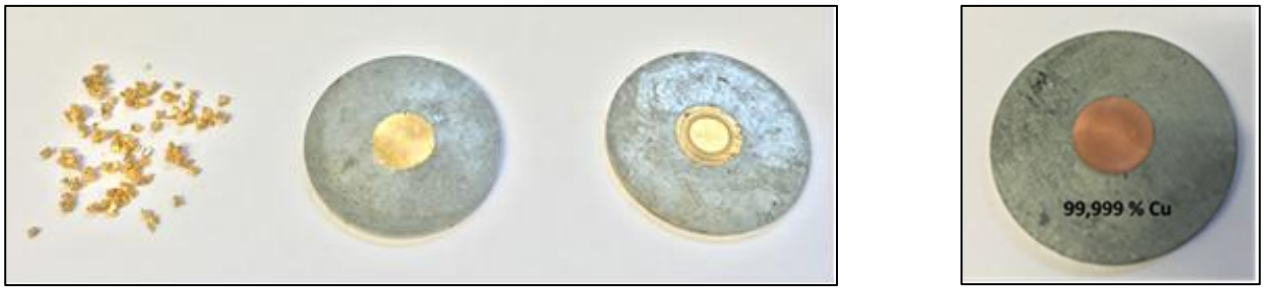
Figure 2: Calibration curves of (a) Se in Ag and (b) Pd in Ag.

2.2. Sample preparation

2.2.1. Sample preparation of conducting materials:

Compact samples with a flat surface with minimum 20 mm in diameter can be analyzed directly. To get a flat surface, the sample can be formed by mechanical treatments like cutting, grinding, rolling or remelting. The finished surface is obtained by etching, polishing and/or treating with a suitable solvent. Other forms like wires, very thin foils, powders, metal chips are prepared by hydraulic pressing in an orifice of metal rings to form a mechanically stable surface (**Figure 3 a, b**).

Non-ductile brittle materials can be pulverized in a mill before pressing. During handling, care must be taken to avoid the risk of contamination. For quantitative analysis, calibration standards can be prepared by doping with solutions of defined concentrations to a pure matrix powder.



(a) **(b)**

Figure 3: Pressings from (a) gold granulates and (b) copper powder in steel discs for GD-MS measurement.

2.2.2. Sample preparation of non-conducting materials:

In order to widen the application field of GD-MS, analysis of non-conducting materials has been developed [10]. Principally there are two different techniques to carry out the analysis of non-conducting materials:

(A) Non-conducting samples are prepared into powder and can then be mixed with quantitative amounts of a high purity conducting agent such as powdered metals (e.g. silver, copper or tantalum), liquid metals like gallium, or high purity graphite powder [9,10,13]. The samples are then homogenized and pressed into pellets. Conducting agent with known content of impurities will act as a sample binder and as a secondary cathode. Such addition can dilute the sample and hence lowering the sensitivities for trace analyses. It has been reported that trace elements in non-conductive alumina to below mg/kg levels can be well detected using high purity graphite powder as a sample binder and as a secondary cathode where helium was introduced as an additional glow discharge gas to argon plasma [14].

(B) Alternatively, non-conducting powders can also be pressed into or onto soft solid metals like indium, lead, or tin which will act as a metallic diaphragm called secondary cathode [15]. High pure tantalum is also commonly used for this purpose. The fine powder samples are pressed directly into a borehole of high pure metal with an inner diameter less than the diameter of the glow discharge spot which will act as a secondary cathode.

Analysis of high purity alumina powder has been carried out in this way [16]. A high purity tantalum target equipped with a borehole of ca. 5 mm diameter was placed on a TaW plate was used as a secondary cathode. Some milligrams of alumina powder were filled in the hole (**Figure 4**), and stable and compact pellets were prepared by pressing the powder with a TaW pressing pin. The used tantalum target is easily resurfaced by grinding or milling for multiple use.

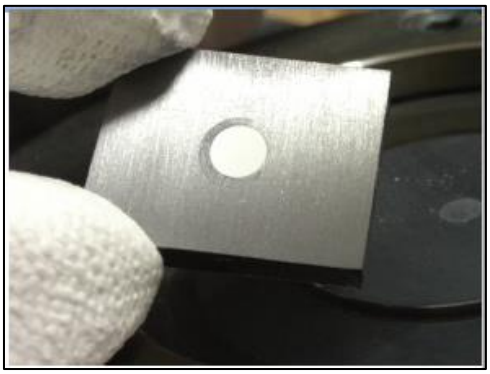


Figure 4: Non-conductive alumina powder sample pressed into a tantalum secondary cathode [16].

