PRODUCTION SUPPORT AND PROCESS CONTROL OF PV MATERIALS BY DIRECT SAMPLING HIGH-RESOLUTION GLOW DISCHARGE MASS SPECTROMETRY METHODS

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ABSTRACT: Direct sampling high resolution mass spectrometry methods, like Glow Discharge Mass Spectrometry (GDMS) equipped with either reduced pressure or fast-flow glow discharge ion sources, are among the most sensitive analytical methods available today for routine analyses of photovoltaic (PV) grade materials. These multielement analytical techniques can quantitatively monitor impurity concentrations in a wide variety of PV grade materials currently considered for large scale productions, such as solar grade (SoG) Silicon, CdTe, CdS or for those which are potentially considered to be used in the near future, like CIGS. Since the GDMS techniques are survey methods, they are especially the most cost effective in monitoring process with 4N to 6N or 99.99 – 99.9999% pure materials when still many impurity elements are of interest.

Keywords: photovoltaic grade materials, impurities, element concentration distributions, GDMS

1 INTRODUCTION

The PV feedstock manufacturing industry requires systematic contamination monitoring, which means it requires trace to ultra-trace level impurity determinations [1]. On the other hand, spectrometric methods for trace impurity evaluations in their conventional performance modes usually involve a few steps prior to the analysis, such as dissolution or sample digestion procedures and, in many cases also analyte-matrix separations or removal in order to eliminate matrix interferences. Unfortunately, the dissolution rate and the residue of non-soluble substances often limit the sensitivity of these standard analytical techniques. Additional impurities could be introduced from the solvent(s). In many instances these “unwanted” contaminations introduced by preparation steps can increase the instrumental limits of detection for many elements by up to several orders of magnitude. Moreover, the digestion of many materials in this field is tedious, time consuming and often necessitates the handling and disposing of highly toxic chemicals.

Direct sampling mass spectrometry methods, especially GDMS and SIMS [2], with minimum sample preparation requirements can overcome these limitations. Generally, the broadly utilized GDMS techniques (reduced pressure and fast-flow) are the most comprehensive direct sampling methods today for quantitative multielement (almost inclusive) impurity determinations for PV grade materials. In addition, an international, standardized test method is currently in development for Solar grade Si for GDMS under the PhotoVoltaics Committee of SEMI.

GDMS techniques are best suited for “4N to 6N” category of materials, like the upgraded metallurgical grade silicon solids (UMG-Si), CdTe and CdS powders, for which a survey of a large number of impurities needs to be and/or it is generally monitored. Other advantages of GDMS are that: a) trace level determinations can be reproduced well (~ 10% for higher level and ~ 25% for lower level concentrations); b) impurity concentrations can be determined within a factor of about 2x to “true” values without having strictly matrix matching reference materials traceable to Standard Reference Materials.

Direct sampling in the dc glow discharge ion sources is accomplished by plasma sputtering. The analyzed material can be introduced to the ion source of the instrument in a variety of forms that serve then as a cathode, the surface of which is bombarded by ions of the discharge gas. This bombardment results in the release of atoms and/or atom clusters from the sample surface, which are subsequently ionized in the discharge and accelerated into the high mass resolution analyzer.

2 GDMS SURVEY ANALYSIS OF BULK IMPURITIES IN PV FEEDSTOCKS

Photovoltaic materials are manufactured, processed or utilized in many different forms, including powders, granules, flakes, chunks or wafers. Photovoltaic feedstocks are diverse in the total contents of impurities, in their electrical resistivity, thermal conductivity and/or stability. Also, having information only from bulk concentrations of impurities is very often not sufficient for clear understanding the impacts of particular trace level impurities on the desired properties or long-term performance of the final photovoltaic devices. Therefore the distribution of elements either in micro- or macroscopic volumes and/or laterally is often looked-for by manufacturers. Thin film technologies require analytical techniques with depth profiling capabilities having variety of depth resolutions, etc. In other words basic analytical needs for this technology are exceptionally broad not only just for the trace level impurity analyses.

GDMS techniques presently available can match many of the analytical requirements demanded by the PV feedstock industry. Survey analysis for bulk impurities in homogeneous solids are relatively straightforwardly performed by GDMS on all kinds of physical forms. However, various sample forms and analytical requirements demand different sample introductory systems. On the other hand not all of these can guarantee the same level of sensitivities for all of the elements in interest, or precise and accurate determinations in general.

