Non-Traditional Spectroscopy for Analysis of Semiconductor and Photovoltaic Thin Film Materials

Fuhe Li* and Scott Anderson†

Air Liquide Electronics - Balazs NanoAnalysis, 46409 Landing Parkway, Fremont, CA 94538

Abstract. Characterization of semiconductor thin films has long been determined by a number of traditional surface analysis techniques; Auger, ESCA/XPS, SEM-EDS and SIMS to name only a few. Depth profiles, contamination in the thin film or quantitative stoichiometry are specific application examples that predicate the technique best suited for the analysis need. The evolution of photovoltaic (PV) thin film compositions with new chemistries and growing importance of atomic layer deposition (ALD) for semiconductor and nanoscale applications provide a sustaining need for thin film analyses along with an avenue for new analytical tools.

In this paper we will discuss the applications of two non-traditional material analysis techniques for the semiconductor and PV applications, glow discharge optical emission spectroscopy (RF GD-OES) and laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS). Depth profiles are available via both techniques with the ability to analyze monolayers (single nm) as well as analysis in the bulk (μm thickness). Depth resolution capabilities allow analysis without surface equilibrium issues seen with other techniques. In addition, the charging effect that can cause issues with electron and ion beam techniques is avoided with RF GD-OES and LA ICP-MS, and thus analysis of both conductive and non-conductive materials is very straight-forward.

Contaminant analysis in thin films is very straight-forward and elements across the periodic table are analyzed in a simultaneous mode with both techniques. Detection limits to part-per-billion levels can be achieved and quantitation at low concentrations up to 99% achieved with LA ICP-MS. Lastly, it will be discussed that for some thin film applications, LA ICP-MS and RF GD-OES provide advantages over more traditional techniques, and these aspects as well as complementary features will be discussed.

Key Words: thin film analysis, depth profiling, depth resolution, contamination, quantitation, laser ablation, glow discharge, semiconductor, PV

INSTRUMENTATION

Glow discharge (GD) is a compact and small-volume plasma, and owes its name to the luminous glow of the plasma [1]. The glow discharge is generated between an anode and cathode inside a cylindrical glass tube filled with argon gas to a low pressure. When a varying RF voltage is applied across the electrodes, a plasma is formed between the electrodes and the entire tube then glows.

The analytical science community took advantage of the glow discharge principle and introduced a powerful material analysis instrument by combining a glow discharge source with an optical emission spectrometer (OES). In RF GD-OES, the GD is the emission light source (Figure 1). The cathode, however, is replaced by the solid sample that requires characterization. The sample can be either conductive or non-conductive. The RF potential is typically applied to the back of the sample.

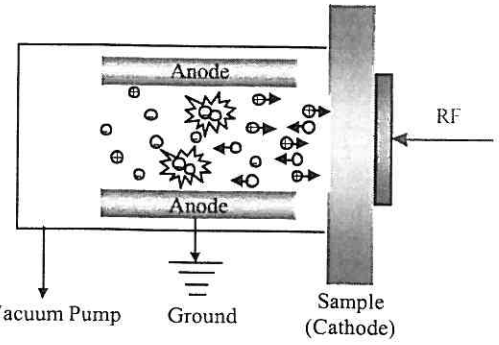

FIGURE 1. Conceptual diagram of Radio Frequency glow discharge emission source (RF GD-OES)

RF GD-OES analysis can be used for surface and bulk analysis of a variety of different materials. Its sputtering rates are typically 1-10 μm per minute, equivalent to about one atomic layer every 6 ms.

* Email: fuhe.li@airliquide.com
† Email: scott.anderson@airliquide.com

CP1173, *Frontiers of Characterization and Metrology for Nanoelectronics: 2009*,
edited by D. G. Seiler, A. C. Diebold, R. McDonald, C. M. Garner, D. Herr, R. P. Khosla, and E. M. Secula

Additionally, the optical emission signals can be recorded at ms speeds. Therefore it is possible for RF GD-OES to accurately profile atomic layer deposition (ALD) films.

Laser ablation in combination with inductively coupled plasma mass spectrometry (LA ICP-MS) has been utilized for more than thirty years to sample and analyze surfaces for metals, but only recently for thin film materials [2]. LA ICP-MS involves the conversion of a solid sample into a plume of particles and gas vapor via a focused pulsed laser beam. The plume is transported in an argon carrier gas to the steady-state RF plasma (ICP) for efficient atomization and ionization. The ions produced by the ICP are then analyzed by either a quadrupole or a magnetic sector based high-resolution mass spectrometer.

