UNIVERSIDAD DE OVIEDO

Departamento de Química Física y Analítica

NEW APPLICATIONS OF CONTINUOUS AND PULSED RADIOFREQUENCY GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY FOR THE ANALYSIS OF ADVANCED MATERIALS

TESIS DOCTORAL

Deborah Alberts

Enero 2011

No one who achieves success does so without the help of others. The wise and confident acknowledge this help with gratitude.

Alfred North Whitehead

Al concluir el presente trabajo, me gustaría agradecer la colaboración de todas aquellas personas, que, de alguna manera, han contribuido y animado a la realización del mismo.

Al Profesor Alfredo Sanz-Medel, Catedrático de Química Analítica de la Universidad de Oviedo, por brindarme la oportunidad de formar parte de su grupo de investigación, siendo esta experiencia de gran ayuda en mi formación.

A la Doctora Rosario Pereiro, Profesora Titular del Departamento de Química Física y Analítica de la Universidad de Oviedo, por ofrecerme la posibilidad de trabajar en el mundo de la glow y por el apoyo que me ha dado pero sobre todo por su paciencia conmigo, día a día.

A la Doctora Nerea Bordel, Profesora Titular del Departamento de Física de la Universidad de Oviedo, por el ayudo en momentos de dudas en la busceda del pre-peak y por la tranquilidad durante sus explicaciones.

To Doctor Johann Michler, Doctor James Withby and Max Aeberhard from 'Swiss Federal Laboratories for Materials Testing and Research' (EMPA) at Thun (Switzerland), for making my stay abroad an interesting and challenging experience. Especially I would like to thank Doctor Peter Horvath for all his help and patience he put forward during our collaboration.

To Professor Philippe Guillot and Doctor Laurent Thérèse from CUFR J. F. Champollion at Albi (France), to welcome me in their laboratory and to offer me help when necessary at any time, even long after leaving and for the nice moments during the Plasma Winter Conference in Florida. Also, I would like to thank Doctor Thomas Nelis for all the discussions about plasmas and pre-peaks.

To Doctor Arne Bengtson from the Corrosion and Metals Research Institute SWEREA KIMAB AB at Stockholm (Sweden) for his hospitality, his spontaneity, his humor and for sharing his knowledge about GD and optical emission and so many more things. Also, thanks to Simone Weyler and Mats Randelius for making my stay in Stockholm wonderful and pleasant, as well as day-to-day life in the laboratory.

To the European Community for the financial support through the Marie Curie Research Training Network (MRTN-CT-2006-035459).

A mis compañeros de laboratorio (de los DOS grupos de investigación) por los buenos momentos vividos juntos, tanto en el día en día como en las cenas, las comidas, las reuniones, los congresos etc.

Cuando uno se marcha de su país y de todo lo que conoce para empezar una nueva aventura fuera de casa, solo puede soñar con encontrar unas personas que le alegran la vida, que le acojan en sus vidas y que le ofrezcan su amistad. Yo tuve mucha suerte y encontré más de una. Primera llegó Emma, quien dejó claro que para ser su amiga había que hablar bien el español, y así fue. Después conocí a Jose Angel, quien fue mi supervisor de tesina, mi Angel de la guarda, pero sobre todo mi mejor amigo. Y a Héctor, mi payaso favorito aunque en el fondo muy sincero y buen amigo. Al empezar la etapa "glow" conocí a Lara, dulce Lara, siempre ahí, escuchando y lista para ayudar; también a Cristina, siempre sincera y con una gran paciencia, sobre todo cuando yo ya no la tenía (o nunca la tuve). Con Cris, vino Chus, dos personas muy grandes, que me enseñaron Asturias, Fitoria, l'asturianu y mucho más. Y a Ana, Adriana, Estela, Bea y Pablo, Juan y Jaime por las risas, por las lagrimas que derramamos juntos, por los momentos duros, por los buenos momentos, por las broncas y por los reencuentros, por los comentarios (aunque no siempre aceptados, pero con las mejores intenciones), por las bromas, por los silencios... Por lo vivido a vuestro lado, ¡Gracias!

Als laatste wil ik graag mijn mamy en papy (en Brigitte) bedanken voor er altijd te zijn met een luisterend oor en goede raad voor al die momenten van frustratie, voor al de kansen die ik gekregen heb en voor de onvoorwaardelijke steun en vertrouwen. Ook wil ik twee belangrijke personen herinneren, die het begin hebben gekend van dit avontuur, maar het einde spijtig genoeg van verder meemaken; bomma en bompa, ik mis jullie.

Voor mamy, papy,
bomma en bompa

The beginning of wisdom is found in doubting; by doubting we come to the question, and by seeking we may come upon the truth.

Pierre Abelard

Summary

Due to the continuous development of new materials arising from surface treatment and nanotechnology, an increasing demand of fast, reliable and low cost characterisation techniques exist, in order to correlate the different properties of materials to their composition and component distribution. Moreover, such techniques are indispensable during the optimisation steps of their synthesis procedures and the quality control of the final products to guarantee their optimal performance. Many of these materials are, partially or as a whole, non-conductive and/or fragile, which complicates their analysis. In this context, radiofrequency glow discharges (rf-GDs) coupled to optical emission spectrometry (OES) offer a most promising analytical potential.

Rf-GD-OES in pulsed operation mode offers advantages compared to its steady-state counterpart, but pulsed rf-GD studies are still scarce in spite of their demonstrated interest. Thus, the analytical performance of rf-GD-OES, used in continuous and pulsed operation mode, has been investigated in this Ph.D. Thesis for the direct solids analysis of advanced materials. This Ph.D. has been carried out in the frame of **Marie Curie Actions for Human Resources and Mobility Activity of the 6th Framework: RTN "Analytical Glow Discharge Network (GLADNET)"** which is a consortium of 16 partners working in the field of GD.

In this general line, different partial objectives have been addressed:

In the first chapter of this work, radiofrequency pulsed glow discharges have been studied, in view of their potential use with optical emission spectrometry, through time-resolved measurements of pulsed emission profiles for a wide range of copper transitions. The characteristic pre-peak signal observed has been related to a lack of self-absorption at the beginning of the pulse. The influence of analyte concentration, discharge and pulse parameters upon the pre-peak behaviour has been evaluated.

In the second chapter, the effect of thin coatings on non-conductors and/or the addition of a magnetic field to the set-up have been studied in order to improve

the analytical performance of rf-GD-OES for the analysis of non-conducting samples. Moreover, a critical comparison of the analytical performance of rf-GD-OES, in continuous and pulsed operation mode, has been carried out for conductive and insulating samples, coated and non-coated, in terms of emission intensities, sputtering rates, emission yields and their potential for depth profiling analysis.

In the last chapter, the potential of rf-GD-OES, in continuous and pulsed operation modes, has been finally investigated for the qualitative and quantitative depth profile direct analysis of nanostructured oxides, particularly alumina nanopores and titania nanotubes, containing conductive nanowires of different elements, as well as nanocomposite coatings doped with TiO_2, deposited either upon titanium or steel substrates.

Resumen

Debido al continuo desarrollo de nuevos materiales, mejorados mediante tratamientos superficiales y empleo de nanotecnología, existe una creciente demanda de técnicas de caracterización rápidas, fiables y de bajo coste, que permitan correlacionar las propiedades del material sólido con su composición y distribución de sus constituyentes de forma directa. Además, este tipo de técnicas resultan indispensables para garantizar un rendimiento óptimo de las etapas de síntesis y en el control de calidad del producto final. En general, estos materiales suelen ser, parcialmente o en su totalidad, no-conductores y/o frágiles, lo que complica su análisis. En este contexto, hoy las descargas luminiscente de radiofrecuencia acopladas a la espectrometría de emisión óptica (rf-GD-OES) constituyen una técnica altamente prometedora para el análisis de este tipo de nuevos materiales.

Aunque está demostrado que la rf-GD-OES en modo pulsado presenta ciertas ventajas frente al modo continuo, los estudios de la rf-GD pulsada son todavía escasos. Por esta razón, en este trabajo de tesis se ha estudiado el potencial analítico de la rf-GD-OES, operada tanto en modo continuo como pulsado, para el análisis directo de materiales avanzados. Dicha Tesis Doctoral se ha llevado a cabo en el marco de las **Marie Curie Actions for Human Resources and Mobility Activity of the 6th Framework: RTN "Analytical Glow Discharge Network (GLADNET)"**, constituido por 16 grupos de investigación que trabajan en el área de las GDs.

En este contexto general, se han abordado los siguientes objetivos parciales:

En el primer capítulo de esta Tesis Doctoral, se ha estudiado la descarga luminiscente pulsada mediante medidas con resolución temporal de perfiles de emisión para un amplio rango de transiciones de cobre. En particular, a partir de estas medidas se ha relacionado la existencia de la señal característica del "pre-peak" con la ausencia de auto-absorción al principio del pulso. Por otro lado, también se ha evaluado la influencia que ejercen la concentración del analito, los parámetros de descarga y las características del pulso sobre el comportamiento de dicho "pre-peak".

En el segundo capítulo, con objeto de mejorar el rendimiento analítico de la rf-GD-OES en el análisis de materiales no-conductores, se ha estudiado el efecto que ejercen la deposición de capas delgadas sobre muestras no-conductoras y/o la presencia de un campo magnético. Además, se ha llevado a cabo una comparación crítica del potencial analítico de dicha técnica, operando tanto en modo continuo como pulsado, para materiales conductores y no-conductores, con y sin capa delgada, en términos de intensidades de emisión, velocidades de arrancado, eficiencias de emisión y ,particularmente, para su aplicabilidad real en el análisis directo de perfiles en profundidad.

En el último capítulo, se ha investigado finalmente el potencial de la rf-GD-OES, tanto continua como pulsada, para el análisis cualitativo y cuantitativo del perfil en profundidad de óxidos nanoestructurados (nanoporos de alúmina y nanotubos de titania rellenos de distintos elementos conductores) y capas nanocomposite dopadas con TiO_2, depositadas tanto sobre sustratos de titanio como de acero.

INDEX

A. RESEARCH OBJECTIVES/OBJETIVOS 1

B. INTRODUCTION 11

B.1. Solid Materials Science 13
B.1.1. Classification of new materials 13
B.1.2. Direct Solids Elemental Analysis 19
B.1.3. Current techniques for the analysis of solid material 20
B.1.4. Comparison of depth and lateral information obtained with different techniques 31

B.2. Glow Discharge in Analytical Chemistry 32
B.2.1. Discharge chamber configuration 33
B.2.2. Fundamental processes and the plasma discharge 35
B.2.3. Generation modes of Glow Discharges 38
B.2.4. Glow Discharge coupled to Optical Emission Spectrometry 45
B.2.5. Analytical characteristics of GD 49

B.3. Glow Discharge for Direct Solids Analysis 52
B.3.1. Bulk analysis 52
B.3.2. Thin film analysis 54

B.4. Glow Discharge Applications 59
B.4.1. Bulk analysis 59
B.4.2. Thin film analysis 61

B.5. References 63

C. EXPERIMENTAL 71

C.1. Rf-GD-OES Instrumentation 73
C.1.1. JY 5000 RF 73
C.1.2. LECO GDS 750 Grimm type 76

C.2. Additional Instrumentation 78

D. RESULTS AND DISCUSSION 81

D.I. Time-resolved measurements of emission profiles in pulsed rf-GD-OES: investigation of the pre-peak 83

D.I.1. Introduction 87
D.I.2. Objectives 90
D.I.3. Results 91
D.I.4. Discussion of the Results 99
D.I.5. References 102

D.II. Investigation of continuous and pulsed rf-GD-OES for the depth profile analysis of coated materials 105

D.II.1. Introduction 109
D.II.2. Objectives 111
D.II.3. Results 113
D.II.4. Discussion of the Results 130
D.II.5. References 135

D.III. Development of new applications of continuous and pulsed rf-GD-OES for the direct analysis of nanostructured and nanocomposite materials 137

D.III.1. Introduction 141
D.III.2. Objectives 143
D.III.3. Results 144
D.III.4. Discussion of the Results 171
D.III.5. References 175

E. CONCLUSIONS/CONCLUSIONES 177

F. SUGGESTIONS FOR FUTURE RESEARCH 185

G. PUBLICATIONS 189

RESEARCH OBJECTIVES/OBJETIVOS

The field of glow discharges (GDs) for direct solids analysis of a wide variety of materials is undergoing a continuous expansion, because of their inherent advantages compared to alternative elemental techniques, which usually require dissolution steps, previous to the final analysis. Due to the demonstrated benefits, including its reliability, fast analysis and few matrix effects, GDs coupled to optical emission (OES) and mass spectrometry (MS) are considered as well-established approaches for the direct determination of major, minor and trace elements and for the depth profiling analysis of solids, with depth resolutions down to a few nanometers. This depth analysis capability is of great importance for the development and characterization of modern coated materials.

Up to date, direct current (dc) GDs have been widely used, due to their simplicity and the well-controlled relation between the various working parameters. Nevertheless, direct analysis using dc-GDs is only possible for conducting samples, a fact that severely limits its application field. Therefore, radiofrequency (rf) GDs are gaining increasing interest as they allow the direct solids analysis of conductive, semi-conductive and insulating samples. However, important limitations still exist regarding thermal-sensitive and fragile samples. These shortcomings can be overcome when operating the GD in pulsed mode (*i.e.* applying a square wave power pulse followed by power termination), offering an additional way of controlling the plasma while relieving thermal stress upon the samples. Moreover, quasi-simultaneous structural, molecular and elemental information can be obtained when using time-gated detection. Although this operation mode is highly promising, basic studies and applications of pulsed rf-GDs are still scarce.

In this context, the main objective of this work, carried out within **the Marie Curie Actions for Human Resources and Mobility Activity of the 6th framework: RTN "Analytical Glow Discharge Network (GLADNET)"** is the further investigation of continuous and pulsed radiofrequency glow discharges coupled to optical emission spectrometry and their application for the analysis of advanced materials.

