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Glow discharge optical emission spectrometry: moving towards reliable thin film analysis–a short review†

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Glow discharge optical emission spectroscopy (GD-OES) is briefly reviewed, with particular reference to topics relevant to the application field of near surface and thin film analysis. The special needs and requirements for thin film analysis, in contrast to coating and bulk analysis, are pointed out. A task list is developed which shows the requirements of further developments to the technique and the fundamentals. The state-of-the-art is presented in measurement technique, GD source control and design, the effect of traces of molecular gases, correction and quantification procedures, contributions of modelling and, finally, reference materials for thin film analysis.

1. Introduction

The GD-OES depth profile technique (based on a Grimm type source[1] and the spectrometer design of Rowland[2]) has a long history since 1970 and a wide range of applications.

In the 1980s, a boom of activities concerning industrial applications and scientific works started worldwide. Within this background a European GD-OES community began to form, finally leading into the European GDS Network at the end of the 1990s.

In practical applications, the analysis of surface treatments and metallic coatings on steel was strongly growing to the level of extensive use. Starting with qualitative profiles, with all the disadvantages in interpretation, efforts were focused on fundamental studies to develop quantification and applicable software routines.

In the late-1990s the high level of expertise led to the first pre-normative research project on quantitative GD-OES depth profiling of zinc and aluminium based coatings, carried out in the European Community in 1997–1998.[3] Furthermore the development of rf-sources for GDS extended the application of depth profiling also to non-conductive materials like organic coating, glasses, ceramics, *etc.*, and particularly to the analysis of thin conducting layers on conducting substrates (where a dc discharge would require a breakthrough which would destroy the layer to be measured). The rf technology has presented new opportunities and challenges for the quantification of depth profiles, but further developments are needed (rapid stabilisation of the source, high voltages to deal with thicker substrates and improved measurement of electrical discharge parameters). The instrumentation currently on the market differs widely, so that no serious comparison can be made. The work is promising but so far not all questions are completely resolved, so this review is mainly restricted to dc discharges.

In the last decade also methods of mathematical modelling have led to a further understanding of the physics and spectroscopy of glow discharge. Based on these results, some GDS phenomena can be numerically described and experimental results predicted.

The state-of-the-art in the general field of depth profile analysis has been presented by a review paper of A. Bengtson and S. Hänström.[4] Within this broad success in quantitative coating characterisation in depth-regions of some μm up to 50 μm and more, new applications of GD-OES depth profiling for thin film (defined by the ISO as "a layer or material, typically less than 100 nm in thickness, deposited or grown on a substrate"[5]) and surface analysis began to develop.[6] The advantages of easy use, high sensitivity, good quantification and high sample throughput force an extension of this field of application. This has led to a requirement for further development in GD-OES techniques and depth profile analysis of a more complex nature, *i.e.*, the reliable analysis of near surfaces and thin films. At an Expert Meeting on Depth Profiling organized by the EC Thematic Network on Analytical Glow Discharge Spectroscopy (Dresden, 1999),[7] Network participants were invited to comment on the problems that should be tackled to improve GD-OES thin film analysis. The resulting discussions have led to the production of this paper. A number of specific topics are considered, which do not necessarily affect only thin film analysis but which are particularly relevant to this application.

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2. Some fundamental aspects of thin film and surface analysis

"The surface was invented by the devil"—Wolfgang Pauli

So it is safe to conclude that life will not get easier for GD-OES depth profiling—and for all the other surface sensitive analysis techniques dealing with thin films and surfaces or near surface regions.

What are the reasons for this? Fig. 1 shows a schematic drawing of a surface formation. In contrast to coating analysis it can be seen that thin film analysis has mainly to deal in a depth-region with a strong presence of

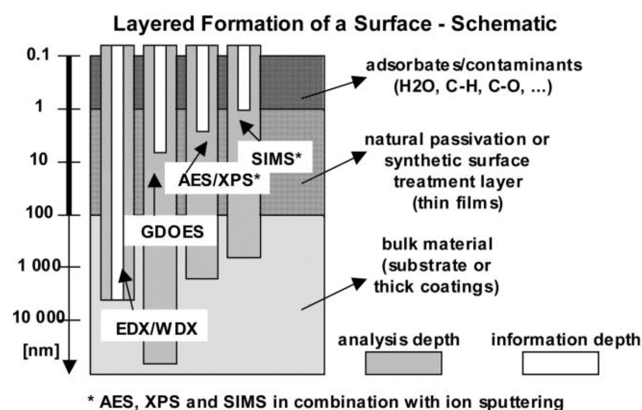
–various species of gaseous elements originating from adsorbed gases and contaminants, such as H_2O, C–H-compounds, O_2, C–O, *etc.*

–a passivation or oxide layer, originating from natural passivation or synthetic surface treatments (different kinds of oxides, hydroxides, phosphates, *etc.*).

The ability of the technique to analyse thin layers or films depends on the information and analysis depths of the measurement technique but also on the surface roughness, crater flatness, *etc.* The information depth, shown in the figure, is the depth region below an ideally flat surface which contributes to analytical information, *i.e.*, the escape depth of the signal. On the other hand, the analysis depth is the depth region of the sample where an analysis can be acquired.

Until now, the applications of GD-OES involved the determination of element concentrations in the μm depth range. In the above scheme, these technical layers, such as hard coating or Zn corrosion protection layers, already belong to the "bulk material" domain. So the challenge for GD-OES thin film analysis is to take into account all these dominant interchange effects of gaseous molecules and passivation layers (with mostly unknown structures and densities) on glow discharge physics and spectroscopy processes. State-of-the-art fundamentals and common models of correction and quantification have to be revised and further developed.

As mentioned above, not only do new influences dominate the plasma, sputtering and excitation processes but also parts of the GDS hardware system influence the ability to analyse



Acronym	Technique	Information depth/nm
SIMS	Secondary Ion Mass Spectrometry	1
AES	Auger Electron Spectroscopy	2
XPS	X-ray Photoelectron Spectroscopy	2
GD-OES	Glow Discharge Optical Emission Spectrometry	6
EDX	Energy Dispersive X-ray Analysis	5000
WDX	Wavelength Dispersive X-ray Analysis	5000

Fig. 1 Schematic drawing of the complex layered formation of a surface showing adsorbates/contaminants, passivation layer and substrate material, together with the different surface analysis techniques and their information depth attainable (approx.) (Hantsche[8]).