2.3. Analysis of Materials

Almost all pure metals and alloys are analyzed directly discharging on the material surface. In order to eliminate surface contaminations, pre-sputtering has to be carried out.

2.3.1. Analysis of pure metals:

For trace impurities with very low concentration level (<1 ppm) in highly pure metals it is necessary to calculate the results by using standard RSF's due to only limited reference materials are available [12,17]. The impurities present in highly pure metals up to 6N can be well analyzed. As an example, an analysis of pure copper is shown in **Table (1)**. In this analysis, the quantification of the most abundant impurities was obtained by external calibration with matrix matched certified reference materials. The sum of all impurities present in pure 6N copper is summarized to 0.92 ppm, and the purity of the metal thus calculated to 99.99991%.

2.3.2. Analysis of metal alloys:

High precision analysis of trace metals in Ni alloys, which is used in the production of aerospace industry such as for the production of turbine blades of aircrafts and rockets, is well achieved by using the pulsed mode of the Element GD Plus GD-MS. The pulsed mode of the glow discharge source results in enhanced overall stability [5]. An accurate composition of most elements present in this alloy characterizes the material. **Table (2)** shows the very precise analysis results of certified reference material (CRM) BAS346A Ni super alloy by GD-MS [6]. It can be seen that an exceptional performance for the routine analysis of the 14 most important elements in Ni super alloys with an excellent performance and high precision concentration determination with high sample throughput, i.e., requiring less than 5 minutes per run. Overall analysis procedure are optimized for efficiency with minimum sample preparation which in turn reduces the analysis time and cost.

Table 1: Analysis report of ultra-trace impurities in pure copper (6N) by GD-MS.

GDMS
Analytical Report

Institut für Materialprüfung
Glörfeld GmbH
Frankenseite 74 – 76
47877 Willich, Germany
Tel. +49 2154 482 73 0
Email: info@img-labor.de

Customer:
Date:
Customer ID:
Sample: **6N Cu**

Element	Mass fraction ppm	Element	Mass fraction ppm
Li	<0.001	Pd	<0.001
Be	<0.001	Ag	0.14
B	<0.001	Cd	<0.005
C	n.d.	In	0.017
N	n.d.	Sn	0.001
O	n.d.	Sb	0.005
F	0.015	Te	0.001
Na	0.009	I	<0.001
Mg	0.001	Cs	<0.001
Al	0.001	Ba	<0.001
Si	0.015	La	<0.001
P	0.003	Ce	<0.001
S	0.369	Pr	<0.001
Cl	0.017	Nd	<0.001
K	0.020	Sm	<0.001
Ca	<0.001	Eu	<0.001
Sc	<0.001	Gd	<0.001
Ti	0.005	Tb	<0.001
V	<0.001	Dy	<0.001
Cr	0.002	Ho	<0.001
Mn	<0.001	Er	<0.001
Fe	0.019	Tm	<0.001
Co	<0.001	Yb	<0.001
Ni	0.002	Lu	<0.001
Cu	**Matrix**	Hf	<0.001
Zn	0.001	Ta	0.001
Ga	<0.001	W	0.006
Ge	0.55	Re	<0.001
As	0.004	Os	<0.001
Se	<0.001	Ir	<0.001
Br	0.017	Pt	0.015
Rb	<0.001	Au	0.163
Sr	<0.001	Hg	<0.001
Y	<0.001	Tl	<0.001
Zr	<0.001	Pb	0.005
Nb	<0.001	Bi	<0.001
Mo	0.001	Th	<0.001
Ru	<0.001	U	<0.001

n. d. = not determined: Total impurities: 0.918 ppm; Cu (Remaining) = 99.99991%

Proceedings: EMC 2019, Vol. 4, pp. 1501-1513

Table 2: Repeat analysis the reference material BAS346A Ni super alloy by pulsed mode in Element GD PLUS GD-MS (Pulse frequency = 4 Hz; Pulse duration = 40 µs) [6].