This general aim has been pursued through the specific following objectives:

I. Time-resolved measurements of emission profiles in pulsed radiofrequency glow discharge coupled to optical emission spectrometry: investigation of the pre-peak.

Pulsed glow discharges (PGDs) are created when applying periodically a high power pulse lasting some milli- or microseconds. During each pulse an atom and ion packet is generated which will diffuse along the discharge chamber. PGDs can offer important analytical advantages, compared to their steady-state counterpart, such as less thermal stress, alleviated plasma instabilities and improved depth resolution for thin film analysis.

A main advantage is the creation of time regimes during which the analyte signal is enhanced and different information can be obtained, in case time-gated detection is used. Unfortunately, information on the excitation and ionisation processes taking place in PGDs is still scarce, even if this knowledge is crucial for their effective analytical use. Therefore, time-resolved measurements of pulsed emission profiles by rf-GD-OES will be carried out, using a wide range of copper transitions as model. The influence of both the discharge (pressure and forward power) and pulse parameters (pulse frequency, duty cycle and pulse length) on the pre-peak behaviour, observed at the beginning of the rf pulse, will be studied and related to the phenomenon of self-absorption taking place in the discharge chamber. The results will provide important information on how to exploit analytically the pre-peak signals to obtain enhanced emission, more linear calibration curves for strongly self-absorbed emission lines (even at high analyte concentrations) and time-gated detection novel applications.

II. Investigation of continuous and pulsed radiofrequency glow discharge coupled to optical emission spectrometry for depth profile analysis of coated materials.

Commonly, glow discharges are generated by dc or rf operated in continuous mode. These discharge types are easy to generate and have been successfully applied in a great number of applications for the direct solids analysis during the last decades. However, in the case of the direct analysis of insulators, limitations still exist related to the low power deposited into the plasma, leading to analytical difficulties, due to a voltage drop developed across the material. It has been demonstrated that the deposition of thin top conductive layers have a

positive influence on the electrical discharge parameters, a fact that should be taken in account in the development of quantification methods.

The increasing demand to carry out the analysis of non-conductive and semi-conducting thin layered materials is forcing the development of new operation strategies. In this vein, the potential of rf-PGDs is being investigated because of the various advantages this mode offers, as compared to the continuous operation mode (pointed out above). Therefore, a critical comparison will be carried out for rf-GD-OES, operating both in continuous and pulsed mode, for the analysis of conducting and insulating samples in terms of emission intensities, sputtering rates, emission yields and crater shapes. Moreover, the potential for depth profiling analysis will be tested through the measurement of conducting and insulating substrates with nanometer-thick coatings. Also, a detailed study will be carried out to determine the influence of thin coatings on a range of insulators with varying dimensions through electrical and optical measurements, demonstrating their potential to obtain more power deposited into the plasma and enhanced emission intensities, in order to overcome the analytical difficulties related to this type of analysis.

III. Development of new applications of continuous and pulsed radiofrequency glow discharge coupled to optical emission spectrometry for the direct analysis of nanostructured materials and nanocomposites.

The development of rf-GDs allowed the extension of the “conventional” glow discharge application field, as the dc-GDs are limited to the direct solids analysis of conductive samples. This development is boosted by the increasing demand for quality control of new materials, e.g. those obtained through miniaturisation and nanotechnology (important properties of such nanostructured materials depend on both their chemical composition and structure). The need of reliable characterisation techniques is indispensable during the optimisation steps of the synthesis procedures to guarantee optimal performance of the final product.

Therefore in this Thesis, rf-GD-OES will be investigated, both in continuous and pulsed operation mode, for its application to advanced materials, such as nanostructured aluminium and titanium oxides filled with metallic nanowires, as well as metal-based titania nanocomposite films, deposited both on titanium or steel substrates.

El campo de aplicación de las descargas luminiscentes (Glow Discharges, GDs) para el análisis directo de sólidos ha experimentado un crecimiento continuado en los últimos años gracias a las enormes ventajas que presentan frente a las técnicas en las que es necesaria la puesta en disolución previa de las muestras. Debido a sus prestaciones, entre las que se incluyen su fiabilidad, rapidez en los análisis y bajos efectos de matriz, la GD con detección por espectrometría de emisión óptica (OES) o espectrometría de masas (MS) se considera actualmente una técnica bien establecida para la determinación directa de los elementos mayoritarios, minoritarios y traza y para el análisis fiable de perfiles de concentración en profundidad, alcanzando resoluciones de unos pocos nanómetros. La obtención de estos perfiles en profundidad es importante a la hora de llevar a cabo un control de calidad, hoy imprescindible en la fabricación de materiales recubiertos.

Hasta la fecha, las GDs de corriente continua (dc) son las más empleadas, debido a su sencillez y a las relaciones bien conocida entre los diversos parámetros de funcionamiento de la misma y sus prestaciones. Sin embargo, la dc-GD únicamente permite el análisis de muestras conductoras, lo que limita bastante su campo de aplicación. Por eso, el gran atractivo de las GDs generadas por radiofrecuencia (rf) es, que además de poder ser utilizadas con muestras conductoras, permiten el análisis directo de semiconductores y no-conductores. No obstante, todavía existen importantes limitaciones en cuanto al análisis de muestras termo-sensibles y frágiles. Estas limitaciones se pueden superar mediante el uso de la GD en modo de operación pulsado, que ofrece una posibilidad adicional para controlar el plasma y disminuye los problemas derivados de efectos térmicos inducidos sobre la muestra. Además, cuando se emplea un sistema de detección con resolución temporal se puede obtener información estructural, molecular y elemental de manera casi simultánea. A pesar de que este modo de operación es muy prometedor, los estudios sobre rf-GD pulsada son todavía escasos.

Por todo ello, el objetivo fundamental de la presente Tesis Doctoral, que se llevó a cabo dentro de **"Marie Curie Actions for Human Resources and Mobility Activity of the 6th framework: RTN Analytical Glow Discharge Network (GLADNET)"** es la investigación a fondo de la descarga luminiscente de radiofrecuencia, comparando el modo continuo con el pulsado, acoplada a espectrometría de emisión óptica, así como su aplicación final para el análisis de materiales avanzados.

El objetivo general se concretará en los siguientes objetivos específicos:

I. Medidas de perfiles de emisión con resolución temporal en una descarga luminiscente de radiofrecuencia en modo pulsado con detección por espectrometría de emisión óptica: investigación de la señal del "pre-peak".

Las GDs pulsadas (PGDs) se crean aplicando periódicamente un pulso de potencia eléctrica elevada, con una duración típica de mili o microsegundos. En cada pulso eléctrico se genera un paquete de átomos e iones de la muestra que se expande y difunde a lo largo de la cámara. Estas PGDs pueden ofrecer importantes ventajas analíticas sobre las que operan en modo continuo: por ejemplo, menos problemas derivados de efectos térmicos inducidos sobre la muestra, mejor estabilidad del plasma y mayor resolución en profundidad para el análisis de capas delgadas.

Otras de las ventajas importantes es la presencia de regiones temporales que permiten discriminar las señales analíticas, ventaja que se puede explotar para el análisis utilizando una detección con resolución temporal. A pesar de estas ventajes, la información sobre los procesos de excitación e ionización que ocurren en el plasma de las PGDs, aunque es crucial para su uso efectivo en análisis, es escasa. En este contexto, y con objeto de obtener un mayor conocimiento de los procesos de excitación en el plasma, este primer objetivo profundizará en medidas de los perfiles de emisión obtenidos en rf-PGD para una gran variedad de transiciones de cobre. Se investigará la influencia de parámetros como la potencia y la presión aplicada, la duración o anchura del pulso, la frecuencia del pulso y el factor de ocupación ("duty cycle") sobre el pico que se observa al principio de la descarga rf pulsada ("pre-peak"). Los resultados pueden hacer posible la explotación analítica del "pre-peak" (*p.e.* para obtener intensidades de emisión mas elevadas y para aumentar la linealidad en calibraciones utilizando resolución temporal).

II. Investigación de la descarga luminiscente de radiofrecuencia, tanto en modo continuo como pulsado, acoplada a espectrometría de emisión óptica, para el análisis directo de materiales con capas delgadas.

Comúnmente, las GDs se generan con dc o con rf en modo continuo. Este tipo de descargas son sencillas de generar y han sido aplicadas con éxito en un gran

número de aplicaciones para la caracterización directa de sólidos durante la última década, aunque para el análisis de no conductores todavía existen limitaciones relacionadas con la baja potencia acoplada al plasma. Este hecho da lugar a dificultades analíticas debidas a una caída de voltaje en el material. Estudios previos han demostrado que esta caída se minimiza mediante la deposición de capas delgadas conductoras debido a su influencia sobre los parámetros eléctricos de la descarga, un factor a tener en cuenta en la cuantificación. Debido a las ventajas comentadas antes de las rf-PGDs y a la creciente demanda de análisis de materiales complejos que está promoviendo el desarrollo de nuevas estrategias de operación, actualmente se ha iniciado la investigación del potencial de las rf-PGDs para dicho propósito.

Así pues, en esta Tesis, se llevará a cabo una comparación crítica entre las rf-GDs, operando en modo continuo y pulsado, para el análisis de muestras conductoras y no conductoras, en términos de intensidad de las señales, velocidades de arrancado, forma de los cráteres, límites de detección, etc. Además, se evaluará el potencial de la técnica para el análisis de perfiles en profundidad, investigando muestras recubiertos con capas de espesores que van desde las micras hasta los nanómetros, así como con capas térmicamente inestables. Asimismo, se llevará a cabo un estudio para determinar la influencia de capas delgadas depositadas sobre muestras no conductoras, de diferentes dimensiones, mediante medidas eléctricas y ópticas. La evaluación de su potencial para un acoplamiento mas eficaz de la potencia aplicada y obtener intensidades de emisión mayores (mayor sensibilidad analítica) es una de las metas del estudio.

III. Desarollo de nuevas aplicaciones de la descarga luminiscente de radiofrecuencia (tanto en modo continuo como pulsado), con detección por espectrometría de emisión óptica, para análisis directo de materiales nanoestructurados y nanocomposites.

El desarrollo de las rf-GDs ha permitido extender el campo de aplicación de las GDs al análisis directo de materiales semiconductores y aislantes, ya que las dc-GDs “tradicionales” sólo permiten el análisis directo de materiales conductores. Este desarrollo está siendo impulsado particularmente por la creciente demanda en el campo del control de calidad de los nuevos materiales que se están sintetizando y produciendo (*p.e.* los nanomateriales que se obtienen mediante

nanotecnología). Durante las etapas de optimización del proceso de síntesis de los mismos resulta imprescindible disponer de técnicas analíticos y de caracterización fiables que garanticen las propiedades del producto final.

Así pues, en este último objetivo de la Tesis abordaremos en profundidad la evaluación de rf-GD-OES, en modo continuo y pulsado, como técnica de análisis directo de sólidos, utilizando materiales nanoestructurados de óxido de aluminio y óxido de titanio rellenos con nanohilos metálicos, así como películas de nanocomposites de óxido de titanio sobre sustratos de titanio o acero.

INTRODUCTION

B.1. Solid Materials Science

The term "Materials Science" emerged in the USA in the early 1950s, denoting a new scientific concept, born out of metallurgy. It can be defined as "*an interdisciplinary field involving the properties of matter and its applications to various area of science and engineering. This scientific field investigates the relationship between the structure of materials at atomic or molecular scale and their macroscopic properties, and deals with fundamental properties and characteristics of materials*". The base of Materials Science involves relating the desired properties and relative performance of a material in a certain application to the structure of the atoms and phases in that material through its characterisation.

At present, radical advances in materials are driving towards new products or even new industries. However, materials science is still indispensable in established industries to secure continuous improvements or to troubleshoot problems still arising with currently used not-so-novel materials. Industrial applications of Materials Science include material design, cost benefit trade-offs in industrial production of materials, processing techniques, etc. Materials Science is of great importance today and in a tremendous array of fields expanding from construction, transport, renewable energies, electronic and telecommunication industry, up to spatial and package industry and the food sector. In order to achieve new advances in this field, it is indispensible to know the internal structure and the properties of the materials employed, so the most adequate one can be selected for each application. All these aspects explain the fact that today we find ourselves in the so-called "New Materials" era, in which new basic concepts should be studied and understood.[1]

B.1.1. Classification of new materials

The different known materials are usually classified into 5 main groups in function of their chemical composition and atomic structure: metals, ceramics/glasses, polymers, semi-conductors and composite materials. It is easy to understand that the improvement of our life quality, bound to such emerging technologies, implies the development of new materials. Actually, and due to the continuous and ceaseless progress in this field, new classifications grouping known materials are emerging. Among them, we would like to highlight the following ones:

○ **Biomaterials.-** This group includes any element designed to be implemented or incorporated inside a living being. The spectacular advance occurring in this field is explained by the possibility to increase both our life quality and expectation, through its application in the biomedical field.

○ **Catalysis materials.-** The appearance of new materials for catalysis has induced the continuous creation of innovating chemical and physical processes (as well as many improvements for already existing processes).

○ **Magnetic materials.-** Both natural and synthetic materials exist able to create magnetic fields, being of technological interest due to a wide range of their applications. Of course, such valuable magnetic characteristics can be altered, or even created, via the development of new materials.

○ **Nanomaterials.-** Such materials exhibit their special characteristics just due to their nanometric size. This discovery has given rise to a new scientific and technological branch focussed and based on their investigation and development, the so-called today "Nanoscience and Nanotechnology". Nanotechnology is directly related to the creation and improvement of useful materials, devices and systems through their control at nanometric scale. The importance of this field is based on the radical change of the sample properties, both physical and chemical, that some materials undergo with dimensions of less than 100 nm. The enormous importance of the exploitation of these new properties and phenomena, emerging out of this nanometric scale, cannot be overemphasized.