Most of the PV grade solids used today can be at the present time analyzed using the reduced pressure glow-discharge (RP GD) ionization sources attributed to the commercial VG9000 (Thermo Group) instruments. Figure 1 shows schematically the most frequently used cell and sample introductory configuration applied in this technique for routine analyses.

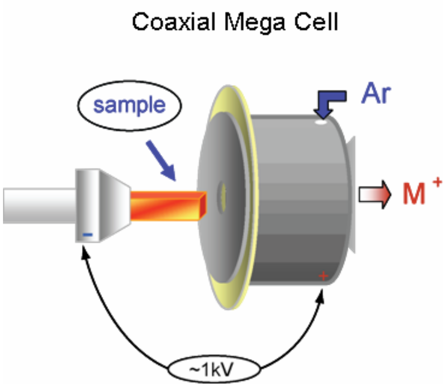


Figure 1: Mega Cell assembly for the VG9000.

The sample for analysis is a pin-shaped piece which is 2-3 mm in diameter and approximately 20 mm in length. The glow-discharge cell is housed in the vacuum chamber of the instrument. The sample and cell are all together cryogenically cooled during the whole time of the analysis. Among other analytical advantages this also permits analyzing, for instance, samples with low melting points. Although the pin shaped sample and cell configuration is generally applicable for survey analyses of a broad range of solids, they are not optimal for analyzing powders or particulate materials and do not provide the means for collecting distribution and/or depth related concentration information.

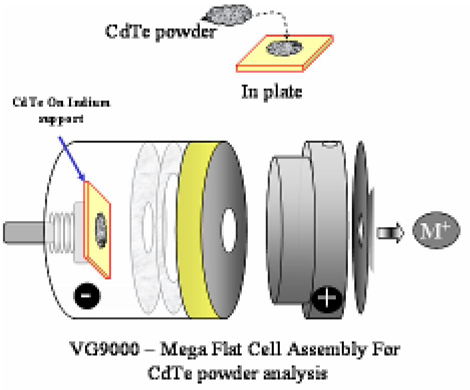


Figure 2: Mega Flat Cell assembly for the VG9000 for analyzing powders or particulate materials.

Figure 2 illustrates the sample introduction into the Mega Flat Cell assembly. This assembly permits analyzing powders and/or particulates without the limitations of the pin geometry. Figure 2 illustrates that the fine CdTe powder is first pressed onto a 99.99999+ purity Indium plate, which becomes not just the sample carrier but also that the Indium plate serves as part of the cathode during analysis and also it is “sealing” the cell. This configuration not just permits analyzing powders, particulates, chunks with equal sensitivity to the classical pin configuration, but makes it possible for acquiring depth related concentration information on flat sample surfaces or coatings.

The most sensitive GDMS measurements can be done in the instruments equipped with the fast-flow direct current glow-discharge (FF GD) cells (Model Element GD from ThermoFisher Scientific) [3]. FF GD is a high power source resulting in high sputter rates (orders higher as compared to the RP GD) and thus better element sensitivities. The sputter rates for Si matrices for instance are in the order of microns per minute in FF GD as compared to 0.05 microns per minute in the RP GD. The detection system of the FF GD instruments offers a slightly wider linear dynamic range as compared to the RP GD instruments. Consequently, the FF GD is the method of choice for high sensitivity measurements. However, the measurements using FF GD instruments are currently limited to thermally stable and electrically conductive matrices. Another limitation of the FF GD technique is in the list of elements, which are currently not possible to determine with high confidence due to the unwanted contributions from GD source components.

Table I shows GDMS typical limits of detections for selected elements for variety of PV materials. This table illustrates that for various PV materials different GDMS methods are needed in order to reach the required sensitivities or precisions.