Table 1 Tasks to improve thin film analysis with GD-OES depth profiling

Improvements for thin film analysis—main topics	Working tasks
GDS measurement technique	Vacuum conditioning/improvements Switch-on behaviour of the power supplies Data acquisition rates Development of new GDS-sources
GD physics and spectroscopy	Plasma effects Excitation and emission effects Sputtering effects Erosion rates and shape Development of modelling
Evaluation procedures	Improvements for correction and quantification models Density calculation
Reference samples—thin film	Thickness and density measurement Homogeneity of layer formation Sputter rate determination

thin films. Therefore, attention should also be paid to the following aspects.

For example, vacuum conditioning (pre-pumping and flushing time, oil-free pumping systems, *etc.*) will be important to reduce the gaseous amount and contaminations in the plasma and on sample surface.

Higher data acquisition rates will improve the ability to analyse thin films due to a higher number of data per unit time.

Reducing the erosion rates will also improve the detection of thin films. This could be done by mixing the carrier gas argon with, for example, He. The admixture of small quantities of hydrogen to argon can also significantly improve the depth resolution of thin films[9,10] when using rf sources. The available rf-voltage often limits the attainable depth resolution, especially for thin layers on non-conductive substrates thicker than ~2 mm. Hence, such gas-mixture procedures of improving analytical figures of merit are welcome.

The development of new pulsed sources promises also a reduction in sputtering power and therefore a slower erosion rate of the sputtered material.

Table 1 highlights some of the main tasks of current activities and works, which are needed to improve thin film analysis with GD-OES depth profiling.

3. GDS measurement technique

Pre-pumping time

In Fig. 2 the influence of pre-pumping time on the reduction of gaseous elements, such as oxygen, nitrogen and hydrogen, is shown. An increasing vacuum leads to the desorption of adhesive molecules and/or contaminants from the surface. The values established in the graph depend on the GDS vacuum system and the cleanness of the lamp. These established results suggest long pre-pumping times. In contrast to this, it can be seen that the carbon signal increases with pumping time. This

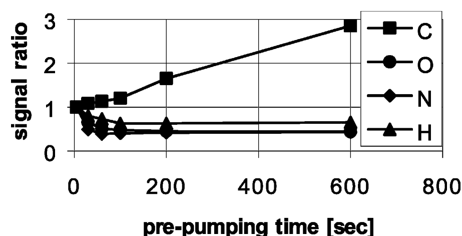


Fig. 2 Ratios of signal intensities of the elements C, H, N, O to initial intensities as a function of pre-pumping time in GD-OES analysis.[11]

phenomenon is interpreted as back-diffusion of carbon from the rotary pump.

Source cleanliness

The influence of GD contamination (from the walls of the GD source, from the sample itself and from the argon atmosphere) on the analytical signals at the beginning of a depth profile and on the depth resolution is critical in particular for thin and very thin film analysis; nevertheless, it can be minimised correspondingly. Previous sputtering of pure materials (ideally silicon) has been shown to minimise the presence and hence the effect of hydrogen as contamination.[10]

The emission of molecular bands is well known in glow discharge spectroscopy and is even exploited in some applications. Normally the emission of molecules over a wide spectral range (typical 10 nm) disturbs the correct measurement of the intensity of atomic lines. Therefore rare gases are used for sputtering, the sources are carefully sealed and vacuum tight samples must be applied.[12] Additionally, other effects occur when molecular impurities containing hydrogen are present in the discharge,[9,13,14] as discussed in Section 5.

Even if the reason for these effects was not known for a long time, the consequences were observed when molecular impurities, like H_2O, N_2, C–O–H, were present at the beginning of depth profiling in the source. Nearly all line intensities decrease in an exponential-like manner until the source is cleaned by sputtering the surface and self cleaning of the source (*e.g.* by gettering). GD-OES users normally warm up their instruments every day to reduce the source contamination and in GD mass spectrometry (MS) cryo-cooling is used to get reproducible discharge conditions with low contamination. The first principle, however, is to avoid contamination by the argon sputter gas (use of high quality gas) and by the vacuum system (*e.g.* oil free pumps, steel tubes).

In a Round Robin test carried out by the European Working Group on Glow Discharge Spectroscopy (EW-GDS), the residual level of contamination was compared for different instrumentation.[7] For that purpose the background equivalent concentration (BEC) of carbon in iron was determined after pre-sputtering of up to 10 min and calibration with low carbon containing iron standard material. The BEC of carbon from 20 participants varied from 9–61 $\mu g\ g^{-1}$, but no systematic result concerning the source of this contamination could be obtained. Two similar systems using "dry" (oil-free) pumps gave values of 10 and 37 $\mu g\ g^{-1}$, illustrating the need to check carefully the cleanliness obtained in routine use. Typical calibration curves for carbon in iron are shown in Fig. 3, which prove that the BEC value also depends on the applied discharge conditions.[15] Most probably there are many small effects, which contribute to this BEC value, because the existing sources were developed with fore-vacuum pumping systems. Systematic studies are needed for further improvements.

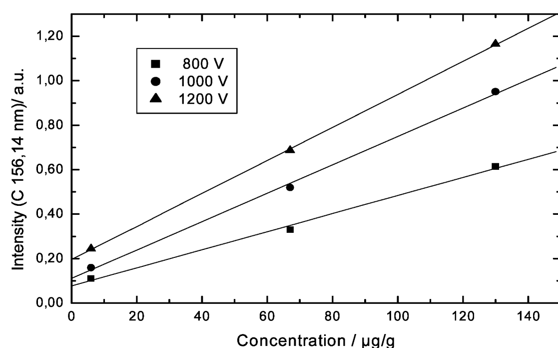


Fig. 3 Calibration curves to determine residual carbon in GD source and to show the effect of the applied voltage on the intensity of carbon.

Fig. 4 Sketch of typical crater profiles: (a) with convex crater edge, (b) with concave crater edge.