○ **Thin coated materials.-** It has been demonstrated that the presence of thin coatings deposited upon base materials can produce important modifications of the material surface. In this way, the solid substrate provides some basic characteristics (mechanical support) or more specific ones (mechanical resistance, magnetic polarisation, etc.) while the coating, or thin film, provides alternative useful properties. Thus, through this combination of substrate plus thin film superior characteristics (in comparison to these of the own substrate) can be obtained.

As mentioned previously, the improvement of our life quality, and the bound development of new technologies, imply the investigation of new materials. The introduction of such new materials in industry is straightforward in the search of valuable products with improved characteristics and quality, and of materials able to replace common strategic materials (such as petroleum or carbon). Other key factor for the development and maintenance of important industry is the elimination of toxic residues and also material recycling. Both environmental requirements are giving rise to the quest for alternative materials which do not generate residuals (besides the possibility of obtaining also new materials out of recycling). Taking in account all those facts, it can be understood that Materials Science is both scientifically as technologically challenged, as the demand for materials more and more sophisticated and specialised, providing higher benefits, with a versatility for a high number of applications is continuously pressing. We will concentrate here on thin coated materials and nanostructured materials.

B.1.1.1. Coatings and thin films

Thin films are deposited onto bulk materials (substrates) to achieve properties unattainable or not easily attainable in the substrates alone, so that such new materials can be employed in new applications. Table 1 shows a possible classification of the properties into five basic categories providing illustrative examples of typical applications within each category. This Table shows clearly that the range of thin film applications is very broad indeed. Often, multiple properties are obtained simultaneously; for example, through the deposition of Cr coatings on plastic parts for automobiles, improved material hardness can be obtained, together with metallic luster and protection against ultraviolet light. This Cr coating achieves the functionality of the same automobile part made from bulk material, but at significant savings in cost and weight.

Additional functionality in thin films can be achieved through the deposition of multiple layers of various materials. Optical interference films, for example, consist of tens, or even hundreds, of layers alternating between high and low indexes of refraction. When such alternating layers consist of nanometer thick semi-conducting materials (*e.g.* as GaAs and (AlGa)As), the result is a “superlattice” that has electrical properties governed by the nanoconstructed periodicity rather than by the atomic periodicity. Thus, multi-layer thin films can behave as completely new, engineered materials with

properties unknown in their bulk form. When this multiple layering is combined with lithographic patterning in the plane of the films, microstructures of endless variety can be constructed in this way. This is the basic technology of the integrated-circuit industry, the optical waveguide circuitry and micromechanical devices, used today for a huge variety of applications.

Table 1. Thin film applications.[2,3]

Thin Film Property	Applications
Optical	Reflective/anti-reflective coatings Interference filters Decoration Compact Discs Waveguides
Electrical	Insulation coatings Conduction coatings Semi-conductor devices Piezo-electric drivers
Magnetic	Memory discs
Chemical	Diffusion barriers Oxidation/corrosion protectors Gas/liquid sensors
Mechanical	Tribological coatings Hardness Adhesion Micromechanics
Thermal	Barrier layers Heat sinks

At the same time, the requirements in modern electronic devices, more and more strict, referring to their operating characteristics (*e.g.* response time, size, sensitivity, stability, etc.), has been the driving force for the achievement of new thin films of improved physical-chemical properties. All this has been possible due to the extraordinary advances made during the last 40 years in both the synthetic deposition processes and the subsequent characterisation techniques. It should be emphasised that the rapidly changing needs for thin film materials and devices are creating new opportunities for the development of new processes, materials and technologies, giving rise to what can be called today "Thin Film Science" (see Fig. 1)[4], a substantial part of this Thesis.

Figure 1. *New processing techniques related to thin film materials and devices.*

Thin Film Preparation Techniques

The continuous development of thin film technologies has led to an increasing specialisation, originating in a wide range of variants depending on the destined application. Therefore, the choice to use one or another technique depends on a lot of factors, such as the material to deposit (composition, structure, etc.), thickness, deposition speed and coating homogeneity, substrate temperature, density and adhesion of the coating to the substrate, purity of starting materials and of the coating, etc.

Various preparation techniques for thin films exist based on different physical-chemical procedures, such as:

- Immersion in hot medium (zinc, aluminium, phosphate deposition processes on steels).
- Enamel and ceramic welding.
- Physical and chemical vapour deposition processes (PVD and CVD, respectively).
- Chemical and electrochemical processes.
- Surface treatments (ion implantation, etc.).

The immersion in hot medium and welding preparation techniques are traditionally applied in metallurgic processes for corrosion protection or for decorative endings. Although a wide range of applications exist in which these techniques are applied for the deposition of coatings, it are the vapour-based techniques which experienced a boom during the last 40 years. They are employed in most of the

technological processes, in such a way that, in various cases, they are gradually replacing the other existing traditional techniques.[3] This technique is based on the deposition of the condensation of a vaporised material upon a substrate as thin film. Generally, this process takes place in vacuum or in controlled atmosphere to avoid interaction between vapour and air, as well as the adhesion of air components to the substrate surface.

Within the vapour-based techniques a wide variety of preparation procedures of thin films exists, which can be classified in three main groups: (a) those based on the vaporisation of the material of interest, (b) those who start from a liquid phase, from which, due to a reaction, a precipitated thin film is obtained, and (c) those obtained through surface treatments in controlled atmosphere. In the last case, rather than a deposited thin film, a superficial film of the same material as the substrate, is obtained with improved properties; so, this group consists of surface modification techniques contrary to the two other groups of deposition techniques.

B.1.1.2. Nanostructured materials

During the last years a great variety of nanostructured materials (nanorods, nanotubes, etc.) have been designed and synthesised, based on metals, polymers, carbon or semi-conductors, with special properties converting them in materials of great interest and utility for the industrial and technological sector. A material is considered to be a nanomaterial when the sizes of the individual building blocks are less than 100 nm, at least in one dimension. This definition is well-suited for many research purposes, where nanomaterials have a high priority.

In nanotechnology, it is frequent to use the “bottom-up” approach while in conventional technologies the “top-down” approach is preferred (Fig. 2). The expression “top down” means starting from large pieces of materials and producing the intended structure by mechanical or chemical methods. Contrary, “bottom-up” refers to the use of atoms or molecules as building blocks to produce nanoparticles, nanotubes and nanorods, or thin films or layered structures. According to their dimensionality, these features are also referred to as zero-, one- or two-dimensional nanostructures (particles, tubes and layers respectively).

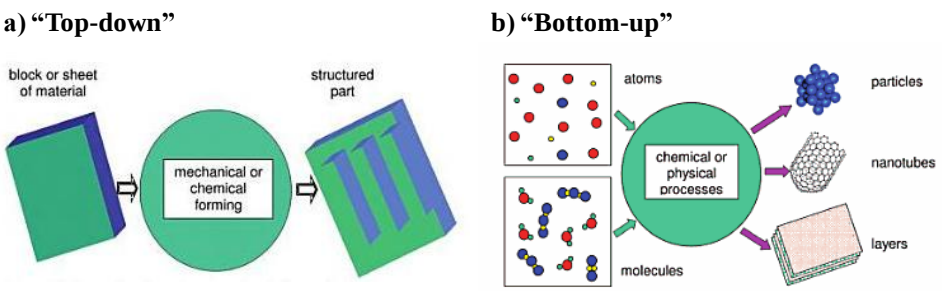


Figure 2. *a) Conventional technology's "top-down" approach, and b) Nanotechnology's "bottom-up" approach.*[5]

For industrial applications, the main importance is the relation price-properties. In most cases, nanomaterials and products using nanomaterials are significantly more expensive than conventional products. Hence, as long as the use of nanomaterials with new properties provides the solution to a problem which cannot be solved with conventional materials, the price becomes not so important.

B.1.2. Direct Solids Elemental Analysis

The direct analysis of solid materials avoids previous dissolution and/or digestion steps, one of the most time-consuming steps of the analysis. Moreover dissolution increases the risks of sample contamination, analyte loss and loss of spatial information, together with a certain increment in overall costs. The advantages offered by direct solids analysis, versus sample dissolution, have led to its continuous development and use of direct solid elemental analysis techniques. A final important consideration in solid analysis is the possibility to obtain region-specific information, either laterally or depth resolved. If this latter information is desired aqueous sample preparation should be practically ruled out. Thus, the principal advantages to be stressed include: (a) reduced analysis time due to the absence of tedious sample preparation steps; (b) reduced analysis cost; (c) less destructive character; (d) possibility to obtain more information (*e.g.* speciation, lateral and depth resolution, etc.); and (e) reduced contamination risks.

Each of the various direct solids analysis techniques available, which will be described at continuation, has its unique analytical characteristics. Therefore, it is interesting to identify the most salient characteristics that the "ideal" spectrochemical source for direct solid analysis should possess (see Table 2).[6] Of course, this "ideal" technique does not exist as not all points can be fulfilled in one design in the real world. However, the choice of the most appropriate technique for a given problem implies the

knowledge of the analytical characteristics of each particular technique and will be determined by the sample type and the desired information.

Table 2. The ideal spectrochemical source for direct solid elemental analysis.[6]

1. Applicability to all possible sample matrices.
2. Easily controlled atomisation/excitation/ionisation rates.
3. Non-destructive character.
4. Rapid, high-precision depth profiling.
5. High degree of lateral resolution.
6. No sample preparation.
7. Easy to operate.
8. Useful for all elements under the same operating conditions.
9. Low capital and maintenance costs.
10. Total element coverage.
11. Linear dynamic range.
12. Easy to quantitate (no matrix effects).
13. Multi-mode operation (*e.g*. Optical Emission, Mass Spectrometry).

B.1.3. Current techniques for the analysis of solid material

The use of direct solids analysis techniques is more than ever extended due to the important advantages previously detailed. This type of technique can be divided into two categories, depending on the information obtained: (a) techniques for the analysis of the global composition of homogeneous solid samples ("bulk analysis"), such as Arc/Sparc Spectroscopy and X-Ray Fluorescence (XRF), and (b) techniques allowing such analysis with lateral and/or depth resolution, representing today the most important tools for surface and thin film analysis. Most of them are of spectroscopic nature, based on the excitation of the material to be analysed with photons or particles (electrons or ions), followed by the detection of the characteristic photons or particles emitted due to the energy-matter interactions.[7,8] In this way, the surface of the sample is bombarded by photons, electrons or ions, affecting the physical condition of the surface to analyse. The range of these effects depends on the nature of the particle that interacts with the surface. Thus, as an example, when bombarding a sample with an ion or electron beam with an energy of 1 keV, most of this energy will be deposited near the surface (1-2 nm). Conversely, a photon beam with the same energy can penetrate to a depth of 1 μm.

When comparing the destructive character of photons, electrons and ions on the sample, photons are generally the less destructive ones and their impact depends on their wavelength. Electrons, in turn, have a more destructive character than photons and their final effect depends on the conducting or insulating nature of the sample, being particularly destructive for organic material. Finally, ion beams generally produce the sputtering of the sample surface and are, therefore, classified as a destructive method. As a result, analytical techniques based on the bombardment of the surface with ions are preferred to carry out in-depth analysis, where the emission intensity or analytical signal (related to the concentration) is plotted as a function of the analysis time (an easily measureable parameter related to the penetration depth).

It is important to highlight here that the effect on the sample surface depends on the strength and nature of the incident beam. Laser ablation techniques are a well-known example: a high power light beam can achieve the vaporisation, excitation and ionisation of a small volume of the solid sample. Also, in static 'Secondary Ion Mass Spectrometry' (SIMS) it is important to highlight that ions are used for the excitation, but they possess very low power and so static SIMS can be considered as "quasi" non-destructive.

Figure 3 collects the principal spectroscopic techniques for the direct elemental chemical analysis of solid samples with lateral and/or in-depth resolution. They are grouped considering the excitation source and the detected particle.

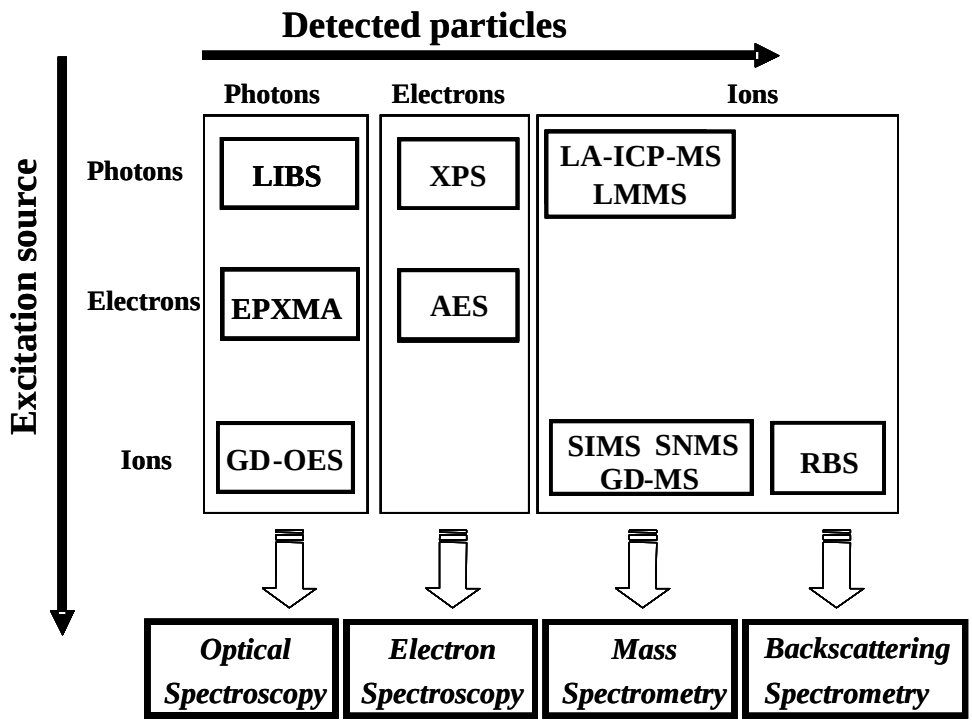


Figure 3. *Classification of the usual techniques used for surface analysis*
***LIBS**: Laser Induced Breakdown Spectroscopy; **EPXMA**: Electron Probe X-Ray Microanalysis*
***GD-OES/MS**: Glow Discharge Optical Emission Spectrometry/Mass Spectrometry*
***XPS**: X-Ray Photoelectron Spectroscopy; **AES**: Auger Electron Spectroscopy*
***LA-ICP-MS**: Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry*
***LMMS**: Laser Microprobe Mass Spectrometry; **SIMS**: Secondary Ion Mass Spectrometry*
***SNMS**: Secondary Neutral Mass Spectrometry; **RBS**: Rutherford Backscattering Spectrometry*

B.1.3.1. Optical Spectroscopy (detection of photons)

♦ Laser Induced Breakdown Spectroscopy (LIBS)

When a sample is irradiated with a laser beam (*e.g.* a solid state laser Nd:YAG), a laser induced plasma is generated and the vaporisation ("laser ablation") of the solid, followed by the excitation of the sample species will occur[9]. The optical emission observed from this plasma, is the basis of Laser Induced Breakdown Spectroscopy (LIBS). In particular, LIBS is very suitable for on-line/on-site elemental analysis. The emission of the photons produced is not simply the effect of the heating of the bombarded surface, but rather the consequence of a variety of processes that include thermal vaporisation and gas dynamics. The analytical capabilities of LIBS are determined by the plasma properties, which depend on various experimental parameters, including the laser pulse (energy, duration, repetition rate and wavelength), the sample (physical properties), and the ambient atmosphere (gas, pressure). Several studies have explored the use of ultra short (pico- and femtosecond) pulsed lasers[10].