Table I: Typical detection limits of GDMS measurements

	Si solid RP pin	Si solid FF flat	CdTe powder RP flat	CdTe solid RP Pin	CdS powder RP flat
Li	0.001	0.0005	0.005	0.001	0.001
B	0.001	0.0005	0.005	0.001	0.001
Al	0.01	0.005	0.005	0.001	0.01
P	0.01	0.002	0.01	0.005	0.01
S	0.01	n/a	0.01	0.005	-
Ca	0.05	0.005	0.05	0.05	0.05
Ti	0.005	0.0001	0.001	0.001	0.001
V	0.005	0.0001	0.001	0.001	0.005
Cr	0.01	0.001	0.01	0.005	0.01
Fe	0.01	0.001	0.01	0.005	0.01
Ni	0.01	0.0005	0.01	0.001	0.01
Cu	0.01	0.0005	0.01	0.001	0.01

Notes: All values are in mass fraction mg/kg (ppm wt); RP – reduced pressure GDMS; FF – fast-flow GDMS

3 CASE STUDY: INVESTIGATION OF DISTRIBUTIONS OF TRACE LEVEL IMPURITIES IN UPGRADED METALLURGICAL GRADE SILICON BY FAST-FLOW GD INSTRUMENT

3.1 Sample selection

Flat samples were cut out from different UMG-Si bricks for this study according to the schematic representation shown in Figure 3.

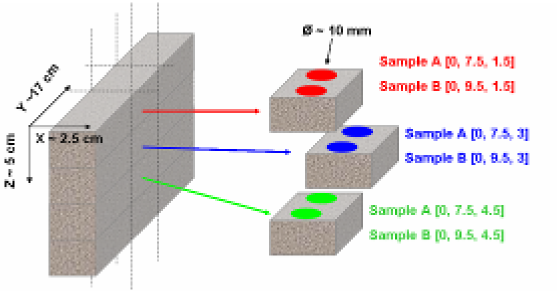
3.2 Analysis

Two spots were analyzed close around the area centered with the co-ordinates described in Figure 3. Three sets of data were taken from every spot. Based on the final crater depth the sputter rate was determined assuming uniform sputtering across the whole sputtered area. Accordingly the three individual readings are representing layers approximately 10 microns apart in depths from each other.

3.3 Calibration

GDMS trace element analysis is basically always “quantitative” measurement, since the trace element concentrations are generally evaluated within a factor of about 2 times to “true” values. This feature of the GDMS methods makes them extremely powerful especially for evaluations of those element concentrations for which there is no certified reference material available. The core of this feature is interrelated to the quantification process, which in the GDMS techniques is based on the measurement of the Ion Beam Ratios (IBR). The IBR is the ratio of the intensity of the analyte element signal relative to the matrix element(s) signal intensity. In the case of Silicon measurements for example, the Silicon intensity is directly measured and the trace elements signals are ratioed to the Si ion beam. In a “true” calibration setup the certified element concentrations are plotted against the measured IBRs of each element. The slope of this “calibration graph” gives the “true” sensitivity or the relative sensitivity factor (RSF) for that element. There are several other analytical techniques, which are based on this or similar calibration procedures. However, the RSF values in the GDMS techniques are close to unity for most of the elements, and they are varying in a relatively narrow range from element to element. In addition, the RSF values in GDMS are not significantly influenced by the nature of the sample matrix, thus calibrations frequently can be done without having multiple reference materials “strictly” matrix matched. This aspect of GDMS led to development of a generalized set of RSF values, analogy to a universal calibration curve, which has proven to be fairly reliable especially for measurements of unknown materials. This generalized RSF set is frequently used as the starting calibration, from which the “true” calibration coefficients are further refined using certified reference materials. As an example, GDMS accuracies for the two most important dopants, B and P, are now traceable to NIST Standard Reference Materials by the use of well-established SIMS Si reference materials (EAG group) for calibrations.

Figure 3: Schematic illustrations of sample selections from an UMG-Si brick (lines indicate the positions where the flat pieces where cut out from the Si brick).



3.4 Case Study Results

Two different UMG-Si bricks sampled the same way were used in this case study. Three test samples were prepared from each of the blocks and three consecutive readings were collected for each of the two different spots per sample. This represents 18 individual readings for each brick taken from various areas or volume fractions from each brick. Altogether fifteen different elements were simultaneously monitored for this study. The obtained results were plotted next to each other for comparing the results representing the two bricks. Figure 4 illustrates for instance the Boron distribution chart. Group of readings labeled Green 1 (G1), Blue 1 (B1) and Red 1 (R1) were obtained on brick #1 (18 left points) and similarly G2, B2 and R2 were obtained on brick #2.