Depth resolution

The concept of depth resolution has been discussed by Quentmeier[16] and Weiss[17] among others. This review only includes points particularly relevant to the analysis of thin films and layers: for a more detailed discussion the above two articles and references therein should be consulted. In early work[18] the depth resolution was defined as "the depth range over which a signal increases (or decreases) by a specified amount when profiling an ideally sharp interface between two media. By convention, the depth resolution corresponds to the distance over which a 16% to 84% change in signal is measured".[19] However, the prerequisite for the use of this equation is that the "measured profile can be approximated by an error function", which is not valid for an optimised depth profile in GD-OES. Here, whilst the central area of the crater bottom is as flat as possible, the edges are either convex (Fig. 4(a)) or concave (Fig. 4(b)). This leads to a measured profile, where for the convex case, a signal from the lower layer B already appears before the sharp transition or, for the concave case, the upper layer A still produces a signal after the sharp transition. In multilayers, therefore, often 16% and/or 84 % values do not exist even if there are still sharp transitions.

More generally, the measured signal can be described by the following equation

$$I(z) = \int_{-\infty}^{+\infty} c(z')g(z-z')\mathrm{d}z'$$

where $g(z - z')$ represents the depth resolution function (DRF). If the measured profile can be approximated by an error function the DRF has a Gaussian shape. This, however, is not at all valid in GD-OES; moreover, the DRF changes with depth. However, for these non-Gaussian DRF or non-symmetrical DRFs and depth profiles, the so-called "inverse maximum slope" method can be applied.

$$\Delta z = \Delta c/(\mathrm{d}c/\mathrm{d}z)_{\max}$$

The depth resolution Δz is determined on this basis at a sharp interface between two layers, where Δc is the difference of the concentration of the corresponding element in the two layers and $(\mathrm{d}c/\mathrm{d}z)_{\max}$ represents the steepest slope of the quantified depth profile at the interface. Of course it is impossible to describe any DRF completely with this one parameter, but this method is independent of any assumption about the DRF and provides an objective quantity. However, one must keep in mind that the depth resolution calculated on this basis is smaller than the thickness of a layer where we would get a plateau of the intensity or concentration from a multilayer sample. This would only be achieved if slope were constant throughout the transition. The physical meaning of this depth resolution value relates to the flatness of the main part of the crater bottom.

For a Gaussian DRF the depth resolution determined by the inverse maximum slope method is slightly higher (2.507σ) than the conventional 16–84% approach (2σ). For a non-Gaussian DRF, a lower or higher depth resolution can result, depending on the actual DRF. This holds true also for the normalized amplitude method, which is described in Briggs[19] and also discussed by Hofmann.[20] In this approach the ratio of the

difference and sum of the maximum and minimum of intensity or concentration of a certain element in two adjacent layers of a multilayer is used for the determination of the depth resolution. This ratio again is an objective measure of the measured depth profile, but the transformation of this value into a depth resolution requires a transformation function, which depends on the DRF. If the DRF is unknown, the transformation function for the Gaussian DRF is used. In this case, intensity changes no longer exist if the depth resolution is twice the layer thickness, whereas for an exponential DRF, 20% oscillations are still observed even if the depth resolution is four times the layer thickness. The physical meaning of the depth resolution thus determined is the area of the crater which is sputtering in a certain layer type. Here contributions from more layers of the same type are also included and it is quite possible that the calculated value of the depth resolution improves even if the crater profile becomes worse with depth.

Simulation of depth profiles[21] and systematic studies at 100 nm multilayer systems[22] confirmed also at this depth scale the knowledge that the crater profile is the most critical factor for the depth resolution in GD-OES (*e.g.* Weiss[23]). The inverse maximum slope method proved to be suitable for optimizing and comparing the depth resolution of GD-OES depth profiles After good optimisation of the crater profile by source design and discharge conditions the depth resolution increases linearly from about 25 nm at 100 nm depth up to 60 nm in 1 μm depth. A linear extrapolation of this dependence to the surface would lead to a depth resolution of about 20 nm at the beginning of the analysis. Because of the varying and non-Gaussian DRF in GD-OES, this is not in contradiction to the fact that we can produce depth profiles of layers that are thinner than 10 nm and gain very valuable analytical information.

There are additional influences, such as impurities, roughness and curvature of the sample, and so on, also affecting the depth resolution, which might limit it even more than the crater shape at the top surface. Moreover, one should have in mind that the diameter of the sputtered area is about 6 orders of magnitude larger than the best depth resolution obtained of some nm. Therefore, a good optimisation of the crater shape (see also Section 7) is an absolute prerequisite for such good depth resolution at the upper surface. Furthermore, it must be mentioned that the electrical conditions with the best crater shape may not be suitable for the analysis of, for example, heat sensitive samples.

4. Developments in GD source control and design

The time dependence of the electrical and emission signals was studied for dc and rf modes and it became clear that the present technique is limited by the time constant (about 20 ms) of the power supplies.[24] At an erosion time of 100 nm s^{-1} this already means sputtering of 2 nm. Mostly, however, the ignition currents are higher than the final value and therefore also the erosion rate is increased. Longer instabilities of the power supply totally disturb the depth profiling at thin layers.

A special problem consists in choosing the working mode of the source. Constant voltage and current must be avoided if the pressure regulation system has a long time constant, although improvements in modern instrumentation are now allowing rapid pressure regulation. Constant voltage and pressure is preferred but sometimes leads to problems at ignition and too high voltages are needed, which destroy the layer structures by the ignition pulse. Here an external ignition could solve this problem. Working at constant current and pressure leads to high voltages on ignition and the same problem as was mentioned before exists.

These difficulties might be overcome by the use of a microwave boosted GD source. The basic concept of Leis *et al.*[25] would have to be modified for this kind of thin film applications by adding an electrode to start a microwave discharge initially—that discharge could clean the source and sample surface without any significant sputtering of the sample. Then, because a discharge is already running, a dc (or rf) sputtering discharge would start with little time delay and no high voltage or current surges.

5. Plasma and discharge mechanisms; effects of traces of molecular gases

For many years there has been interest in the discharge mechanisms taking place in Grimm-type GD, *e.g.* the work at the National Physical Laboratory, Pretoria, South Africa in the early 1980s (*e.g.* Ferreira *et al.*[26]). It is important that such investigations are carried out by as many techniques as possible—optical emission and absorption[26,27] and by mass spectrometry. More recently, additional understanding has been provided by modelling work.[28] One topic of particular current interest is the effect of traces of molecular gases (*e.g.*, hydrogen and nitrogen) in the noble plasma gas. These traces may arise from the sample itself or from contamination in the source. They affect the analytical quantification procedure in general, but become particularly important in thin film analysis as (i) it is not possible to use long preburn times to clean the source and (ii) many of the films themselves contain such elements as a constituent.