The OES and MS techniques have different advantages. RF GD-OES provides improved depth resolution along with analysis of metals and H, C, N and O, and spot size analysis of approximately 4 mm. While LA ICP-MS can analyze only metal and semi-metals, the sensitivity of the ICP-MS surpasses that of OES, and the spot size is approximately 4 μm. Both techniques can be applied to any type of surface material without surface equilibrium or charging issues at the sample or in the resulting data.

DEPTH PROFILING ALD FILMS

Figure 2 shows a RF GD-OES depth profile of an ALD metal oxide thin film on silicon substrate using a specific precursor material. This type of film is expected to be used as a future "high-k" gate dielectric due to its high-permittivity and low gate leakage when CMOS devices are scaled down to the sub-65 nm level and beyond.

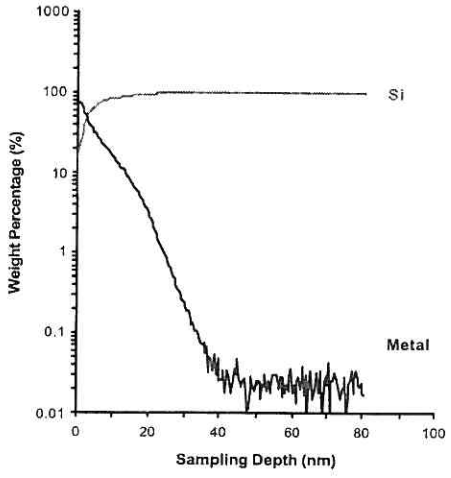

FIGURE 2. RF GD-OES depth profile for an ALD film indicates metal has been driven into the silicon substrate.

The physical thickness of this ultra-thin film was only a few nm and the film was post thermal anneal. The purpose of the RF GD-OES analysis is to examine how the proprietary metal element distributes vertically after annealing. Prior to the profile experiment, there was no sample preparation or pre-surface modification required. The RF GD-OES depth profile in Figure 2 clearly shows the effect of the post deposition thermal annealing as the metal has been driven into the silicon substrate slightly.

DEPTH PROFILING THIN FILMS ON GLASS/OPTICS

Analysis of poorly conductive materials such as glasses, ceramics, and thin films on glass is a very challenging process for Auger, SEM-EDS, and SIMS techniques due primarily to surface charging. This charging effect is well known, and can be so severe that stable signals can not be obtained, let alone the accuracy and precision. Fortunately there is no electron or ion beam involved with glow discharge or laser ablation sources. With RF GD-OES, an effective depth profile can readily be obtained for a metal nitride thin film on a glass substrate (see Figure 3).

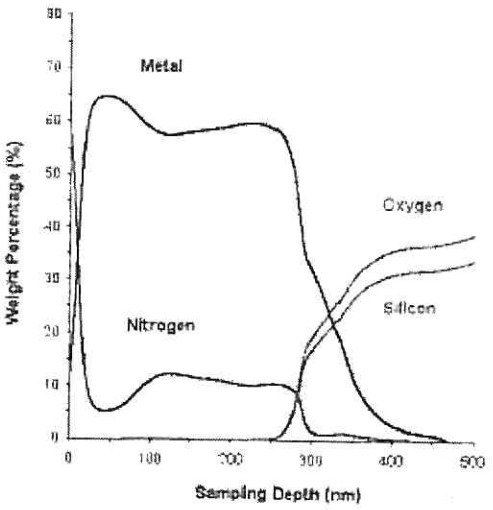

FIGURE 3. RF GD-OES depth profile of a film on glass with high nitrogen at the surface being detrimental to film properties.

The metal nitride film in Figure 3 was grown using metal-organic chemical vapor deposition (MOCVD). The process engineer claimed that the film was defective, even though the average weight percentages (%w/w) of proprietary metal and nitrogen in the film were consistent with the expected values. The RF GD-OES profile revealed the vertical distributions of metal and nitrogen was very uneven. In

addition, a very high concentration of nitrogen was found on the surface that proved to be detrimental to the film property. After reviewing the RF GD-OES profile, the engineer realized an issue with the deposition process and corrected the problem.

A non-conductive optical coating/part is also a straight-forward profile with LA ICP-MS as shown in Figure 4. In this case, a much deeper depth profile can be obtained by simply firing the laser through the different layers of the coating/optic. In both 3 and 4, these films would not be easily profiled with other surface techniques as multi- and initially-unknown element monitoring is not straight-forward while the thick profile in Figure 4 is not amenable to SIMS or XPS.