The element distribution charts for B, Al, Fe and As in Figures 4, 5, 6 and 7, respectively, clearly reveal differences in distribution characteristics for different elements. Boron mass fractions are about two to three times higher on average in the first brick as compared to the boron levels in the second brick. These results indicate a much more uniform distribution of boron and arsenic in the second brick in all three directions as compared to the first brick. On the other hand, iron and aluminum charts point out more random distribution of these elements in the second brick as compared to the first brick.

Trends in the distribution of elements can indicate unwanted contamination related issues. For example the first reading of aluminum for each spot i.e. the reading closest to a surface is always higher than the other two readings, which are results from deeper sub-surface regions. The elevated level of aluminum closer to the surface of the tested samples is pointing towards contamination issues caused by the cutting tools and/or insufficient surface cleaning before analysis. Iron distribution is generally more random as compared to the aluminum distributions. Thus, presence and concentration levels of iron and its distribution in the brick is most likely characteristic of the stage in the manufacturing process.

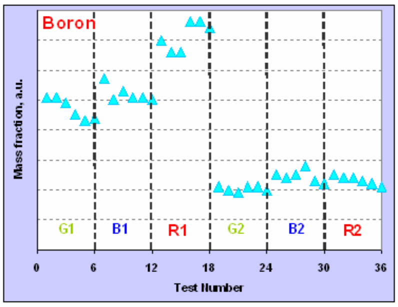


Figure 4: Boron distribution chart

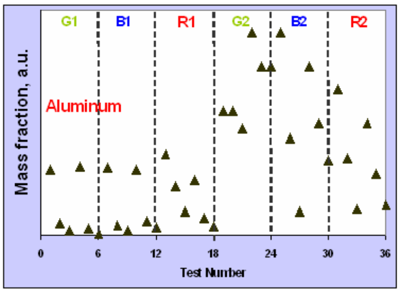


Figure 5: Aluminum distribution chart

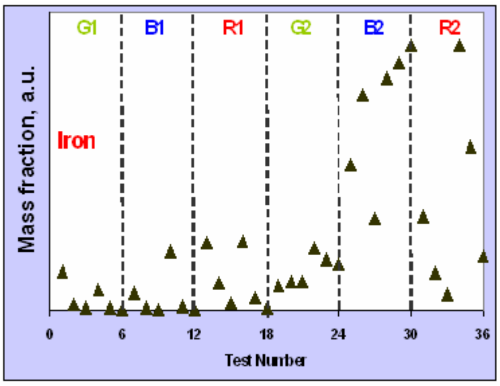


Figure 6: Iron distribution chart

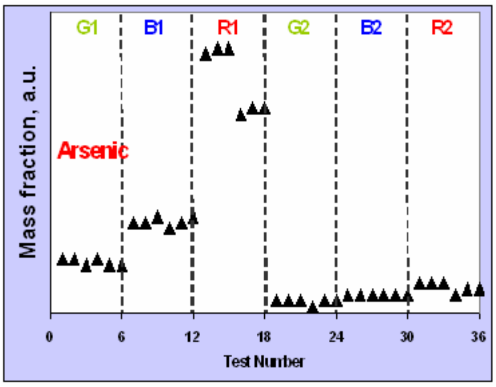


Figure 7: Arsenic distribution chart

4 SUMMARY

a) The main purpose of the case study was to demonstrate that the FF GD technique is an excellent tool for providing very sensitive distribution information as related to variations in “macroscopic” volumes in MG/UMG-Si samples.

b) There are many different routes proposed for up-grading (significantly reducing unwanted impurities from the material) of metallurgical grade Silicon (MG-Si) to the so-called UMG-Si (residual impurities in the ultra-trace levels). Detailed information about the changes in distributions of trace elements in various steps could be essential for fine tuning process parameters.

c) This case study indicates that trace impurity distributions in MG-Si and/or in the “intermediate” material processed on the route towards the UMG-Si goal are generally not uniform.

d) The actual range of non-uniformity (randomness, trends) is element dependent. Some impurities in some sections show trends, others are strictly random.

e) Trace elements distribution graphs can be used to determine what material to exclude or where representative samples should be taken.

5 REFERENCES

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