Many investigations on the effects of hydrogen, nitrogen and oxygen have been made (see review by Wagatsuma[29] on the effects of nitrogen and oxygen and Fernández *et al.*[30] for the effect of nitrogen, hydrogen and oxygen in rf discharges), but frequently, in these cases, the molecular gas is a major constituent of the plasma gas. Extensive studies of the effect of small amounts of hydrogen (0.01–2% v/v hydrogen), using both OES and MS, have been carried out by Hodoroaba.[9,10,13,14,31] It has been shown that when TiH layers are used as the sample, the hydrogen concentration in the plasma gas is $\sim$0.2–1% v/v,[9,13] depending on the source used. On the other hand, hydrogen concentrations $\sim$0.02% v/v can produce significant changes in the sputtering rate, in the intensities of both argon and sample lines and in the discharge resistance. Higher concentrations ($\sim$0.2% v/v) produce an underlying hydrogen continuum in the region 200–400 nm. MS measurements have shown that small traces of hydrogen produce a drastic reduction in the Ar^+ signal and a strong ArH^+ signal. Some of the mechanisms involved have been discussed by Hodoroaba *et al.*, and an extensive review of possible interactions has been given by Bogaerts *et al.*[32] and calculations presented for a VG9000 MS flat discharge cell.[33,34]

Investigations on the effect of small quantities (up to $\sim$2% v/v) of nitrogen in the plasma gas have recently been reported by Šmíd *et al.*[35] These confirm to some extent and extend the earlier results of Fischer *et al.*[36] Again, the intensities of the plasma gas and sample lines are strongly affected by the presence of nitrogen. The plasma resistance increases but to a lesser extent and in a more complex way than with hydrogen. The effect on the sputtering rate depends strongly on the sample used; 0.1% v/v nitrogen produces an 80% drop in the sputtering rate for a titanium cathode but only a 20% drop for an iron cathode.[35] Sputtering a TiN sample in a pure argon discharge gave a nitrogen signal corresponding to about 0.05% v/v nitrogen using a titanium sample. Further investigations are continuing.

The effects are even more complicated when traces of hydrogen and nitrogen are present simultaneously in the plasma gas. Dorka and Šmíd[37] have made MS measurements using small quantities of nitrogen in argon. In a nominally pure argon discharge, a strong ArH^+ signal was observed. When nitrogen was added the ArH^+ signal was almost completely suppressed, indicating a change in the various discharge

reactions occurring. Similar results have been reported very recently by Jackson and King.[38]

Investigations on these effects of molecular gases are continuing. Corrections for the effect of hydrogen on quantification algorithms have been suggested by Payling *et al.*[39,40] but much further work is required before the effects of the molecular gases are more fully understood and appropriate modifications made to quantification procedures.

6. Developments in correction and quantification procedures

It has been a widely held opinion that GD-OES is not a suitable technique for near-surface or very thin film analysis. This opinion was previously justified by the fact that the glow discharge was often observed to be rather unstable during the first few seconds of sputtering. However, the improvements in source design and control over the years have changed this picture. It has been shown that the minimum information depth and depth resolution of GD-OES can be comparable with those of secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES).[22]

An example of the very high depth resolution obtained for a series of alternating 5 nm Ni–Cr layers is shown in Fig. 5. The depth profile was recorded at SIMR Stockholm with a LECO GDS 750A spectrometer, operated in the constant current–constant voltage mode, with active pressure regulation to stabilise the discharge. The instrument used has a time constant of about 100 ms for pressure regulation, which allows the operator to work in this preferred mode for quantification. A preliminary test must be performed to ensure that the pressure at ignition is not too far from the pressure needed to run at the given voltage and current. The depth profile was quantified using a standard emission yield calibration based on steel and nickel bulk reference materials. The depth resolution of this profile has been evaluated according to the normalized amplitude method by S. Hofmann.[41] He found that Δz increases from 4.5 nm initially to about 6 nm in the middle of the multilayer stack. An apparent slight decrease of Δz between 50 and 80 nm indicates some degree of "positive interference" between adjacent layers in the depth profile.

Interestingly, applying the inverse maximum slope method to this profile gives a result similar to that quoted in Section 3 above, *i.e.*, the depth resolution decreases to about 20 nm in 100 nm depth. It is therefore evident that in GD-OES with a non-Gaussian DRF, the method used to determine the depth resolution has a strong influence on the result and its meaning and therefore *must* be reported by the authors. Certainly, the results give further evidence that GD-OES is capable of analysing layers much thinner than 20 nm.

Another example of the high resolution of thin layers that can be obtained with GD-OES is shown in Fig 6.[42] This shows the depth profile of a 100 nm GaN layer obtained using a GDA

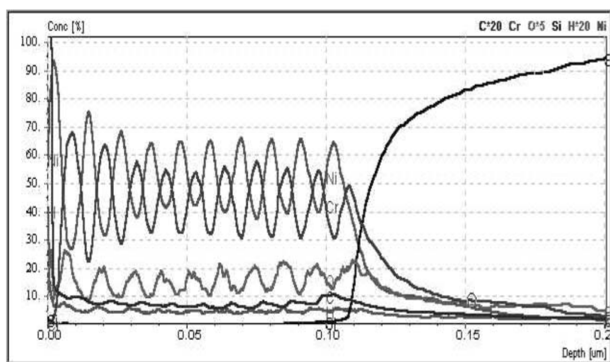


Fig. 5 Quantitative depth profile of 20 alternating Ni–Cr layers, each 5 nm thick, on a silicon substrate.