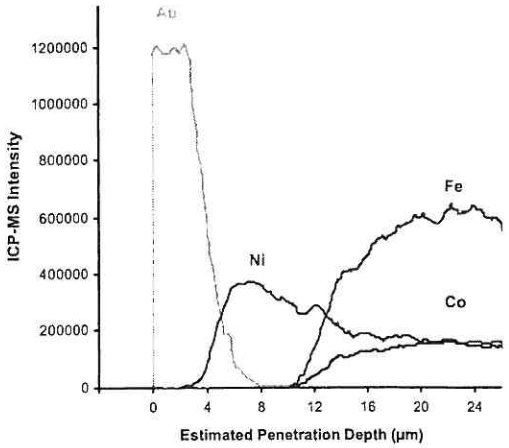

FIGURE 4. LA ICP-MS of thick optical coating/part

ANALYSIS OF SURFACE COMPOSITION/ CONTAMINATION

The surface modification of a material can produce a far superior product in terms of increased corrosion resistance, improved optical transparency, and decreased electric contact resistance. With a photovoltaic circuit, it could mean less recombination effects, better compatibility between films, and ultimately higher energy conversion efficiency. Both RF GD-OES and LA ICP-MS have the capability to show properties such as film stoichiometry and elemental contamination in a thin film.

Starting in 5A with a standard alloy structure, Figure 5 shows three RF GD-OES depth profiles of a 100 nm thin film and the effect of chemical exposure on the surface. Mixture B enriches the immediate surface with metal X by depleting the metal Y, whereas

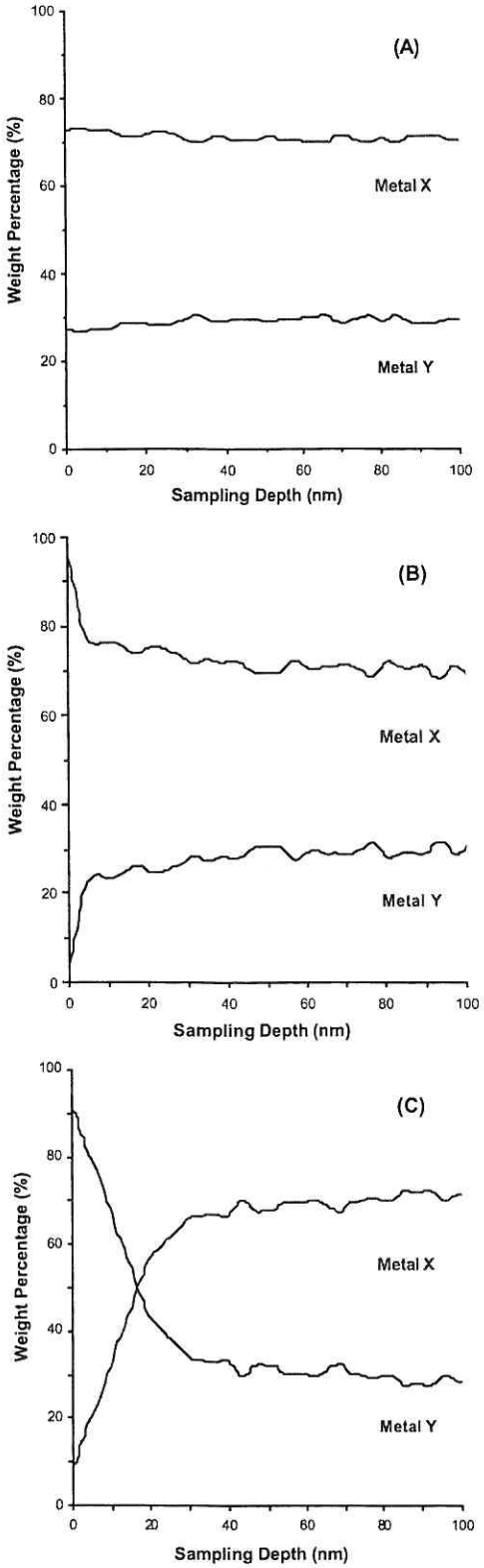

FIGURE 5. RF GD-OES Depth profiles from an alloy thin film after chemical surface treatments: normal A, mixture B, and mixture C. Proprietary metal Y is depleted at the surface with mixture B while Metal Y is enhanced in mixture C.

mixture C instead made the surface enriched with metal Y. Such properties could translate to different functional properties of a film and in the case of PV, efficiency in the final module. RF GD-OES has a ready ability to analyze and profile such compositions on the surface and near surface regions of a thin film. Any indication of a surface equilibrium phenomenon [3], a difficulty frequently encountered with SIMS analysis, is not observed with RF GD-OES.