For direct solid samples analysis, LIBS permits a depth profile resolution of several nanometers, while the lateral resolution can reach 1 μm. The detection limits for the direct analysis of metals, glasses, pottery and even organic samples are in the range of mg/g - μg/g for different trace elements.[11] An important drawback of this technique is associated to quantification difficulties, due to serious matrix effects.

♦ Electron Probe X-Ray Microanalysis (EPXMA)

The technique Electron Probe X-Ray Microanalaysis (EPXMA) is defined by IUPAC as follows: "*an analytical technique which uses the excitation and evaluation of the characteristic X-ray spectrum of a solid specimen by a focussed electron beam (typically of a diameter of less than 1 μm). Qualitative and quantitative X-ray analysis is its main feature.*".[12] When a sample is irradiated with high-energy electrons, core electrons are ejected, resulting in the ionisation of sample atoms. The ejected electrons have a wide range of kinetic energies, called secondary electrons, and are very useful for imaging purposes as in scanning electron microscopy (SEM); microstructures in shapes such as defects, precipitates, grain boundaries and so on, are easily observed by SEM. The hole of an inner electron orbital, resulting from the irradiation with energetic electrons, may be filled by an electron from a higher level and the energy difference between the core and the higher orbital is released as the emission of an X-ray photon, containing analytical information. The photon energy of a characteristic X-ray is well defined by the energy difference between the two energy levels of the corresponding electron orbitals, and this is the basis of EPXMA techniques.

Through physical calculations of the trajectory of the incident electrons, it is known that the interaction volume of the electrons with matter has a form of the type represented in Fig. 4. The electron speed decreases while penetrating into the material and, at some moment, its energy will be less than the critical ionisation energy (Ec) meaning that no X-ray production can take place, determining this way the size of the interaction region. Thus, by increasing the energy of the incident electrons this volume will increase and deeper interaction will take place. The higher the atomic number of the elements composing the sample, the smaller and more spherical the interaction volume becomes.

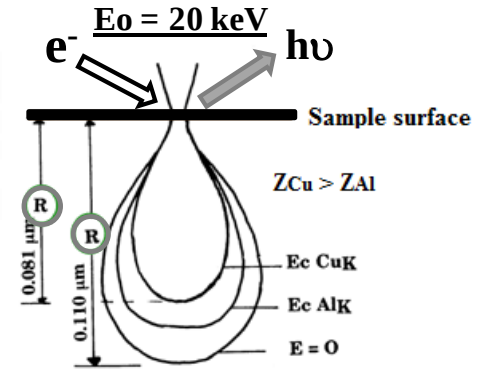


Figure 4. *Interaction volume of the electron with the sample for copper and aluminium. R: penetration/excitation depth; E_0: energy of the incident beam; E_c: critical ionisation energy.*

An important feature of EPXMA is the low depth resolution (>1 μm). Related to its applications, the analysis of conducting samples is easily viable, because the circulation of electrons minimises the problems associated to the generation of negative charge on the surface. However, isolating materials should be covered with a small conducting film. Other difficulties of this technique are related to the analysis of light elements and the required high vacuum (increasing in such a way the analysis time and overall costs).

♦ Glow Discharge (GD)

Glow Discharges (GD) are low-pressure electrical discharges in a noble gas (at 0.1-10 Torr), generally in an inert atmosphere, produced through a voltage between two electrodes, which are in contact with the discharge gas (most commonly Ar). When this voltage exceeds a threshold value, the Ar will be ionised and a current flow will be established between the two electrodes, generating a plasma in this way. Therefore, GD is as an atomisation, excitation and ionisation source, because (a) the sputtering of sample surface material through the collision of the Ar ions generates atomisation; and (b) the presence of Ar ions and electrons in the plasma leads, through a great number of collisions, to the excitation and ionisation of sputtered sample atoms.

This technique for direct solids analysis can be coupled to Optical Emission Spectrometry (OES) or to Mass Spectrometry (MS) providing elemental information and allowing both qualitative and quantitative analysis for almost all

the elements of the periodic table. Due to the sputtering effect, it is a destructive technique but, on the other hand, the analysis of concentration profiles with high in-depth resolution (range of nm) can be obtained, compensating its relatively poor lateral resolution (range of mm). In fact, the GD enables rapid and detailed characterisation of the near-surface layer, interfaces and bulk composition, if the spectral line intensities of the elements of interest are recorded simultaneously.[7] It should be highlighted that comparatively few matrix effects are observed using GDs, as a consequence of the spatial and temporal separation of the atomisation, excitation and ionisation processes in this source. This direct solid analysis technique will be covered in more detail in Parts B.2-B.4, considering its predominance in this Thesis.

B.1.3.2. Electron Spectroscopy (detection of emitted electrons)

In techniques based on electron spectroscopy, the bombardment of the solid sample with photons or electrons leads to the ionisation of the surface atoms. The analysis of the kinetic energy of the originated photoelectrons (electrons emitted through the action of photons) or of the Auger electrons (electrons emitted corresponding to the energy of internal generated processes) will allow the identification of the corresponding atoms from the ionised surface. The following techniques provide information of the first atomic layers.[3]

♦ X-Ray Photoelectron Spectroscopy (XPS)

Also known as Electron Spectroscopy for Chemical Analysis (ESCA), X-Ray Photoelectron Spectroscopy (XPS) is based on the ejection of an electron from a core electron orbital when irradiating a sample surface with a monochromatic high energy X-ray photon beam (~ 1 keV). This electron emission is due to the energy transfer from the incident photons to the electrons in the internal atomic levels. Figure 5 represents this photoelectron emission process where an X-ray beam of energy, **hν**, produces the ionisation of an internal atomic level.

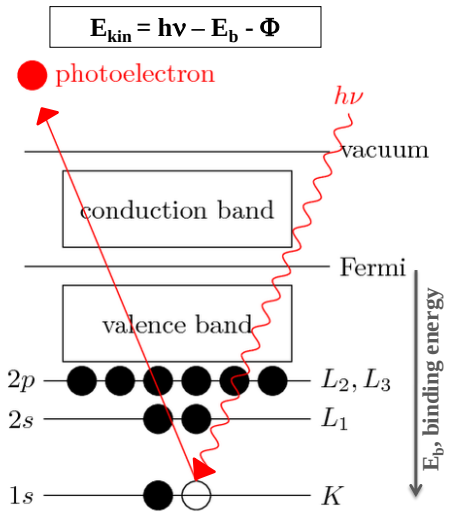


Figure 5. *Excitation and emission process of a photo-electron in XPS.*
E_b: binding energy; E_v: valence level energy; Φ: working function of the spectrometer.

The kinetic energy (E_{kin}) of the emitted electron is measured by an electron spectrometer and will be approximately equal to the incident radiation energy (**hν**) minus the binding energy of the electron in the atom and a term denominated as working function of the spectrometer (Φ). The binding energy of the internal electrons is characteristic for the atom and so it defines each specific atom.[9]

XPS allows the qualitative analysis of conducting and isolating samples with thicknesses of 1 Å to 100 nm, in a non-destructive way, obtaining information on the first atomic layers while providing information of all the elements (except for H and He) present at concentrations above 0.1%, offering at the same time important structural information as well as the identification of the oxidation states of the element. Depth profile information can be obtained when coupling the technique to others which "sputter" the sample surface. The main inconvenience of this technique is its high instrumental cost, the high vacuum required (0.075 μTorr) and the extreme long analysis time necessary for in-depth analysis (various hours for 100 nm).[13]

♦ Auger Electron Spectroscopy (AES)

In Auger Electron Spectroscopy (AES), both the excitation particles and measured/emitted ones are electrons (called Auger electrons). These are energy-analysed when a focused electron beam is irradiated at a spot size of 100 μm

down to several 10 nm in diameter. The measurement of the kinetic energy of the Auger electrons allows the identification of different atoms (except H and He). This technique is similar to XPS, as in both cases the electrons of the atom core levels are detected. However, while the emission process of the electron in XPS is obtained in one step, in AES it takes place in two (Fig. 6), generating an Auger electron which energy does not depend on the excitation beam energy but on the energy of the internal process induced by the beam.[7] The emission process of an Auger electron is competitive with the emission of an X-ray photon, and the predominating process depends mostly on the atomic number of the element. Therefore, while with AES major sensitivity is obtained for elements with low atomic number, XRF and EPXMA are more adequate for elements with atomic number above 14.

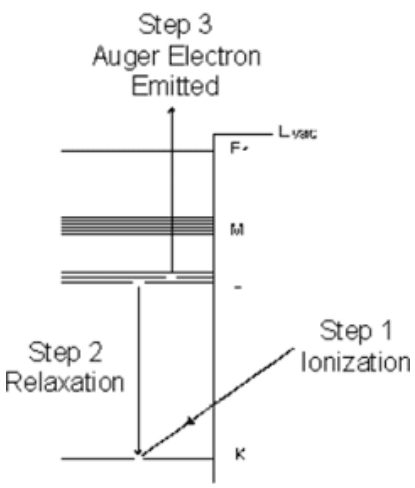


Figure 6. *The Auger process. Step 1: Electron emission. Step 2: Electron drops down to fill the vacancy created during step 1. Step 3: The energy released in step 2 causes the emission of an Auger electron.*

AES allows both qualitative and quantitative analysis, but problems for the analysis of insulating samples are observed, due to "charge accumulation" on the surface. High lateral (0.1-1 μm) and depth (15 Å-100 nm) resolution can be obtained[14] and detection limits in the order of 10^3-10^4 μg/g have been reported. As for the case of XPS major limitations are: the high overall cost and high vacuum requirements (<1 μTorr).

B.1.3.3. Mass spectrometry (detection of ions)

This part summarises the direct solids analysis techniques wherein the detected particles are the generated ions after the excitation of the solid surface.[8]

♦ Laser Microprobe Mass Spectrometry (LMMS)

This technique is based on the action of a laser beam upon the sample surface (similar to LIBS) able to evaporate, excite and ionise a small and well-defined volume. When applying high intensity lasers, dense microplasmas will be formed from the solid sample, breaking up the molecules in their atomic constituents and forming ions, providing elemental information. On the other hand, when a low power laser is used, only laser desorption is achieved and so molecular information is obtained. The combination of a pulsing laser with a 'time-of-flight' mass spectrometer makes it a practical analytical tool.

Lateral resolutions of 1 μm can be obtained and the detection limits reach the range of μg/g for elemental analysis; depth profile analysis, however, is not frequently carried out with this technique.[15]

♦ Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS)

Similar to the previous technique (LMMS), Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) is based on the interrogation of the sample surface with a focused laser, able to volatise the surface atoms. The sputtered sample atoms will be dragged towards the ICP, in the form of a gaseous aerosol, by an inert gas. Thus, excitation and ionisation of the particles is achieved in the ICP, where the ions are analysed by an appropriate mass analyser (*e.g.* a quadrupole).

As other LA techniques, it can be applied to both conducting and insulating samples. The detection limits are in the ng/g (ppb) range or better, depending on the mass spectrometer used. Both the lateral (between 5-300 μm) and the depth resolution achievable are defined by the used laser characteristics.[10,16]

♦ Secondary Ion Mass Spectrometry (SIMS)

Through the bombardment of the sample surface with a primary ion beam, ions penetrate into the solid surface to different depths (in the range of 1 to 10 nm) transferring their kinetic energy through binary collisions to the atoms of the sample. In this way the sample atoms are displaced from their original sites,

colliding with other sample atoms and, so, producing a collision cascade until the transferred energy is insufficient to cause atom displacement. Collision cascades reaching the surface may cause the sputtering of sample material, which consists mostly of neutral particles and some charged ones, from the first atomic layers. Those "secondary" ions are sampled, separated adequately in a mass analyser and finally detected. The neutral particles can be detected as well after a post-sputtering step for further ionisation which is the basic principle of Secondary Neutral Mass Spectrometry, described further on.