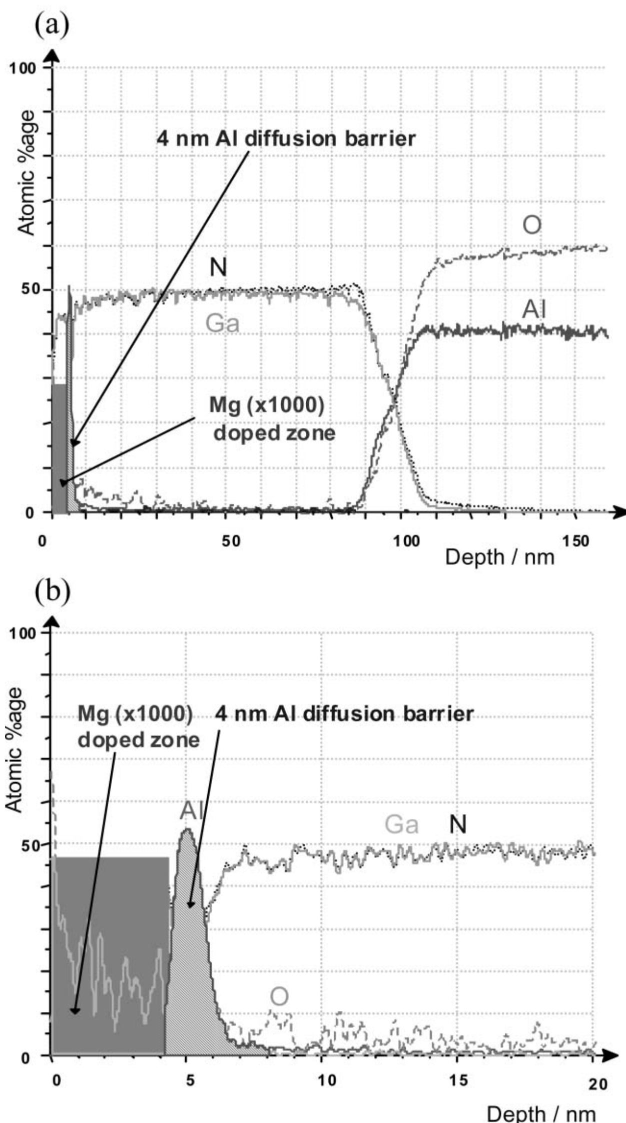


Fig. 6 Depth profile of 100 nm thick gallium nitride layer on an aluminium oxide substrate. All concentrations scaled to 100 % at./at., except that for Mg, which is scaled to 0.1 % at./at. (a) Full depth profile, (b) expanded view of first 20 nm.

750 HP instrument (Spectruma Analytik GmbH, Germany). All elements are scaled to 100% at/at, except that magnesium is scaled to 0.1 % at./at. The Mg doped zone a few nm thick on the outer surface and the Al diffusion barrier (thickness $\sim$4 nm) is clearly resolved.

When profiling very thin films $<$100 nm, the analysis time is very short, sometimes less than a second. Even if the layer itself does not contain any hydrogen, it is inevitable that a certain amount of hydrogen is present in the plasma during the first seconds, from, for example, adsorbed water in the interior of the source. In addition, several very thin technical layers of interest do contain substantial amounts of hydrogen. As a consequence, the effect of hydrogen on the emission yields is often very strong in thin film analysis. The introduction of the "matrix correction" for compensation of this effect is therefore of considerable importance in order to get more accurate results. The correction is effected according to the following formula:

$$I_{corr} = I \times e^{k(\lambda) \times I(H)/I(Href)}$$

where I_{corr} is the matrix-corrected intensity; I is the raw intensity; k(λ) is a line-specific constant; I(H) is the measured

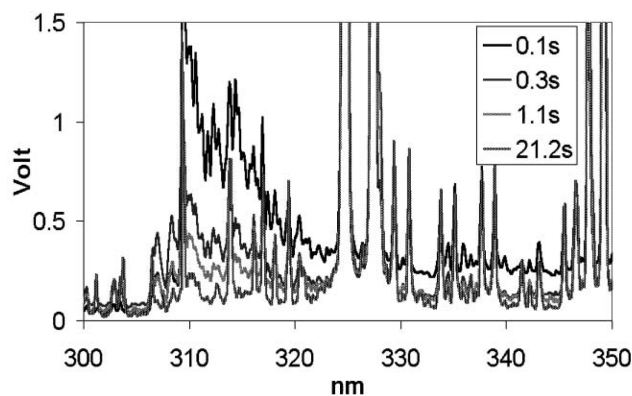


Fig. 7 Spectra in the range 300–350 nm from copper sample, slightly contaminated with grease, Spectruma GDA150 CCD spectrometer, resolution 0.2 nm. Molecular band emission as a function of the time after initiation of the discharge.

hydrogen intensity; *I*(Href) is a hydrogen reference intensity, conveniently determined using a setting-up reference material.

In addition, recent work has revealed that short-lived molecular band emission may also distort the depth profile in the near-surface region. A CCD spectrometer (Spectruma GDA150) with the spectral range 150–450 nm, resolution 0.2 nm and a readout rate of 10 spectra s^{-1} was used for the experiment. A pure copper sample was first dry linished to a surface finish of 220 grit, then very lightly contaminated with grease on the surface. Spectra were recorded both on clean and contaminated surfaces. Fig. 7 shows spectra in the range 300–350 nm from the contaminated surface at various time intervals after the initiation of the discharge.

From the shape of the observed spectra, the existence of molecular band emission is clearly evident. The band structure has been identified as the 0,0 bandheads of the $A^2\Sigma^+ - X^2\Pi$ system of OH,[43] with the first bandhead at 306.4 nm and the most intense at 309.2 nm. If present in the beginning of the discharge, this molecular emission will cause interfering signals at several analytical lines present in this range, *e.g.*, V 318 nm and Zn 330 nm. Although not shown here, weak band emission was also observed for the clean surface. It is suggested that "unexpected" near-surface peaks of certain elements are in fact due to this type of transient molecular emission in many cases. Although these phenomena remain largely unexplored to date, a mathematical tool in the form of a "dynamic" line interference correction has been developed to deal with this problem.[44] Basically, this correction allows the user to define line interference from, *e.g.*, carbon, with defined rise time and decay time. The underlying assumption is that if carbon forms part of the emitting molecular species, there is a time-dependent connection to the carbon atomic emission. This is illustrated in Fig. 8, where the intensity as a function of time from a C line and the CH 0,0 bandhead[43] are shown. Clearly, there is a strong correlation between the two species, but in the very beginning the molecular band is much more intense on a relative scale. This is assumed to be due to some dynamic process in the beginning of the discharge, which can be modelled by assuming a line interference with a defined rise time and decay time.