Depth profiles are obviously critical analyses for any thin film. An important metric that is often not measured due to difficulty in analyses or simply issues in finding traceable standards is quantification of contaminants in a thin film. Often the understanding and subsequent elimination of metal contamination in a thin film can improve the efficiency of the final circuit. With the increased sensitivity of LA ICP-MS (down to ppb levels for some elements) and the availability of meaningful and NIST-traceable standards, quantification of metallic contaminants can be performed at low and high concentration ranges. With this data, a process engineer can see real differences in different thin films or a source of contamination. Quantitation examples via LA ICP-MS are shown in Table 1 and 2.

TABLE 1. Analysis of Bulk Impurities in CdTe Films via LA ICP-MS; CdTe-3 shows more contamination.

Analyte	CdTe-1 PPM (µg/g)	CdTe-2 PPM (µg/g)	CdTe-3 PPM (µg/g)
Li	< 1	< 1	2
Na	< 0.5	15	4500
Mg	< 1	4	2300
Al	< 1	26	170
K	< 5	8	230
V	< 0.5	< 0.5	50
Cr	< 1	< 1	16
Mn	< 0.5	13	53
Fe	< 5	67	340
Co	< 1	< 1	20
Ni	< 0.2	22	87
Cu	< 0.5	< 0.5	20
Zn	< 1	< 1	90
Ga	< 1	< 1	12
Ge	< 1	< 1	76
As	< 1	< 1	< 1
Sr	< 0.2	< 0.2	12
Zr	< 0.2	< 0.2	82
Mo	< 0.5	< 0.5	3400
Ag	< 0.5	< 0.5	<0.5
Cd	Major	Major	Major
Sn	< 1	< 1	89
Sb	< 0.5	< 0.5	23
Ba	< 0.2	< 0.2	230
Pb	< 0.2	16	560

In Table 1, a comparison of different CdTe films shows that CdTe-2 has slightly more metal contamination than CdTe-1, and that CdTe-3 contains a gross amount of metal contamination. In Table 2, contamination in two different indium films is observed with a tell-tale stainless steel indicator evident with Fe, Cr, Ni, and Mo present. The source of this contamination was determined via analysis of the original indium *target* where the stainless steel contamination signature was congruent with that in the *new* indium film. The simultaneous and multi-element analysis scheme of LA ICP-MS, coupled with the availability of NIST-traceable standards, make this analysis a powerful tool for contamination identification, both qualitative and quantitative.

TABLE 2. Purity Analysis of Indium Films and Target via LA ICP-MS; the indium target indicates stainless steel contamination that is also found in the new indium film.

Analyte	Old Film PPM (µg/g)	New Film PPM (µg/g)	New Target PPM (µg/g)
Li	< 1	< 1	< 1
Na	< 0.5	< 0.5	< 0.5
Mg	< 1	< 1	< 1
Al	< 1	< 1	< 1
K	< 5	< 5	< 5
V	< 0.5	< 0.5	< 0.5
Cr	**< 1**	**13**	**12**
Mn	< 0.5	< 0.5	< 0.5
Fe	<5	**120**	**130**
Co	< 1	< 1	< 1
Ni	**<0.5**	**35**	**39**
Cu	< 0.5	< 0.5	< 0.5
Zn	< 1	< 1	< 1
Ga	< 1	< 1	< 1
Ge	< 1	< 1	< 1
As	< 1	< 1	< 1
Sr	< 0.2	< 0.2	< 0.2
Zr	< 0.2	< 0.2	< 0.2
Mo	**< 0.5**	**9.2**	**9.6**
Ag	< 0.5	< 0.5	< 0.5
Cd	<0.5	<0.5	<0.5
Sn	< 1	< 1	< 1
Sb	< 0.5	< 0.5	< 0.5
Ba	< 0.2	< 0.2	< 0.2
Pb	< 0.2	< 0.2	< 0.2

SIMULTANEOUS MULTI-ELEMENTAL PROFILING

The multi-element aspect previously discussed is especially important with finding unknown contamination. With this capability, RF GD-OES can be used to profile multi-layer magnetic recording media for the disk drive industry, and look for contaminants on the surface and in the interfacial regions.

Figure 6 shows two RF GD-OES profiles obtained from good and bad disk materials with no known root cause for disk failure. These materials were previously analyzed by XPS and no distinct difference was found between "good" and "bad" materials. The same disks were then quickly profiled by RF GD-OES and the unwanted surface and interfacial impurities (X and Y respectively) in the bad disk were observed. In this case, XPS was just not sensitive enough to reliably detect those impurities at or below 0.5% (w/w) level. The depth profiles indicate an excellent ability to simultaneously monitor multiple elements while also probing different vertical regions of a material for unknown contamination.