According to the energy of the primary ions, two different types of SIMS can be distinguished, as the effect on the surface and the information obtained are very different.[17]

○ ***Dynamic SIMS.*** The bombardment of a sample with a dose of high energetic primary ions (1-20 keV) results in the destruction of the initial surface and near-surface regions, allowing depth profile analysis, and providing both elemental and isotopic information. The sensitivity is high, with detection limits in a range of ng/g (ppb) and sample tri-dimensional images of the composition can be obtained. Because the probability of ionisation is very dependent on the matrix and on the element of interest, the quantification process is quite problematic.[7,15]

○ ***Static SIMS.*** The primary ion beam has a much lower density than the one used in dynamic SIMS, around 10^{12} ions/cm². The low-energy primary beam produces a low density current flow and a negligible damage of the sample (less than a tenth of an atomic layer). Therefore, this technique can be considered "quasi" non-destructive (typical surface destruction <1%)[7] to analyse the superficial layer and is able to provide molecular information. Bi-dimensional images can be obtained.

♦ Secondary Neutral Mass Spectrometry (SNMS)

As commented previously, the quantification by SIMS is problematic due to matrix effects, derived from the fact that the sputtering and ionisation processes of the sample elements occur simultaneously. Nevertheless, 95% of the emitted particles during the ion bombardment are neutral and, therefore, important

advantages can be offered by the detection of these neutral atoms after an ionisation step, following their initial sputtering.

So, in Secondary Neutral Mass Spectrometry (SNMS) the sample is bombarded with an ion beam (energy in the range of 0.5-5 keV) to sputter atoms from the surface which will be then ionised in a further step (of course in SIMS the analysis is based on the extraction and direct analysis of those initially formed secondary ions). This post-sputtering step can be accomplished by the use of lasers or by the electron bombardment of the atoms before entering the mass analyser.

SNMS provides easier quantification of elemental atomic concentrations than SIMS, and can even be employed for quantitative depth profiling of non-uniform matrices.[18] However, due to instrumental limitations, the detection limits obtained up-to-date with SNMS are of the order of parts per million (ppm), almost three orders of magnitude worse than those obtained with SIMS.[17]

♦ Rutherford Backscattering Spectroscopy (RBS)

During a Rutherford Backscattering Spectroscopy (RBS) experiment, high energy (up to MeV energies) He^{2+} ions are directed onto the sample and the energy distribution and yield of the backscattered ions at a given angle is recordered. Since the backscattering cross-section for each element is known, it is possible to obtain quantitative depth profiles from the RBS spectra (for thin films of less than 1 mm).

RBS is a non-destructive compositional analysis technique with high sensitivity for heavy elements. Important to highlight here is that no reference materials are needed to obtain quantitative data. Moreover, it should be taken into account that the incident ion penetrates into the material, providing information on both the layer composition and layer thickness.[19] In other words, it is possible to determine concentration profiles of heavy elements, distributed in a matrix of light elements, as both signals can be easily separated.

♦ Glow Discharge Mass Spectrometry (GD-MS)

The characteristics of Glow Discharge have already been briefly covered and will be more detailed in Part B.2-B.4. As mentioned, GD can also be coupled to Mass Spectrometry. GD-MS is now a mature and versatile technique for the direct determination of trace elements and depth profiling in a variety of solid materials.[20] GDs have been coupled to different mass spectrometers including quadrupole, sector field (SF), and time-of-flight (TOF) mass analysers. Several commercial instruments have been available during the years (*e.g.* TS Sola quadrupole, Kratos, VG Glo-Quad and VG 9000). However, the only current commercially available instruments are based on GD-SFMS and GD-TOFMS. The GD-SFMS instruments provide low LODs (ppb) and high mass resolving power (> 3000) but have, in most cases, a sequential analyser. Alternatively, TOF mass spectrometers offer high mass spectra acquisition rates for quasi-simultaneous multi-elemental detection of fast transient signals, making TOFMS especially suitable for depth profiling applications and for its coupling to pulsed GD sources.

The main capabilities of GD-MS are the high depth resolution (to nanometers) achievable with recent marketed instruments,[21] the achievable fast sputtering rate (in the order of $\mu m\ min^{-1}$), the isotopic information,[22] the low limits of detection ($\mu g\ g^{-1}$ to $ng\ g^{-1}$) and its multi-elemental analysis capabilities. Particularly, the latter two capabilities constitute the most important advantages of GD-MS compared to GD-OES.

B.1.4. Comparison of depth and lateral information obtained with different techniques

Figure 7 shows a comparison of the capacity for lateral and depth resolution obtainable with the different commented surface analysis techniques. As can be observed, the lateral resolution for GD (in the range of millimetres) is obviously worse than that for the other methods because it is limited by the size of the anode tube (1-8 mm). Nevertheless, the capacity of depth resolution for both GD-OES and GD-MS is in the range of a few nanometers, both among the techniques providing better depth information.

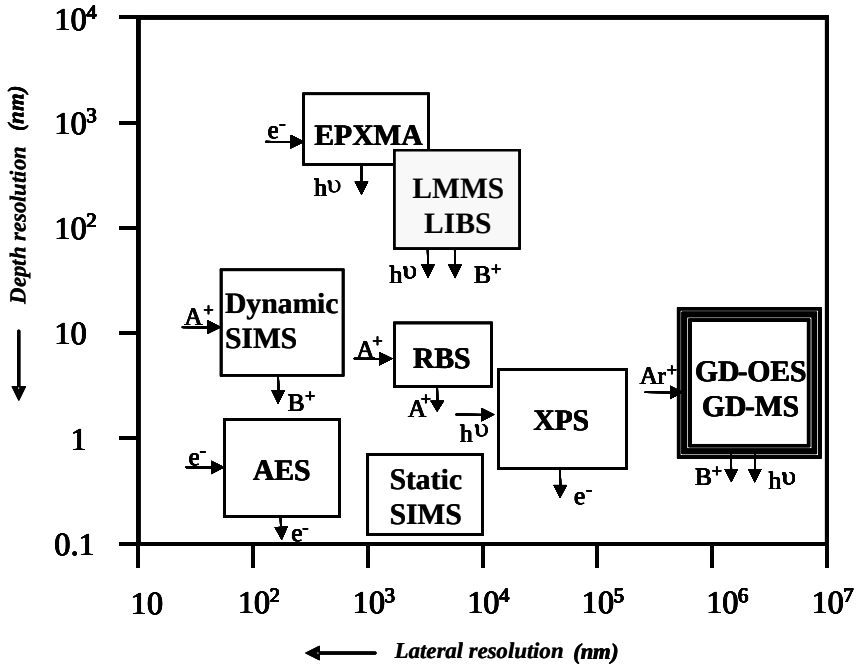


Figure 7. *Comparison of the capacity for lateral and depth resolution for the different direct solids analysis techniques.*
A^+ and B^+: incident and emitted ions, respectively; e^-: electrons and hυ: photons

B.2. Glow Discharge in Analytical Chemistry

Nowadays, Glow Discharges (GDs) are employed for a wide variety of applications in science and technology. The micro-electronics industry represents one of the widest and most important application field where glow discharges are used for thin film deposition. Analogously, they are extendedly used in material industry for the deposition of thin films, coatings, superficial layers and, additionally, for surface cleaning treatments, pre-treatment and modification processes. Analytically, the glow discharge is widely used as atomisation/excitation/ionisation source with important analytical chemistry applications.[23] GD, coupled to either optical emission or mass spectrometry, is a fast, versatile and easy technique allowing the elemental analysis of homogeneous bulk materials, coatings and interfaces. Moreover, GD techniques are not only applicable for direct solid analysis but can also be used for the analysis of liquids[24-26] and the detection of gaseous samples.[27-29]

In 1967 Grimm described his, then new, analytical source[30] as follows "*the combination of a glow and a hollow-electrode discharge lamp allows the spectrochemical analysis of the major elements in a disk or sheet sample in less than 2 minutes*", words that marked the beginning of the modern era of Glow Discharge –

Optical Emission Spectrometry for depth profile analysis of solid specimens. Grimm created a new, rapid, versatile and stable source mounting the sample external to the source, allowing the direct analysis of a wide range of sample geometries, and combining a hollow anode with a hollow cathode block. Grimm's new source attracted immediate scientific interest which has been steadily growing during the 40 years elapsed since the publication of his paper. In fact, the vast majority of the commercial GD systems currently available for analytical purposes can still trace their origins back to the Grimm design.

B.2.1. Discharge chamber configuration

Different types of GD chamber geometries have been described and used as ion and photon sources. They are designed to analyse efficiently different types of samples from liquids (through an adequate sample introduction system) to small samples with sharp forms and metallic alloy blocks, allowing, as a whole, to include a large number of applications. The principal GD chamber configurations are the following: the hollow cathode, the coaxial cathode and the flat cathode configuration.

○ **The hollow cathode.** Hollow Cathode Lamps (HCL) have successfully been used in the direct analysis of solid materials, but great part of their applications are related to their use as lamp for both atomic absorption and fluorescence spectroscopy. Because of the efficient excitation/ionisation, GDs based on HCL offer good analytical sensitivity[31] and are therefore often used as excitation - sputtering sources in the analysis of different sample types, inserted inside the hollow cathode, such as metallic chips, powders and even liquids in microvolumes.[23] Typical operation conditions for this configuration include: voltages between 200-500 V, electrical current intensities of 10-100 mA and pressures of 0.1-10 Torr.[32]

○ **The coaxial cathode.** This configuration is very popular for GDs coupled to mass spectrometry.[33] Its design allows the analysis of samples with varying forms and dimensions such as cylindrical tubes, discs, tips, etc. which are located at the end of a direct insertion probe. This probe is introduced inside the discharge chamber through a vacuum interface to maintain the low pressure inside the chamber. The sample will act as cathode, while the discharge chamber will act as grounded anode. The discharge will be formed at the extreme end of

the sample and the ions will be extracted from the plasma towards the mass analyser. Typical operation conditions for this configuration include: voltages between 500-1000 V, electrical current intensities of 1-5 mA and pressures between 0.4-2 Torr.[32]

○ **The flat cathode.** Discharge chambers with flat cathode configuration (Fig. 8) are broadly employed in OES analysis[34] (nowadays, it is the basic design in all commercial GD-OES instruments), although their use in mass spectrometry is becoming more common. The original design of this chamber was proposed by Grimm at the end of the 60's to obtain an atomic emission source[30,35] and is therefore often referred to as "Grimm type source". Here, the cathode is located outside the chamber, making the sample change easier while serving simultaneously to close the chamber to maintain the vacuum. The discharge is enclosed in the inner zone of the cylindrically shaped anode, meaning the cathode surface submitted to sputtering is equal to the area of the cylinder base. The main advantage of this design is its capability for depth profile analysis, whereas, its main limitation is the necessity of flat samples. Typical operation conditions for this configuration include: voltages between 500-1500 V, electrical current intensities of 3-30 mA and pressures between 2-6 Torr.[32]

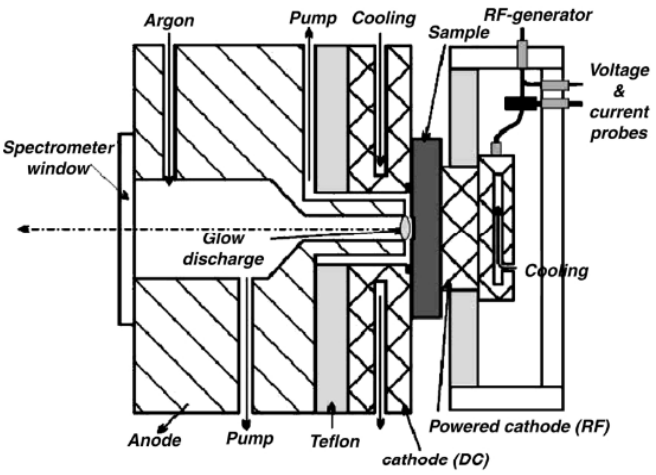


Figure 8. *Flat cathode or Grimm type source for dc or rf operation.*[36]

B.2.2. Fundamental processes and the plasma discharge

B.2.2.1. Different discharge regimes

The luminosity of the glow discharge is caused when both the electronic energy and electron density are high enough to generate visible light due to the excitation of energetic states through the occurring collisions. Nevertheless, discharges are not only distinguished by their luminescence but also by their current-voltage characteristics, that is, current density and breakdown voltage. These main characteristics depend on the vessel and electrode geometry, the plasma gas and the electrode material. The electrical behaviour of discharges covers different situations reflected in the current-voltage curve characteristic for a discharge tube, represented in Fig. 9. According to this curve, characteristic of a direct current electric discharge, the GD constitutes the second of the three regions: the dark discharge, the glow discharge and the arc region (see Fig. 9). In turn, each of the three discharge regions is defined by different electrical regimes, that is, the evolution of a glow discharge consists of different transitions which obey an electric response.

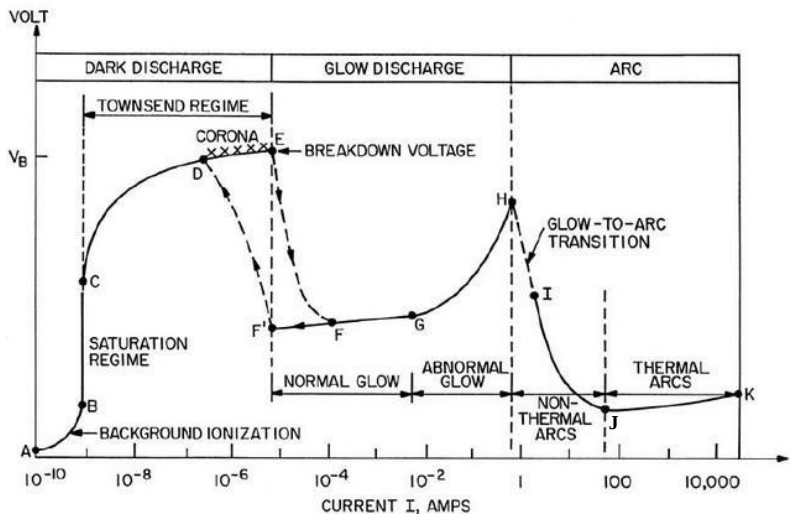


Figure 9. *Voltage-current characteristic of a DC low pressure electrical discharge tube.*

○ **The dark discharge.-** The region from point A to E n Fig. 9 is termed "dark discharge" because (except for a *corona discharge* and the *breakdown* itself) the discharge remains invisible to the eye due to the reduced density of excited species. *In the Townsend regime* (B-C) the electrons obtain sufficient energy from the electric field that will ionise some neutral gas atoms, giving rise to a rapid increase of the current as a function of the voltage. During the unipolar

corona discharges (D-E) the electrical field is the dominant parameter, rather than the potential difference between the electrodes. The *electrical breakdown* (point E) occurs when the ions reaching the cathode have enough energy to generate secondary electrons and the discharge will move into the normal glow discharge region.