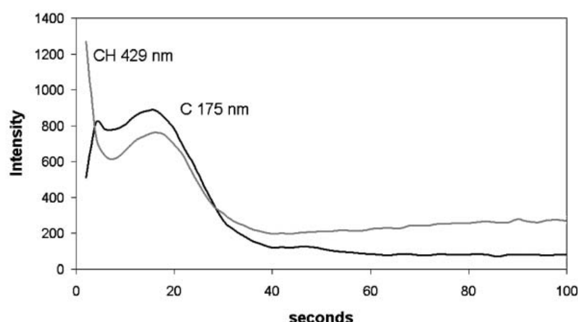


Fig. 8 Intensity of the C 175.2 nm line and the CH 428.6 nm 0,0 bandhead as functions of time.

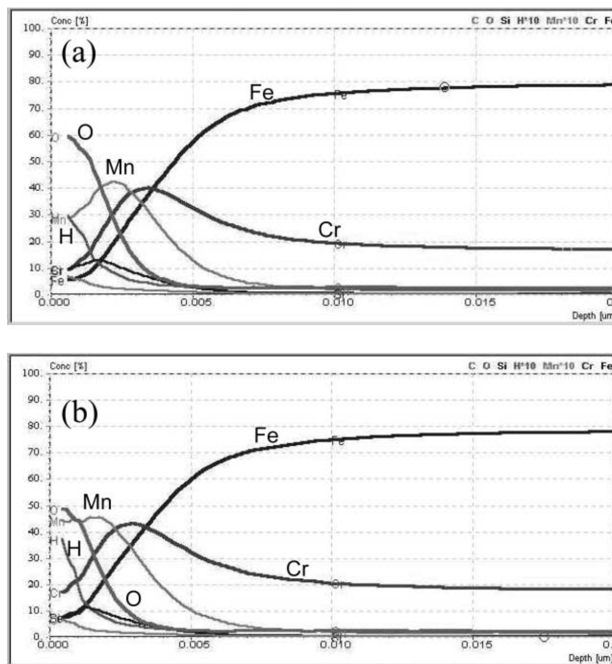


Fig. 9 Quantitative depth profiles of passivation layer on chromium steel: (a) uncorrected, (b) corrected for hydrogen and molecular emission.

Fig. 9 is an example of a quantitative depth profile of a passivation layer on a chromium steel, illustrating the effect of applying "matrix correction" for hydrogen and a "dynamic line interference" for carbon on the oxygen profile. The largest correction is due to the "hydrogen effect"; in this case a small "dynamic" molecular interference correction was additionally implemented to give a "reasonably" accurate oxygen concentration. It has, to date, not been possible to verify experimentally that molecular emission exists at the 130 nm oxygen line.

With the improved source design of modern GD-OES instruments, and the improvements in quantification models, the technology is now ready for "pre-normative research" with the aim of developing new standards for thin film analysis based on GD-OES. The advantages in terms of easy use and high sample throughput over, *e.g.*, SIMS and AES, are expected to make such standard methods very attractive to industrial users.

7. Developments in modelling, particularly related to sputtering and crater profiles

In recent years, a comprehensive modelling network has been developed by Bogaerts *et al.* for analytical glow discharges in dc, rf and microsecond pulsed mode (*e.g.*, refs. 28,45,46). The purpose of this numerical modelling work is to obtain a better understanding of the glow discharge processes, in order to improve the analytical capabilities of glow discharge sources. These advances provide a new tool for future source development. They allow the prediction of the effect of changes in source geometry on, for example, crater profiles, and can therefore be used to investigate whether proposed changes will have the desired effect, avoiding the need for costly production of many prototypes.

The modelling network consists of several sub-models to describe the behaviour of the various plasma species, and it has

Table 2 Overview of the species considered in the modelling network, and the models used to describe their behaviour

Species	Models
Ar gas atoms	Assumed to be thermal + uniformly distributed Or: heat transfer equation (gas heating) Or: computational fluid dynamics (gas flow)
Fast electrons	Monte Carlo model
Thermal electrons	Fluid model
Ar^+ ions	Fluid model
Ar^+ ions in cathode dark space (CDS)	Monte Carlo model
Fast Ar atoms in CDS	Monte Carlo model
Ar atoms in 64 excited levels	Collisional–radiative model
Sputtering of the Cu cathode	Based on empirical formula + flux energy distributions of bombarding species
Thermalization of the sputtered Cu atoms	Monte Carlo model
Cu atoms and Cu^+ ions, both in the ground state and in various excited levels	Collisional–radiative model
Cu^+ ions in CDS	Monte Carlo model

been applied to an argon glow discharge with copper cathode. The species taken into account in the modelling network, and the models used to describe their behaviour, are summarized in Table 2. The models are all coupled to each other due to the interaction processes between the various plasma species, and they are solved iteratively until final convergence is reached. More details about these models and the coupling procedure can be found in refs. 28, 45 and 46 and the references therein. We will only briefly describe the sputtering process and the behaviour of the sputtered atoms, because it is particularly relevant for this paper.

As is shown in Table 2, the sputtering process is described with an empirical formula for the sputtering yield as a function of energy of the bombarding particles,[47] multiplied with the flux energy distributions of the bombarding particles (*i.e.*, Ar^+ ions, fast Ar atoms and Cu^+ ions), which are calculated in the Monte Carlo models. This product gives the flux of sputtered Cu atoms from the cathode. When the atoms are sputtered, they have typical energies in the order of 5–10 eV, which they lose very rapidly by collisions with the Ar gas atoms, until they are thermalized. This thermalization process is described with a Monte Carlo model, and it results in a thermalization profile, *i.e.*, the number of Cu atoms thermalized as a function of distance from the cathode. The product of the flux of sputtered Cu atoms and the Cu atom thermalization profile is used as input in the so-called collisional–radiative model, which describes the behaviour of the thermalized Cu atoms (transport by diffusion, ionization and excitation), as well as of the Cu atoms in various excited levels, and the Cu^+ ions in the ground state and in various excited levels. In the following, a few calculation results will be illustrated to show the possibilities of the modelling for depth profiling and surface analysis. Although the results obtained up to now (and presented here) are not specific for thin film analysis but more in general for surface analysis, the model is of course also applicable to thin film analysis.