	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6	Spot 7	Spot 8	Average	Standard Deviation	RSD	Certified Concentration	Confidence Interval
Mg24	131.1	132.8	132.0	134.1	128.7	131.3	132.7	131.6	131.8	1.6	1.2%	130	7
Zn66	28.8	29.2	29.1	28.6	28.7	29.0	28.6	28.7	28.8	0.2	0.8%	28.8	1.4
Ga69	49.3	52.0	49.5	49.5	49.5	49.4	49.5	49.9	49.8	0.9	1.8%	49.6	2
As75	51.1	51.3	50.9	51.6	50.3	50.6	50.7	51.9	51.0	0.5	1.0%	50.4	2.5
Se82	6.3	5.2	5.5	5.8	6.2	5.5	5.2	5.5	5.6	0.4	7.2%	5.7	0.8
Ag107	42.7	42.7	42.9	42.6	42.6	43.1	43.0	43.4	42.9	0.3	0.7%	42.5	0.9
Cd111	0.35	0.37	0.41	0.40	0.41	0.43	0.37	0.39	0.39	0.03	6.5%	0.37	0.04
In115	19.6	20.5	20.0	20.1	19.9	19.8	20.1	20.2	20.0	0.3	1.3%	20	(Info)
Sn117	92.8	92.5	92.1	92.9	92.1	93.6	93.9	94.5	93.1	0.9	0.9%	93	8
Sb121	44.1	45.0	44.7	44.8	44.4	44.4	45.5	45.0	44.8	0.4	1.0%	45	4
Te130	10.0	8.9	9.0	9.6	10.0	9.1	8.7	9.1	9.3	0.5	5.4%	9.3	0.8
Tl205	1.88	1.88	1.91	1.94	1.84	1.94	1.86	1.91	1.90	0.04	1.9%	1.9	0.3
Pb208	21.8	21.9	21.6	21.9	22.0	22.4	22.3	22.8	22.1	0.4	1.8%	22.2	1.2
Bi209	9.4	10.0	9.7	9.3	9.9	10.3	10.5	9.9	9.9	0.4	4.0%	10.3	0.6

2.3.3. Analysis of non-conducting materials:

Non-conductive oxide powders in general and alumina in particular require severe conditions for wet chemical dissolution in order to be run on ICP-MS [7]. Direct analysis from the solid provides a cleaner sample preparation method, using a secondary electrode for analyses with GD-MS.

Trace elements determination in high purity Alumina powders reference material (CRM 8007a) using Tantalum as a secondary cathode by using a Thermo Element Plus GD-MS under pulsed mode was carried out [16] and the analysis results can be found in **Table 3**. It shows very high precision data of the analysis even at low concentration level of 0.01 ppm by µs-pulsed operation mode which proves that this combination is ideally suited for reproducible and trace metal quantification of high purity alumina powders.

Table 3: Semiquantitative analysis results of the high purity alumina reference material (CRM NMIJ 8007a) using a tantalum secondary cathode (Pulse frequency = ~4 kHz; Pulse duration = 50 μs) [16].

Element	Measured conc.	Standard Deviation of Repeat Analysis	Certified Concentration
Fe	5.0	0.3	5.01 ± 0.25
Si	19.5	1.3	17.1 ± 0.4
Zr	2.5	0.6	1.80 ± 0.20
B	1.08	0.09	0.21 ± 0.08
Ca	2.4	1.0	0.92 ± 0.14
Cr	1.15	0.09	0.84 ± 0.09
Cu	1.25	0.06	0.92 ± 0.08
Mg	3.1	0.2	2.8 ± 1.1
Sr	0.025	0.007	0.022 ± 0.009
Ti	0.35	0.06	0.26 ± 0.08
Th	0.010	0.003	—
U	0.030	0.003	—

4. Technical Application of GD-MS in the analysis of various areas

High resolution glow discharge mass spectrometry is applied for the analysis of various areas which include in the photovoltaic, X-ray technology, medical, chemical, aerospace and electronics industries.