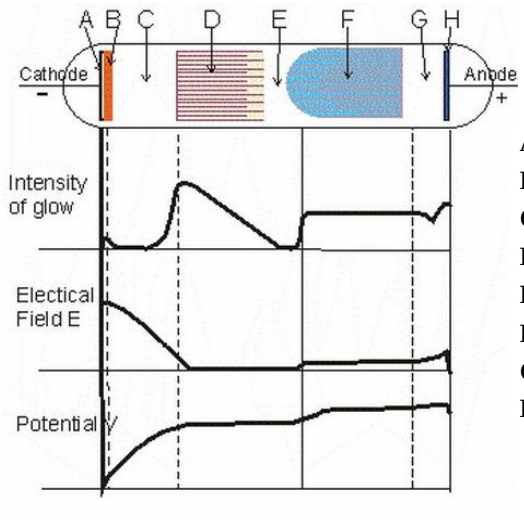
○ **The glow discharge.-** This regime owes its name to the typical luminous glow that can be observed. After the gas breakdown (point E), the electron energy and density are high enough to generate excited gas atoms through collisions, which will relax to their ground state through photon emission. After a discontinuous transition from point E to F, the ***normal glow region*** (F-G) is reached, in which the voltage is almost independent of the current over several orders of magnitude. As the current increases (F-G), the fraction of the cathode occupied by the plasma increases, until the plasma covers the entire cathode surface at point G. The discharge voltage remains constant over a large range of current variation. At this point, where the voltage increases significantly with increasing current, the discharge changes into the so-called ***abnormal glow region*** (G-H) and behaves likewise a normal resistance.

○ **The arc discharge.-** After a given point H, the electrodes become sufficiently hot so the cathode will emit electrons thermo-ionically. If sufficient current is supplied to the discharge, *a glow-to-arc transition* (H-I) will be undergone. During the arc regime, from point I to K, the discharge voltage decreases while the current increases until large currents are achieved (point J). The combination of the high vaporisation degree of the cathodic surface, together with the excitation/ionisation processes through collisions in the plasma, have made of this arc discharge a useful technique for the spectrochemical excitation and analysis of metallic samples.

B.2.2.2. Phenomenology of the 'abnormal' discharge

Figure 10 is a schematic representation of the normal glow discharge and its different discharge regions.[37] Three major regions can be distinguished in the discharge: the cathode region (A-C), the glow region (D-E) and the anode region (F-H).

The Cathode Dark Space and the Negative Glow region are always present in a glow discharge. The latter corresponds to the plasma zone and most excitation processes occur here and, therefore, most of the emission light to be detected for analytical purposes is produced here. The different regions represented of the GD in Fig. 10 are in case of the normal discharge mode. However, the GDs used in this Ph.D. Thesis, and those generally employed for the characterisation of solid materials, are operated in the abnormal mode. Except for its brighter luminosity, the abnormal GD characteristics are very similar to those of the normal GD. Thus, the characteristics described before are still valid for our system.



A. Aston Dark Space
B. Cathodic Glow
C. Cathode Dark Space
D. Negative Glow
E. Faraday Dark Space
F. Positive Column
G. Anodic Glow
H. Anode Dark Space

Figure 10. *Geometry of the normal GD and its different discharge regions.*

It is important to comment the so-called Cathode Dark Space and Negative Glow regions.

○ **The Cathode Dark Space (Crooks, Hittorf region) (C in Fig. 10).-** The region on the right of the "cathodic glow" is a relatively dark region that has a strong electric field, a positive space charge and a relatively high ion density. The energy distribution of electrons and ions depends on the pressure and the applied voltage. In this region electrons are accelerated by the electric field and the positive Ar ions will be accelerated towards the sample cathode while their kinetic energy increases during their pathway. When an energetic ion impacts with the solid surface of the cathode, it can be reflected or penetrate inside the solid and so transfer its energy to the surface atoms. In the latter case, the potential energy of the ion provokes the emission of secondary electrons, while

its momentum and kinetic energy are transferred to the atomic structure through elastic and inelastic collisions. This will result in a collision cascade inside the structure spreading freely towards the surroundings. The result will be the sputtering of the sample atoms during which those atoms can escape out of the solid and enter the gaseous medium (if the energy transferred during the collision is higher than the binding energy to the surface). The sputtered atoms will reach the negative glow region by diffusion.

○ **The Negative Glow (D in Fig.10).-** This region, right next to the cathode dark space, emits the brightest and most intense light of the whole discharge. This region is characterised by a weak electric field, and with the highest dimensions and its intensity maximum is situated on the border with the cathodic dark space. The electrons carry almost the entire current in the negative glow region. The sputtered atoms from the cathode dark space diffuse into this region, where they will undergo collisions with particles with sufficiently high energy to produce the excitation and ionisation of these atoms. These collision processes are the ones maintaining the plasma and depend on the working conditions of the discharge and the chamber geometry. The ability of the GD to produce efficient atomisation and excitation/ionisation of the present elements, constituting the sample, is responsible for its present extensive use as analytical atomic spectrometry source: measuring photons at the spectral lines characteristic of each element (analyte) in the plasma allows optical spectrometry analysis, while the efficient ionisation of the sample atoms allows the analysis by mass spectrometry.

B.2.3. Generation modes of Glow Discharges

The vast majority of glow discharge applications deals with the analysis of solid-state specimens, but not all solids are alike. Important differences occur, not only in chemical composition, but also in physical characteristics. The most relevant difference with regard to GD analysis is the electrical conductivity of the sample, not only for the bulk, but also in the region of the sample surface. If the surface (or bulk) of the sample is electrically insulating, there is no chance for charge movement within the sample matrix and so the simple electrical circuit cannot be completed. In non-conducting samples, a positive charge accumulates on the surface under ion bombardment up to the point where the applied potential is insufficient to maintain the discharge. In the case

that a discharge can be ignited (*i.e.* an amount of ions and electrons exists in the gas phase) the process is analogue to the charging and discharging of a capacitor. The negative potential initially located on the sample surface to initiate the discharge will be neutralised with the arrival of positive ions. Thus, it is clear that while a conventional direct current potential is effective for the analysis of conducting samples, this is not a viable approach for, partially or whole, insulating samples.

The variety of electrically insulating materials is very large and is growing day by day as new materials of unique chemical or/and physical properties are being developed. Three different basic approaches for the analysis of non-conductors have been reported: (a) converting the sample into a conductive one[38], (b) placing a conductive metal layer on the sample surface[39], and (c) using radiofrequency potentials to power the plasma. The first approach precludes the possibility to obtain in-depth profile analysis (while increasing the risk of contamination during the transformation step). The second approach puts limitations on the sample geometry and tends to be complex in terms of optimisation. The radiofrequency approach is more straightforward as it is the only technique where the sample does not need to be chemically modified, avoiding any risk of contamination.

Next, the different generation modes of the GD discharge and their particular characteristics are described.

B.2.3.1. Direct Current Glow Discharge (dc-GD)

Dc-GDs are better-known, compared to radiofrequency GD, due to the large amount of studies carried out on this discharge type. Moreover, the relation between the various working parameters (current, voltage and pressure) determining the discharge, are well-controlled.

It is not possible to select simultaneously all three parameters of the dc-GD: current (in the range of mA), voltage (oscillating between 300 and 1500 V) and chamber pressure. Hence, depending on which parameters are chosen to be fixed, and which to be allowed to find their own values for each sample, several modes are possible in dc operation (depending on the application and sample) as detailed in Table 3. Because of the possibility to control the value of two out of the three parameters, reliable quantification methods could be developed for the analysis of coated samples.

As a matter of fact, commercial instruments employ the operation mode with varying pressure (constant current and voltage) due to the fact that the corresponding quantification method is considered to be the most precise if working at constant electrical resistance.[40]

Table 3. Operation modes in dc-GD.[23]

Constant Parameters	Variable Parameters	Commonly used for
Pressure and voltage	Current	Bulk analysis and surface cleaning
Pressure and current	Voltage	Depth profiling with good resolution
Current and voltage	Pressure	Quantitative analysis

B.2.3.2. Radiofrequency Glow Discharge (rf-GD)

The attractive character of a glow discharge generated by radiofrequency, besides its use to analyse conducting samples (as direct current discharges do), is its ability to carry out direct solids analysis of semi-conductors and insulators.[41,42] This fact is opening a new world of possibilities and applications for the analysis of glasses, pottery, painted materials, polymers, organic materials, plastics, etc., with depth resolution capabilities.[43-45]

To sputter an insulating sample in a typical analytical rf glow discharge device, the sample is placed in contact with one of the conductive electrodes. If a negative dc high voltage is suddenly applied to the electrode, the surface potential of the insulating sample will drop instantaneously to approximately the applied potential, due to the alignment of electric dipoles within the insulator. If this potential is sufficiently large, the inert gas in the discharge cell will breakdown electrically, initiating the glow discharge. The positive ions formed, will bombard the insulator which will be neutralised this way at its surface. The resulting loss of electrons in that surface causes the surface potential to rise towards zero. Since no net current can flow through the insulator, this potential rise will continue until the surface potential becomes too small to sustain the discharge and the plasma is extinguished.

The challenge to sputter insulating materials in an efficient way consists in the continuous restoring of the electrons lost from the surface, due to the ion bombardment, in order to maintain the necessary negative surface voltage. Using high-frequency

excitation, the surface would be bombarded alternately by positive ions and electrons and the electrons lost due to the neutralisation by positive ions in one half-cycle would be restored by electron bombardment during the next half-cycle. This approach does not only enable efficient sputtering of insulating materials, but also continuous sputtering.

Considering the effect of a bipolar rf potential applied to the electrode, first, the same process explained before will occur in Fig. 11; the potential on the surface insulator drops to approximately the applied potential (-1000 V for example). The discharge is initiated and the surface is bombarded with positive ions so the surface voltage rises towards zero. However, before the surface potential rises far enough to extinguish the discharge, at -950 V, the polarity of the applied voltage is switched to positive, resulting in a +2000 V change in the surface voltage to a value of +1050 V, so the surface will be bombarded by electrons, causing the surface potential to drop to less positive values. Since electrons are faster than positive ions, they are more efficient at neutralising the surface potential, and thus, the voltage will drop lower under electron bombardment than it had risen under positive ion bombardment in the preceding half-life. At this point, the potential polarity is switched back to negative obtaining a surface potential lower than the initial one, and the whole cycle restarts.

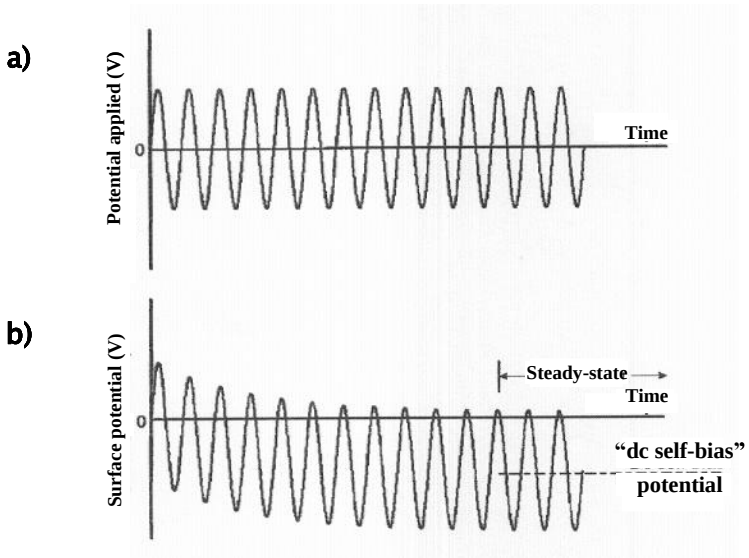


Figure 11. *Establishment of the "dc self-bias" voltage in an analytical rf-GD device. a) Applied rf potential to the electrode; b) resulting surface potential.*[46]

After a number of cycles, a steady-state condition will be attained in which the surface voltage is negative most of the time, meaning a negative "dc self-bias" voltage is acquired by the surface of the insulator. It is the presence of this dc bias that results in

the nearly continuous sputtering of the insulating sample. Important to point out is that its establishment is also accomplished for conductive sample matrices via the inherent capacitance of the impedance matching networks, employed in almost all rf plasma devices.[9] Thus, both conducting and insulating samples can be analysed.

It should be noted that, in the approach discussed, the discharge device is assumed to be highly asymmetric (*i.e.* the ratio of the effective electrode surface areas is large), that the sample constitutes the smaller electrode and that the rf-power is capacitively coupled and applied to the sample. Finally, the utility of frequencies within a range of 2-30 MHz has been studied, resulting that lower frequencies are more adequate for atomic absorption, while excitation and ionisation require higher frequencies.[46, 47] The most common rf-GD is operated at 13.56 MHz, an adequate frequency for analytical aims. Despite the increasing analytical interest in rf-GD, the devices are less developed than those for dc but it constitutes a present and highly important actual investigation field. Particular problematic and object of research today is the difficult control of the various operating parameters (*i.e.* voltage between the electrodes, the applied and dissipated power, etc.), an important aspect to be tackled because it complicates the development of quantification methods for depth profile analysis.[48]

B.2.3.3. Pulsed Glow Discharge

Although both dc and rf-GDs are most commonly powered in continuous mode, the analytical interest in pulsed GDs (PGD) is now steadily increasing.[49,50] A pulsed GD is created by applying periodically an electrical pulse of high power during milliseconds or even microseconds. During each pulse, an atom/ion packet from the surface material is generated and will expand along the discharge chamber. PGDs allow an additional way of controlling the plasma by selecting the pulse parameters (*e.g.* pulse and period lengths). For example, high instantaneous powers, leading to increased atomisation, excitation and ionisation processes, can be used without sample thermal degradation by just varying the duty cycle of the pulses.[51] At the same time, less plasma instabilities are observed in pulsed mode due to the lower mean power value. This involves an important advantage when carrying out the analysis of delicate samples which could break (*e.g.* glasses) or degrade (*e.g.* organic coatings) due to their excessive warm-up when measuring in continuous mode.