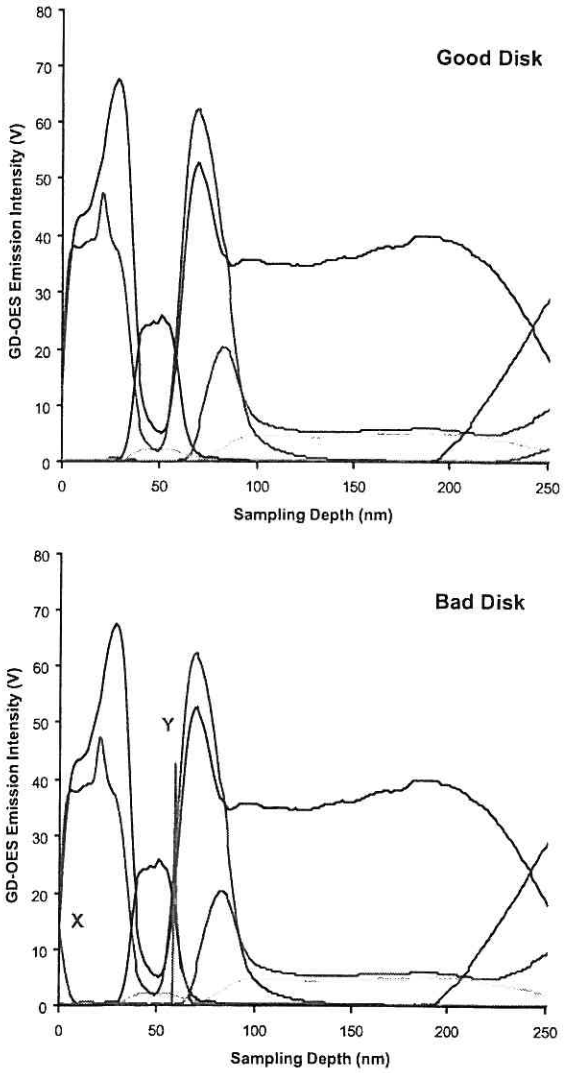

FIGURE 6. Analysis of Bulk Impurities in CdTe Films via LA ICP-MS; CdTe-3 shows more contamination. Depth profiles obtained from good and bad hard disk materials via RF GD-OES. Elemental composition is proprietary as well as contaminants in the bad disk (elements X and Y).

CONCLUSION

The RF GD-OES and LA ICP-MS techniques have been previously shown to possess unique metrology characteristics as both a complementary and supplementary technique to traditional surface analysis techniques such as Auger, XPS, SIMS and EDS. Beyond the complementary aspect, both glow discharge and laser techniques are also stand-alone analyses that in many instances provide the "best available tool" to solve particular surface analysis needs.

RF GD-OES has the ability to simultaneously depth profile more than 40 elements in a material with nm depth resolution approaching that of SIMS. At a typical sputtering rate of 10 nm per second, the sample analysis/data collection is much faster and more cost effective than SIMS as well. When using as an elemental survey technique, both RF GD-OES and LA ICP-MS are more sensitive than Auger and XPS. The typical RF GD-OES detection limits are ppm and LA ICP-MS ppb (w/w) compared to ~0.5% (w/w) by Auger or XPS. LA ICP-MS does not approach SIMS or RF GD-OES on a depth resolution scale, however for thick films or forays into the bulk LA ICP-MS is highly advantageous.

In the end, each surface analysis technique has certain features that provide best utility for the required analysis. A depth profile for dopant concentration is the hallmark of SIMS while chemical state identification is the bailiwick of XPS. RF GD-OES and LA ICP-MS have analytical utility for specific analyses as well. With the development of new materials in photovoltaic and nanotechnology, and with the inherent need to improve thin film and chemical processes, LA ICP-MS, RF GD-OES and all surface techniques will be required to provide practical acumen and proper data.

REFERENCES

1. T. Nelis and R. Payling, *Glow Discharge Optical Emission Spectroscopy, A Practical Guide*, edited by N.W. Barnett, Cambridge, Royal Society of Chemistry (RSC), 2003.
2. F.H. Li and S. Anderson, Using Direct Solid Sampling ICP-MS to Complement SEM-EDX and SIMS in Characterizing Semiconductor Materials, in *Characterization and Metrology for ULSI Technology*, edited by D. G. Seiler et al (Ed.), New York, American Institute of Physics Press, 2003, pp. 715-7192.
3. T. Nelis, M. Aeberhard, R. Payling, J. Michler, and P. Chapon, *Journal of Analytical Atomic Spectrometry* **19**. 1354-1360 (2004).