Analysis for Photovoltaics industry (Si, Cu, Cd)

Analysis for X-ray technology (W, Mo, Pb, Zr)

Analysis for Medical industry (Ti, Ti-alloy, Co-Cr alloy, Mg)

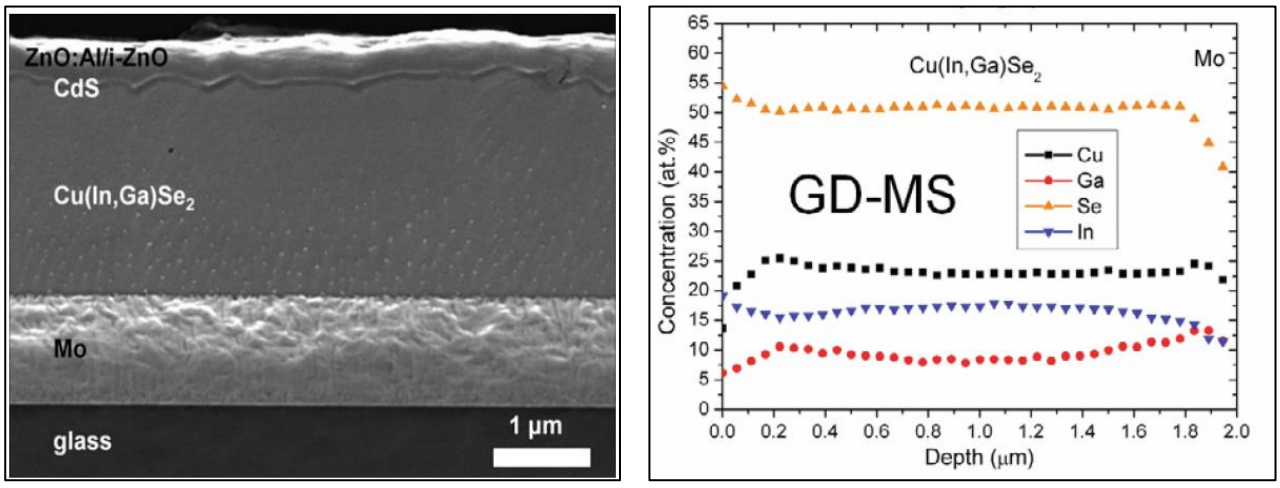
Analysis for Chemical industry, aerospace industry (Ni alloy) [6,12]

Analysis of Semiconductors (Si, GaAs, InP, CdTe, CdTeHg) [2]

5. Depth-profiling

Compositional depth profile analysis of multilayer coatings, transition zones between individual coating layers between coating and base material are usually performed by using GD surface analytical techniques [3]. This method proves that quantitative information of major components and important minor elements with a high speed of analysis. Elemental mass fraction as a function of analysis time enables a depth profile. In this analysis, the registered intensity versus time profiles is converted into the desired concentration versus depth profiles (At different sputter times a depth of the coated layer was determined by the time-depth conversion). To carry out depth profiling, care must be taken not to contaminate the surface while handling the samples.

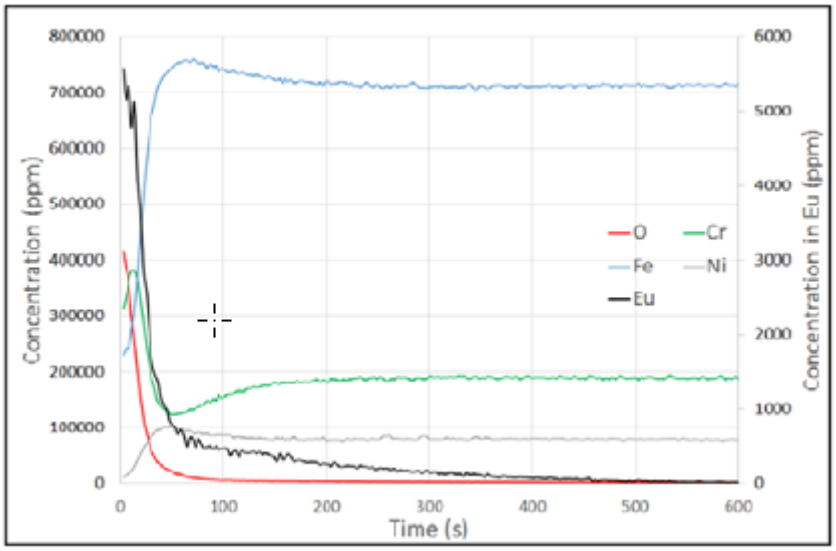
Depending on analytical task, the focus might be set on full quantification at trace level for layers from minimum several hundred of nanometer thickness to a maximum of approximately 100 µm, or at the determination of just key elements in layered systems from single digit nanometer thickness and higher. Depth profiles are typically recorded as semiquantitative data, minimizing the effort for calibration, while the depth scale needs to be determined offline. As a consequence, fast flow GD-MS serves mainly as fast screening techniques for depth profiling, yielding mostly semiquant data at high sensitivities enabling profiles even down to the sub ppm range. A coating depth determination of Cu(In,Ga)Se_2-thin film for solar cell [18] is shown in **Figure 5**.