Moreover, different discharge processes take place at different times within a single pulse (*i.e.* there are different time-regimes in a pulse) and this allows, when coupled to MS and a time resolved signal acquisition detector to achieve quasi-simultaneous structural, molecular and elemental information of the sample.[52,53] Also, using this detection mode analyte signals will be detected at times different from the signals of the plasma gas.[54] Therefore, when synchronising adequately the moment of detection with the moment of pulse generation, it is possible to obtain spectra where the analytical lines dominate, while the Ar or other contamination signals are diminished.[55] These pulsed discharges offer also lower sputtering rates and high sensitivity, so providing an exceptional capability for the analysis of thin layers (depth profile analysis of semi- and non-conductors).

Most of the earlier work on PGDs focused on dc discharges.[56] However, the actual interest is mainly limited to its application to solid conducting sample analysis. Conversely, basic studies on pulsed rf discharges are still scarce and increasing efforts are being made during the last years to better understand its operation and to develop analytically useful pulsed rf-GDs.[50,57] Some specific reported applications have already shown the promising analytical potential and performance of PGDs for the analysis of thin film solar cells,[69] coated glasses[58] and polymers.[59,60]

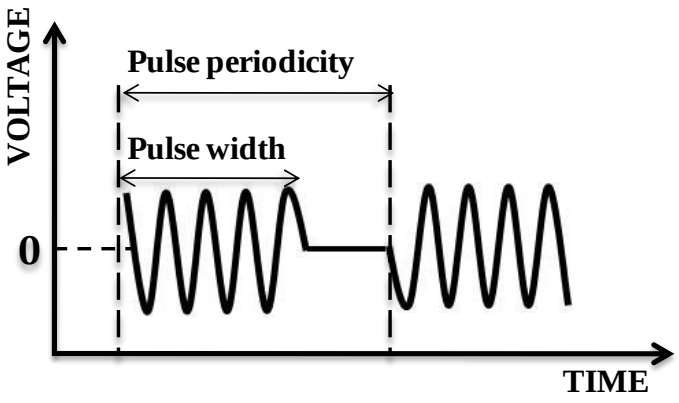


Figure 12. *Schematic representation of a pulsed rf discharge and the pulse parameters.*

Figure 12 collects important pulse parameters: pulse width and pulse period. The duty cycle is the ratio between the pulse width and the whole pulse period (sum power-on and power-off time) and is written in Eq. (1). The pulsed width normally varies within the range of ms to μs and the duty cycle values between 6.25-50%. So a standard

rf discharge (13.56 MHz) with a pulse width of 1 ms and a duty cycle of 25% means that during 1 ms 13,560 rf cycles are applied (power-on time) and during 3 ms the voltage is equal to zero (denominated as power-off time).

$$\text{duty cycle} = \frac{\text{pulse width}}{\text{pulse period}} \tag{1}$$

$$\text{pulse frequency} = \frac{1}{\text{pulse period}} \tag{2}$$

Three temporal regions can be distinguished within the pulsed discharge (represented in Fig. 13): the pre-peak, the plateau and the after-peak or afterglow region, which are each characterised by specific processes occurring in the plasma.

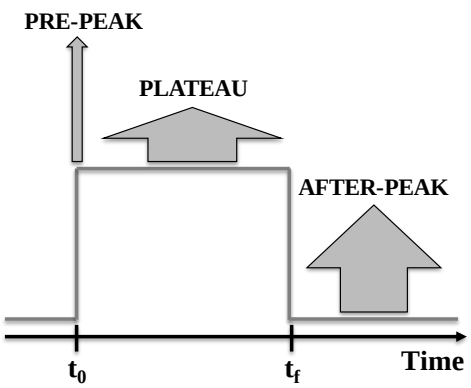


Figure 13. *The different temporal regions within the pulsed discharge.*

○ **Pre-peak.-** This region corresponds to the primary instants of the discharge pulse. In this region, ionisation processes occur through electron impact and elemental information can be obtained.

○ **Plateau.-** The region behind the pre-peak to the end of the pulse is the plateau region. During this period the plasma reaches a pseudo-stationary state with similar characteristics to the one obtained when applying a continuous discharge.

○ **After-peak or afterglow.-** The after-peak region occurs after the end of the pulse. It is characterised by a considerable increase of the metastable argon population that will interact with the sputtered sample ions to ionise them through Penning Ionisation.[61]

B.2.4. Glow Discharge coupled to Optical Emission Spectrometry

Glow discharges for analytical purposes can be coupled to two types of detection techniques, to optical detection or, alternatively, to mass detection.[62,63] Thus, analytical applications of present glow discharges for gas, liquid and direct solid sample analysis, are carried out by coupling them to Optical Emission Spectrometry and Mass Spectrometry instruments[60, 64, 65] (see Fig. 14). The latter MS-based techniques fall beyond the scope of this work.

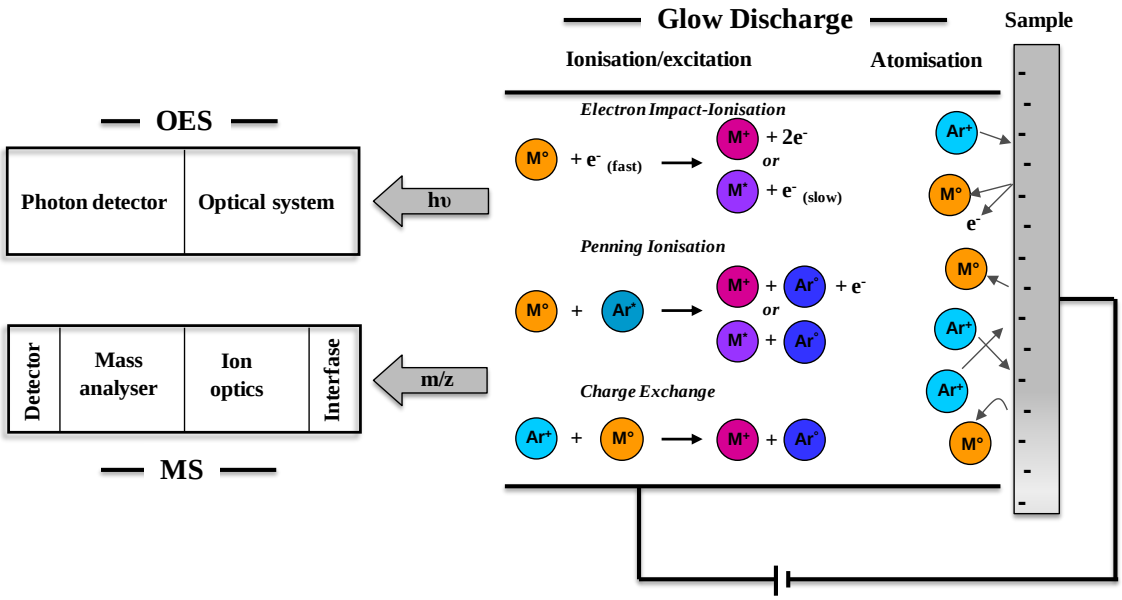


Figure 14. *Basic processes and instrumentation for GD-OES and GD-MS.*

Generally, optical emission instruments include various basic components: (a) a stable spectrochemical source emitting radiant energy (in our case this will be the GD source), (b) a device to isolate a restricted region of the spectrum (a wavelength) for its measurement, (c) a radiation detector (transducer) to convert the radiant energy in a measurable signal (generally electrical) and (d) a data acquisition system. The most significant parts of such optical spectrometers include:

♦ **The spectrometer.**

With the glow discharge source itself (with its associated gas and power supplies, vacuum pumps and controls) the spectrometer is the most important part of a GD-OES instrument. To make appropriate use of the analytical capability of the GD source, the spectrometer should have a sufficient spectral resolution and an adequate spectral range.

Although different types of spectrometers exist, the dispersive type (including poly- and monochromators) is widely used in UV-VIS regions, due to its capability to carry out continuous wavelength scanning and its wide wavelength range. Depending on the application, a commercial spectrometer can cover the wavelength range from 110-800 nm, which contains the most sensitive lines of the elements as Li, Be, B, C, etc. and molecular gases (H, O, N, Cl, etc.). A high spectral resolution is required to avoid spectral interferences of analyte lines with emission lines of other elements, of the sample or of the discharge gas.[7]

The most commonly used designs are the *Paschen-Runge polychromator* configuration (Fig. 15a) for simultaneous detection and the *Czerny-Turner monochromator* (Fig. 15b) for sequential analysis. In the Paschen-Runge mount, the concave grating focuses the spectral line intensities of pre-selected elements onto fixed exit slits, which are positioned on the Rowland circle (represented in Fig. 15a). Up to 64 elements can be detected simultaneously in this way.

In the Czerny-Turner mount only one exit or secondary slit is present. Thus, only a line of quasi-monochromatic radiation is observed at the exit slit. By rotating the plane grating around its axis it is possible to scan a spectral range (line spectrum) and to profile an emission line, by minimising background radiation and excluding neighbouring spectral lines.

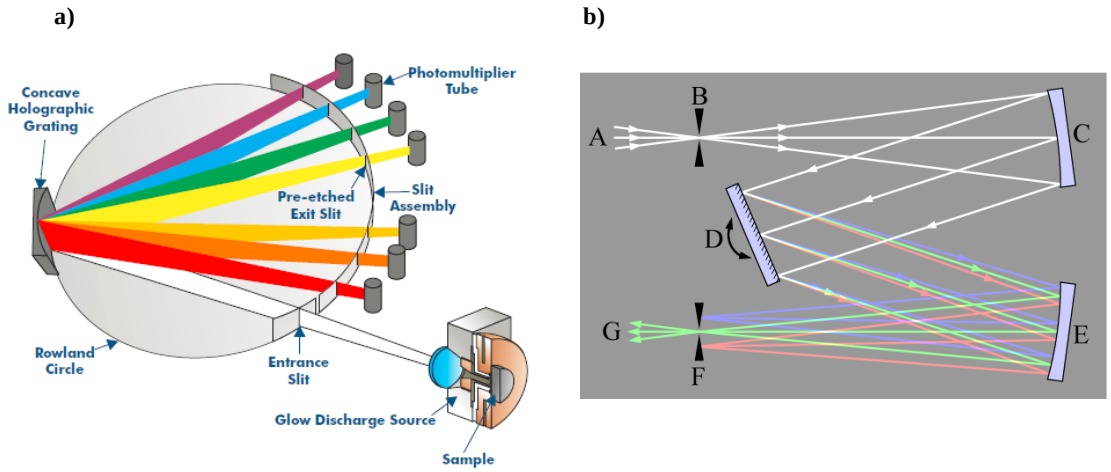


Figure 15. *a) Paschen-Runge polychromator design, and b) Czerny-Turner mount monochromator.*
A: GD source, B: entrance slit to provide a rectangular optical image, C: collimating lens or mirror to produce a parallel radiation beam, D: grid to disperse the radiation into its individual wavelengths, E: focussing element to project the image upon the focal plane, F: exit slit to isolate the desired spectral band, and G: detector.

♦ **Optical emission detectors (photodetection).**

The "monochromatic" desired optical radiation passing the exit slit(s) of the spectrometer is transduced to a signal and finally measured by the detector system. The ideal transducer should present a high sensitivity, a high signal-to-noise ratio and a constant response in a relative wide wavelength interval. Also, a fast response time and an exit signal equal to zero in absence of illumination are required and, finally, the electrical signal produced by the transducer should be directly proportional to the radiation power of the spectral line. The analogue output signals are amplified, converted into digital information and transferred to a computer for further data processing and read-out. Two main different types of photon detector are used:

The photomultiplier tube (PMT).- The first photomultiplier tube documented was in 1934 by Iams and Salzberg from RCA Coorperation, integrating the photoelectric effect and a single secondary emission amplification stage in a single vacuum envelope.[66] Nowadays, it is the most commonly used UV-VIS detector in most commercial spectrometers. In the polychromator system each detection channel is equipped with an individual exit slit, a PMT and the corresponding high voltage supply. Each supply can be

adjusted individually to afford appropriate sensitivity for each analyte element required to match the selected analytical conditions.

The PMT consists of a glass envelope with a high vacuum inside, which houses a photocathode and a series of dynodes, represented in Fig. 16. When radiation strikes upon the photocathode's surface, photoelectrons are emitted as a consequence of the photoelectric effect. These generated photoelectrons are accelerated towards the first dynode, sustained at a higher positive potential than the cathode, from which additional electrons are emitted by each strike of a photoelectron upon its surface through secondary emission processes. The geometry of the dynode chain is such that a cascade occurs with an ever-increasing number of electrons being produced at each stage (10^6-10^7 electrons for each incoming photon striking the photocathode). Finally, this electron cascade is collected at an anode, where the resultant electrical current is measured.