Erosion rate

The calculated flux of sputtered Cu atoms can be interpreted in terms of erosion rates, by the following conversion:

$$ER = J_{sput,net}\frac{M}{N_A \rho}$$

where ER is the erosion rate (in cm s^{-1}), $J_{sput,net}$ is the net sputtered flux (in cm^{-2} s^{-1}), M and ρ are the atomic mass (g mol^{-1}) and density of the sample material (ρ_{Cu} = 8.92 g cm^{-3}),[48] and N_A is the Avogadro constant. Note that the net sputtered flux is used here. Indeed, a considerable fraction of the sputtered atoms (order of 50%) is redeposited on the cathode as a result of back-diffusion. Hence, the net sputtered flux is equal to the total sputtered flux minus the flux of redeposited atoms.

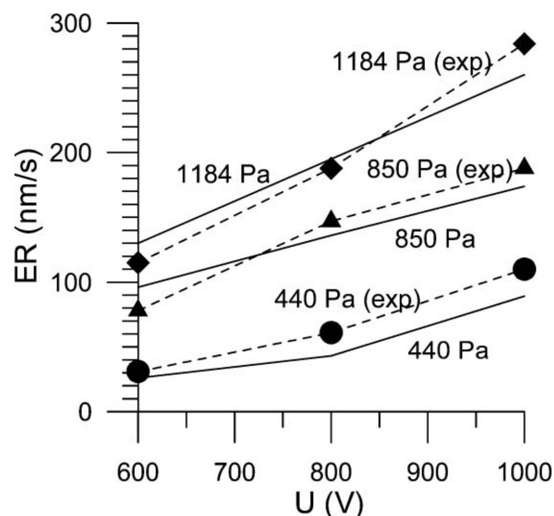


Fig. 10 Calculated (continuous lines) and measured (broken lines + symbols) erosion rates as a function of voltage at three different pressures, for a Grimm-type cell geometry.[49]

Fig. 10 illustrates the calculated erosion rates for a dc Grimm-type glow discharge as a function of voltage at three different pressures (solid lines) in comparison with experimental data (dashed lines + symbols).[49] The agreement between modelling results and experimental data is fairly good, both with respect to the absolute values and to the effect of voltage and pressure.

Crater profile

Based on the calculated flux energy distributions of the bombarding species at the cathode, as a function of radial position, the crater profile as a result of sputtering can be

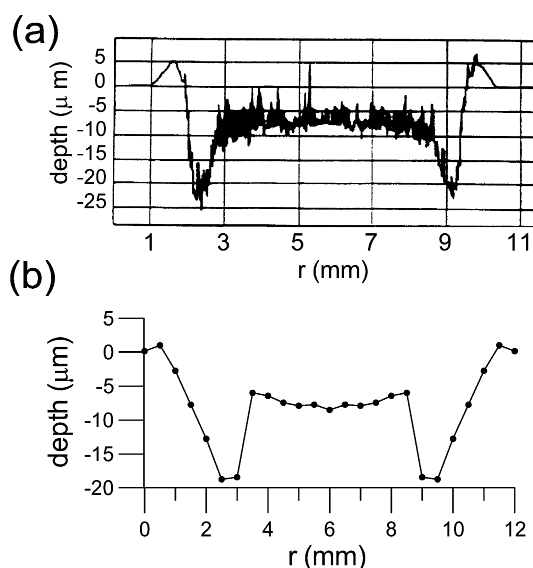


Fig. 11 Examples of modelling technique: (a) measured and (b) calculated crater profiles after 45 min of sputtering in the VG9000 standard glow discharge cell for analyzing flat samples at 1000 V and 3 mA.

predicted with the models, as illustrated in Fig. 11 for the VG9000 glow discharge flat cell.

The reason for the pronounced crater edge effect in this cell can be found in the cell geometry, and the potential distribution in front of the cathode, calculated for this cell geometry.[50–52] Owing to the small distance between cathode and anode front plate, the equipotential lines are not completely parallel to the sample surface, but they are bent in such a way that the plasma species are slightly focussed and bombard the cathode to a larger extent at 0.3–0.4 cm from the cell axis. This results in more sputtering at this radial position, and hence in a much deeper crater at the sides than in the centre, as is illustrated in Fig. 11(a) and 11(b).

Based on modelling results, it can be seen that it is possible to predict how the crater edge effect can be reduced or even eliminated. It appears from the model calculations that changing the discharge conditions (pressure, voltage, current) cannot fully eliminate the crater edge effect of the glow discharge cell,[53] which is in agreement with experimental data. To fully eliminate the crater edge effect, some more fundamental alterations (*e.g.*, in the cell geometry) would have to be carried out. A discussion about these possible alterations can be found in ref. 53.

8. Reference samples for thin film analysis

In general, the requirements for reference standards for depth profiling differ from those for bulk analysis in that there may be two or more major constituents, rather than a major component and many other elements at trace level. With this in mind, a series of zinc standards has recently been specially developed[54] for the analysis of zinc coated steels. For thin layers, the problem is yet more complex. The vast majority of thin layers are electrically non-conductive, due at least to the natural passivation of the most metallic materials, *i.e.*, formation of a very thin (some nm) oxide layer. It is well-known that the GD-OES quantification of non-conductive materials is not yet as reliable as that of conductive materials. The accurate measurement of the rf-GD-electrical parameters, in particular of the discharge current, is difficult, but progress is continuing. Another reason is the lack of certified reference materials (CRM) containing large amounts of light elements such as oxygen, nitrogen and hydrogen needed for the calibration. The calculation/measurement of the density in such cases is a very critical point.

A promising alternative to the conventional bulk CRMs is the use of the so-called *layered CRMs* or *CRCs* (certified reference coatings). Thin layers of well-defined composition and thickness have been produced with steadily increasing accuracy. However, their production and certification is a very costly process. Layered CRMs can be successfully used for GD-OES quantification purposes as check standards. A more realistic evaluation of the depth resolution and its dependence on the depth is possible if multilayer stacks are used. Erosion and sputtering rates can also be determined more accurately. Additionally, layered CRMs help the GDS (-OES and -MS) user to check the condition of the GD system from time to time.