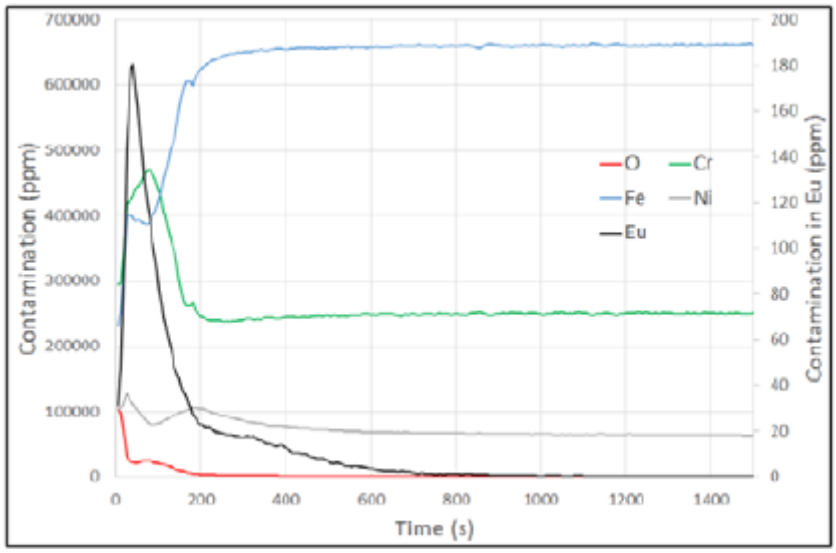
(a) **(b)**

Figure 5. (a) Cross- sectional scanning electron micrograph of the stack solar cell ZnO:Al/i-ZnO/CdS/Cu(In,Ga)Se_2/Mo/glass (b) Elemental distribution of Cu(In,Ga)Se_2-system (~ 2 µm thickness) determined semiquantitatively by the Thermo Scientific Element GD Plus GD-MS [18].

The decontamination of the contaminated oxide layer on metallic surfaces before and after applying by means of laser was also analyzed by GD-MS [19]. The GD-MS profiles for an oxide layers obtained after laser preliminary treatment on 304L stainless steel sheet is shown in **Figure 6**.



(a)



(b)

Figure 6: GD-MS profiles of a Eu-contaminated oxide layers on 304L SS (a) before decontamination treatment (b) after decontamination treatment [19].

6. Conclusion

Most achievements of modern technology are possible by the use of high-tech materials such as metals, alloys, semiconductors or ceramics with excellent material properties. These materials are often characterized by their high purity i.e., in term of the presence of small traces of impurities. Therefore, production and quality control require analytical methods with precise and accurate determination of such impurities and also for very low level of doping.

Fast-flow GD-MS is shown to be a powerful tool for a wide range of modern high-tech materials. Due to its high detection power, high resolution capability, and linear detector response, the Thermo Scientific Element GD Plus can be used for analysis in a wide range of metals, from complex alloys to the highest metal purities available. Besides routine semiquantitative determinations, best accuracies are obtained with few dedicated calibration samples. Currently evolving application fields have just recently been opened to Fast-Flow GD-MS by introduction of modulated (pulsed) operation. This extends the usability of the instrument to non-conductor analysis and advanced depth profiling.

7. References

[1] MATSCHAT, R., HINRICHS, J., KIPPHARDT, H. (2006): Application of Glow Discharge Mass Spectrometry to Multielement ultra-trace Determination in ultrahigh-purity Copper and Iron: a Calibration Approach Achieving Quantification and Traceability, Anal Bioanal Chem, 125–141, 386 (1).

[2] SANDERSON, N. E., HALL, E., CLARK, J., CHARALAMBOUS, P. & HALL, D. (1987): Glow Discharge Mass Spectrometry- A Powerful Technique for the Elemental Analysis of Solids, Mikrochim. Acta, 275 – 290, I, Wien.

[3] TECHNICAL SPECIFICATION (2009): Surface Chemical Analysis-Glow Discharge Mass Spectrometry (GD-MS)-Introduction to Use, ISO/TS 15338, 1st Edition, Geneva.

[4] STUEWER, D. (1990): Glow Discharge Mass Spectrometry - A Versatile Tool for Elemental Analysis, Fresenius J Anal Chem, 737 – 742, 337.

[5] HINRICHS, J. & McSheehy DUCOS, S. (2017): Calibration Factors in Fast Flow Glow Discharge Mass Spectrometry (FF-GD-MS): Continuous versus Pulsed Mode, 17. GDS-Anwendertreffen, Thermo Fisher Scientific, Bremen, Germany.

[6] HINRICHS, J. (2016): High Throughput Analysis of Ni Super Alloys by GD-MS: Efficient Quality Control, Application Brief AN43375, Thermo Fisher Scientific, Bremen, Germany.

[7] NELIS, T. & PALLOSI, J. (2006): Glow Discharge as a Tool for Surface and Interface Analysis, App Spectro Reviews, 227 – 258, 41.

[8] ALDAVE DE LAS HERAS, L., ACTIS-DATO, O. L., BETTI, M., TOSCANO, E. H., TOCCI, U., FUOCO, R., GIANNARELLI, S. (2000): Monitoring of Depth Distribution of Trace Elements by GD-MS, Microchemical J, 333 – 336, 67.

[9] CAROLI, S. (1987): Low-Pressure Discharges: Fundamental and Applicative Aspects. A review, J Anal At, 661 – 680, 2.

[10] BOGAERTS, A. & GIJBELS, R. (1999): New Developments and Applications in GD-MS, Fresenius J Anal Chem, 367 – 375, 364.

[11] VIETH, W. & HUNEKE, J. C. (1991): Relative Sensitivity Factors in Glow Discharge Mass Spectrometry, Electrochimica Acta 137 – 153, 46B (2).

[12] HINRICHS, J. & ROTTMANN, L. (2016): GD-MS Analysis of Trace and Ultra-trace Elements in Nickel Super Alloys, Application Note 30219, Thermo Fisher Scientific, Bremen, Germany.

[13] EHRLICH, G., STAHLBERG, U., HOFFMANN, V., SCHOLZE, H. (1991): Glow Discharge Optical Emission Spectroscopy as Applied to the Analysis of Powdered Materials, Spectrochimica Acta Part B: Atomic Spectroscopy, 115 – 124, 46 (2).

[14] JUNG, S., KIM, S., HINRICHS, J., (2016): Determination of Trace Elements in high Purity Alumina Powder by Helium enhanced Direct Current Glow Discharge Mass Spectrometry, Spectrochimica Acta Part B: Atomic Spectroscopy, 46 – 51, 122 (1).

[15] MILTON, D. M. P. & HUTTON, R. C. (1993): Investigations into the Suitability of using a Secondary Cathode to Analyse Glass using Glow Discharge Mass Spectrometry, Spectrochimica Acta Part B: Atomic Spectroscopy, 39 – 52, 48 (1).

[16] HINRICHS, J. & PUTYERA, K. (2016): Analysis of Alumina Powders using the Thermo Scientific Element GD Plus GD-MS, Application Brief 43222, Thermo Fisher Scientific, Bremen, Germany.

[17] HINRICHS, J. (2018): Routine Analysis of 6N High Purity Copper, Application Brief 30489, Thermo Fisher Scientific, Bremen, Germany.

[18] ABOU-RAS, D. et al., (2011): Comprehensive Comparison of various Techniques for the Analysis of Elemental Distributions in Thin Films, Microsc. Microanal. 1 – 24.

[19] CARVALHO, L., PACQUENTIN, W., TABARANT, M., MASKROT, H. & SEMEROK, A., (2017): Growth of Micrometric Oxide Layers for the Study of Metallic Surfaces Decontamination by Laser, EPJ Web of Conferences, 07038, 153.