There are many layered CRMs commercially available. However, the individual prerequisites necessary for GDS depth profiling require special properties of layered CRMs. First of all, they must be rigid, due to the mechanical stress exercised on the sample as part of the GD source. The surface must be flat and smooth, so that, respectively, the necessary vacuum can be reached and the attained depth resolution partly improved. In order to make possible several GDS "shots" on the same sample, layered CRMs must provide at least several square cm of analysable surface. The concentration of light elements (in particular) and the thickness must be laterally homogeneous and stable over long periods of time as well. In view of the high temperature developed locally in the near surface region during the sputtering, the CRMs (mainly concentration of light elements) must be thermally stable. An appropriate preparation of the substrate surface guarantees, especially for metallic substrates, not only a minimal roughness, but a good adhesion of the coating on the substrate as well. More useful details on optimised depth profiling procedures of the layered materials by GD-OES and comparisons with other competitive analytical techniques can be found in refs. 55 and 56, respectively.

The restrictions enumerated above recently forced the GDS Subcommittee ISO TC201/SC8 associated with the ISO TC201 on Surface Chemical Analysis to perform a survey on the world-wide availability of layered CRMs for GDS depth profiling. The result was that no layered CRMs were found which fulfil the requirements described above.[57] BAM has therefore taken the initiative of producing and evaluating some suitable layered CRMs, especially intensively after 1998 in the frame of a project of the Surface Chemical Analysis Technical Working Area TWA2 of the Versailles Project on Advanced Materials and Standards (VAMAS).[58–60]

For various technological and industrial reasons, the following stacks of thin layers have been selected as potential layered CRMs.

(i) *5 × (250 nm Al/100 nm Ti)/100Cr6 steel* and *5 × (100 nm* SiO_2*/100 nm* TiO_2*)/BK7 glass.*

The Al–Ti multilayers were prepared at BAM by dc-sputtering. Typical precautions have been taken into account, *e.g.*, keeping the temperature during deposition below a critical threshold which prevents the formation of intermetallic phases.

The SiO_2–TiO_2 non-conductive multilayer stack was prepared at Schott Glas, Mainz, Germany, by ion-assisted reactive electron beam evaporation.

Both layer stacks are already included in the BAM Catalogue 2002 *Certified Reference Materials*[61] as "under development". Their completion date will be in 2003.

(ii) *Thick (3 μm) coatings* such as *TiN* and *VN* produced by PVD at BAM.

These have been tested in a round-robin exercise, organised in the frame of the EC Thematic Network on Glow Discharge Spectroscopy for Spectrochemical Analysis, Working Group A. (For a preliminary report, see the EC GDS Network website.[7]) Nitrides and carbides are absolutely necessary for the GDS calibration of nitrogen and carbon in higher concentrations. These are not thin layers, but meet almost the same requirements as those for thin layers and can, of course, be used as reference materials for the analysis of thin layers. TiN and VN thick layers together with TiC and VC ones are also in the final phase of preparation at BAM and will be commercially available in 2003.[61]

(iii) *Thin multilayer metallic stacks of (100 nm CrNi/100 nm Cu)* deposited on conductive silicon wafers by PVD at IFW-Dresden.

These were also included to the round-robin mentioned above. The use of such materials has been proved to be helpful in further development of GDS instrumentation and methodology, *e.g.*, comparison of dc–rf excitation[18] or even for the testing of pulsed GD-OES by V. Hoffmann.

With respect to the characterisation of the layers produced, non-destructive techniques such as grazing incidence X-ray diffraction (GI-XRD) for the Al–Ti multilayers, and spectroscopic ellipsometry for the transparent non-conductive layers, have been applied in order to estimate layer thickness and composition.[35] Other destructive techniques, such as (i) scanning electron microscopy (SEM) and transmission electron microscopy (TEM) on cross-sectioned witness samples and (ii) ball grinding, have been also used in order to determine the coating thickness.[35]

Rutherford backscattering spectroscopy (RBS) was found to be an appropriate technique for the analysis of composition and thickness of the nitride and carbide layers. Nuclear

reaction analysis (NRA)[62] is already established as successful as a standard method for the determination of quantitative depth profiles, in particular of hydrogen, in thin and very thin layers.[63]

The GD-OES quantification concept requires the knowledge of the density of the reference coatings, so that the erosion rates can be converted to sputter rates. However, contrary to the bulk CRMs, where the accurate determination of the density is rather trivial, the determination/certification of the density of CRCs remains a critical point. Efforts from both analysts and sample producers are expected, so that the CRC certificate contains the certified density as well as the element concentrations and thickness.

Summing up, one can remark that there are numerous problems with the production and certification of layered CRMs. Nevertheless, their recent developments can be considered promising, thus offering to the GDS user new possibilities of reaching more accurate results in thin film analysis.

9. Conclusions

GD-OES for depth profile analysis has become an established analytical technique for a wide range of applications, primarily metallic coatings on steels but also some further specific applications. This fact is evidenced by the extensive work on international standardisation currently in progress dealing with GD-OES depth-profiling of zinc-based coatings on steel.

In addition, GD-OES is still a rapidly developing technique, particularly in the fields of rf discharges for non-conductive materials and near-surface analysis of very thin layers.

In recent years work on the task of thin film and near-surface analysis has been very successful, providing continually expanding knowledge of practical applications and improving measurement techniques. For thin film applications, it is demonstrated that state-of-the-art GD-OES systems are capable of a depth resolution similar to SIMS and AES. These encouraging experiences lead to further activities in fundamental research work. Major research efforts are aimed at improving the quantification methods for such applications. For the quantification of very thin layers, the hydrogen correction must be considered. In addition, it is shown that short-lived molecular emission can influence the analytical results. Work in modelling is in progress and ready to be applied on GD-OES data. Erosion rates and crater shapes are calculated by models, which will lead to improvements in depth resolution and in lamp design. The development of the first thin-film certified reference materials has also been successful and will help to improve the fundamental understanding and modelling activities. The report shows also that there are some requirements to improve GD sources for the task of thin film analysis.

Summarising, it can be stated that thin film analysis with GD-OES is continually in progress but the demand for further development activities is clearly evident.

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