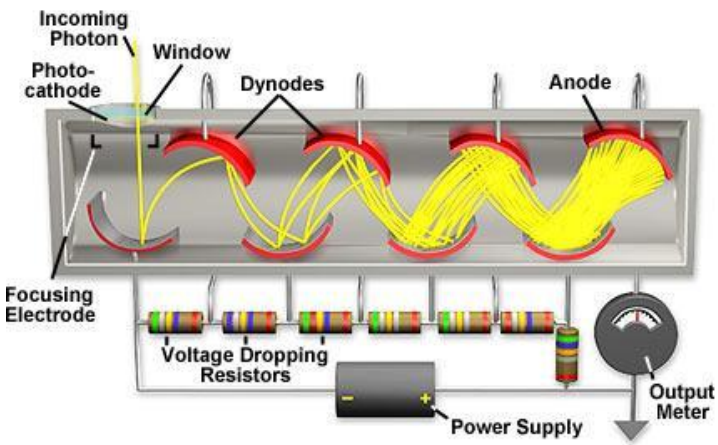


Figure 16. *Transversal view of a photomultiplier tube.*

Solid State Detectors.- These detectors are also called Semi-conductor Radiation Detectors in which a semi-conductor material such as Si, Ge, CdTe, HgI_2 or CdZnTe constitutes the detecting medium. The best detector for a given application depends on several factors. Their working principle consists of collecting the charge generated by ionisation radiation in a solid. The applied high voltage generates a 'depletion layer' (layer depleted of free charges) and any charge created by radiation in this layer is collected at an electrode (see Fig. 17). The charge collected is proportional to the energy

deposited in the detector and therefore, these devices can also yield information about the energy of individual photons of radiation. Different types of solid-state detectors exist today including photodiodes, avalanche photodiodes, diode arrays, charge-coupled devices, [67] etc. and their application field is very broad. [68]

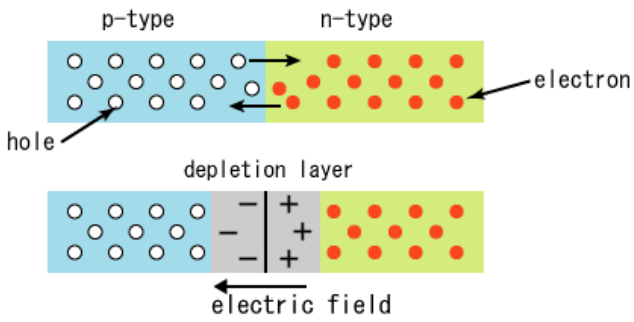


Figure 17. *Working principle of a solid-state detector.*

B.2.5. Analytical characteristics of GD

The continuous increase in popularity that glow discharge has had in the last years is due its advantageous properties as a direct solids analysis technique. Some of the principal performance analytical characteristics of GDs are briefly commented in the following paragraphs, so a general impression can be attained of the capabilities of this technique:

1. Minimal matrix effects.- Due to its intrinsic behaviour (the sputtering in a glow discharge distinguishes this source from most of the other spectroscopic ones for direct solids analysis) a natural separation exists between the initial sputtering process (atomisation) and the excitation and ionisation processes. Atoms sputtered out of solid sample matrices loose the chemical information of their past environment as they dilute into the inert Ar atmosphere. It is in the discharge plasma where excitation and ionisation occur and this mechanism accounts for the low comparatively matrix effects usually observed with GDs.

2. Sample versatility.- The glow discharge does not only allow the direct solids analysis of conducting samples, but also of semi-conducting and insulating samples, when the discharge is generated by radiofrequency instead of using direct current.[69-71]

3. High sensitivity and multi-element analysis.- The source allows multi-element detection (sequential or simultaneous, depending on the use of a mono- or polychromator) and the limits of detection are in the range of μg g^{-1} (ppm) for optical emission spectrometry and of ng g^{-1} (ppb) for mass spectrometry.

4. Sputtering rate and its uniform response.- The high sputtering rate of the solid sample, achieved by GD, allows the study of relatively thick coatings (~100 μm) in short time intervals (in the range of minutes). Moreover, all the elements of a given sample show relative uniform sputtering yields, defined as the number of atoms sputtered for each Ar ion impact.

5. Uniform sputtering and high in-depth resolution.- This is one of the most important characteristics of glow discharge. Due to this uniform sputtering, depth profiles with a high resolution (in the range of nm) can be obtained.

6. Low gas consumption.- The flow rate of the discharge gas is very low (<1 L/min) compared to flows used in, for example, ICP reducing considerably the overall operation cost.

7. Choice of discharge gas.- Although the most commonly used discharge gas in GD is high purity Ar, other gases can be employed as well. Noble gas mixtures, such as Ar/He or Ar/Ne, affect the plasma processes through the modification of the ionisation potentials, the metastable population and the emission yields.[72,73] On the other hand, the presence of small amounts (less than 0.1%) of certain elements (H or N) in the Ar discharge gas can produce different effects on both the sputtering rates and the emission intensities.[74,75]

8. Sample-to-sample reproducibility and plasma stability.- The reproducibility depends on the reproducibility of sample positioning and discharge conditions (voltage, current, power and pressure), parameters which can adequately be controlled, in order to obtain a constant atomic population out of the solid sample. Moreover, it has been demonstrated that the plasma stability or the time to reach a steady-state is very short under typical discharge conditions.[23]

9. Auto- and surface cleaning.- A critical step in the determination of trace elements is the elimination of superficial contamination without introducing new contaminants during this cleaning step. As the glow discharge is able to produce layer-by-layer sputtering, atomic sample polishing via previous sputtering of the sample with a high purity gas (eliminating in this way the superficial layers which could be contaminated) before the final analysis is possible.[76]

10. Low pressure and power.- Typically, the glow discharge is employed at low pressure, within a range of a few torr, so high vacuum conditions are avoided which simplifies the instrumentation and decreases the overall cost. Moreover, powers lower than 100 W are applied (with exception of the pulsed mode) so a small and cheap source is adequate to carry out the desired analysis.

11. Versatility of the detection mode.- The use of the GD as spectrochemical source allows the versatile coupling of it to different detection systems.[77] Of course, the discharge chamber configuration should be modified, according the chosen detection system. Different measurement types can be carried out, leading to different analytical techniques such as Atomic Absorption Spectrometry, Optical Emission Spectrometry, Atomic Fluorescence Spectrometry and Mass Spectrometry.

○ **Atomic Absorption Spectrometry.-** The glow discharge is particularly appropriate to generate atoms for AAS because the overwhelming majority of the sputtered species are neutral. However, this is not a very popular experiment.

○ **Optical Emission Spectrometry.-** As a fraction of the atoms sputtered from the solid sample surface is excited in the plasma, the subsequent decay produces the emission of photons with wavelengths characteristic for each element constituting the sample. Thus, GD-OES constitutes a rapid and modern technique for surface, coating, interface and homogenous solids analysis.[78]

○ **Atomic Fluorescence Spectrometry.-** The atoms produced in the GD are excited by an external optical source (*e.g.* laser) with energies suitable for

fluorescence measurements. The technique is similar to OES but a previous absorption of light from a laser takes place.

○ **Mass Spectrometry.-** Given that some of the generated atoms from the solid sample can be sufficiently excited in the discharge as to lose an electron, the resultant ions can directly be sampled and measured in a mass spectrometer. The GD ion source has gained popularity because of its stability, sensitivity and simplicity of operation. Elemental analysis by GD-MS offers critical advantages over competing techniques as this source can be applied to metal and non-metals exhibiting high sensitivity, offering minimal matrix effects and providing isotopic information.

Although most GD measurements are designed to use only one of these approaches, simultaneous application of more than one is possible, denominated "tandem" spectrochemical sources. Here, an alternative source is used to increment the generation efficiency of excited atoms and ions. This is the case of Furnace Atomisation Non-Thermal Excitation Spectrometry in which the glow discharge only acts as excitation or ionisation source, coupled to the graphite furnace.[79] Laser-assisted techniques constitute another example, in which a more efficient ionisation is obtained by laser.[80]

B.3. Glow Discharge for Direct Solids Analysis

As mentioned previously, one of the most important applications of glow discharges coupled to optical emission detection is the direct analysis of solid samples of various matrices within a wide range of concentration. Moreover, both "bulk" and "in-depth" analysis can be carried out. "Bulk" analysis refers to the determination of the elemental composition of homogenous solids, while "in-depth" analysis consists of revealing the identity and determining the concentration of the elements composing the sample as a function of their depth, relative to the sample surface.

B.3.1. Bulk analysis

Thanks to the analytical characteristics of this technique, a quantification method for homogeneous materials has been established, using both the direct current and the

radiofrequency glow discharges, which is the basic formulation of the "standard model".[81] The standard model can be used as a reference to define the 'expected' behaviour of different spectral lines and their groups. Any deviations from that 'regular behaviour' that cannot be explained within this standard model (*i.e.* through a proper choice of its parameters) can be treated as matrix effects and requires additional explanation.

As mentioned before, an important quantity of the glow discharge technique is the sputtering rate, usually denoted as Q_M, and defined as the amount of sputtered sample from the surface within a time unit. This rate depends on the matrix and the discharge conditions.[82,83] The index M specifies the matrix, *i.e.* the analysed material. If a series of materials is analysed, containing an element E at various concentrations $C_{E,M}$ and if a selected emission line λ(E) of this element is recordered, its emission intensity $I_{\lambda(E),M}$ will depend on the concentration of the element E as:

$$I_{\lambda(E),M} = C_{E,M} \cdot Q_M \cdot R_{\lambda(E),M} \qquad (3)$$

where $R_{\lambda(E)}$ is a proportionality factor called the emission yield of that particular line. In the case the discharge conditions are kept constant throughout the whole series of measurements, $R_{\lambda(E)}$ is assumed to be characteristic of that particular line and independent of the analysed matrix.[84] The standard model is by its nature a semi-empirical scheme and not all its parameters are related in a simple way to the fundamental quantities and physical parameters of the glow discharge plasma. However, this model describes real-life GD-OES analysis with a high level of accuracy in many common situations and is widely used in analytical practice.[23]

Both the calibration as the analysis should be carried out at constant working conditions to avoid errors due to sputtering rate and emission yield variations in time and between each sample. During the calibration, reference materials with a homogeneous composition are used. It is suggested to use the internal standard method, where relative intensities are represented to these of a reference element, usually the major element of the matrix, as a function of the ratio of the respective concentrations. Implementing this information in eq. (3) and considering Q_M is constant in a given sample we obtain:

$$\frac{I_{\lambda(E),\,M}}{I_{\lambda(E),\,ref}} = \frac{C_{E,\,M}}{C_{E,\,ref}} \cdot \frac{R_{\lambda(E),\,M}}{R_{\lambda(E),\,ref}} \qquad (4)$$

where $I_{\lambda(E),ref}$, $C_{E,ref}$ and $R_{\lambda(E),ref}$ are the emission intensity, the concentration and the emission yield of the reference element, respectively.

B.3.2. Thin film analysis

Due to the layer-by-layer ablation in glow discharges with flat cathodes, depth profile analysis was found to be one of the most important analytical features of glow discharges, as demonstrated by Berneron and Green and Whelan in the seventies.[85,86] A commercial prototype was made available in 1978, based on the work of Berneron exploring the use of GD-OES for depth profiling analysis.

Between 1978 and 1985, GD-OES emerged as a promising technique among the most widely used for surface analysis and for the in-depth analysis of relatively thick layers (within the range of micrometers), particularly for galvanised and painted steels[87,88] and occasionally for the depth profile analysis of thin films.[36,89] Traditionally, it has been considered that the outermost surface regions of the solid sample were not accessible, by both GD-OES and GD-MS, due to the often observed discharge instabilities at the beginning of the analysis. Nevertheless, recent studies related to the source design and improved control[90] of the different parameters changed that previous picture, demonstrating the analytical potential of the GD for the analysis of thin layers (less than 100 nm).[91,92]

When analysing layered samples by glow discharge qualitative and quantitative in-depth analysis should be differentiated. Qualitative analysis refers to the plot of variation of the emission intensities of the different emission lines, of the respective elements present in the sample of interest, as a function of the sputtering time (see Fig. 18a). However, for quantitative analysis the variation of the concentration of the corresponding elements is plotted versus the corresponding depth (relative to the sample surface), as can be observed in Fig 18b.

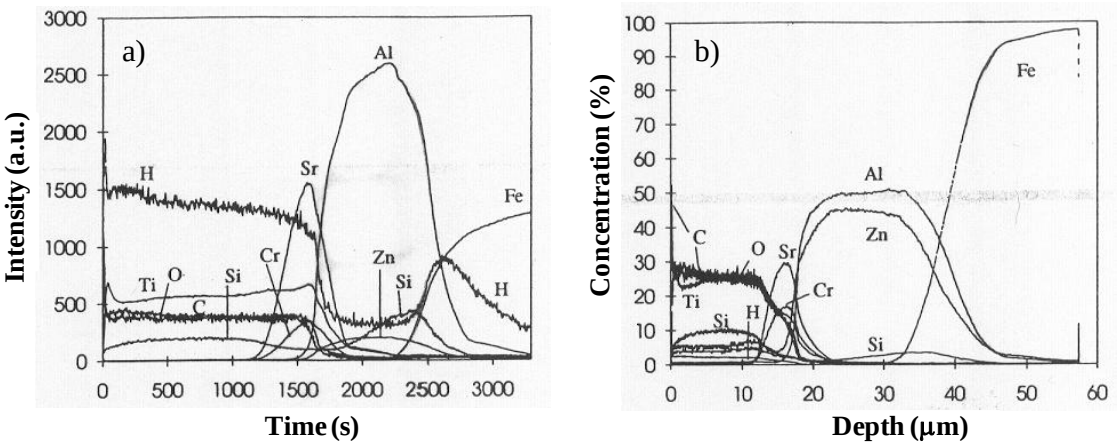


Figure 18. *Depth profiles of a galvanised steel with a superficial paint coating. a) Qualitative depth profile. b) Quantitative depth profile.*

B.3.2.1. Qualitative in-depth analysis

The possibility to study, by GD, the variation of the composition of a material as a function of its distance from the outer layer of the surface is due to the characteristic layer-to-layer ablation, occurring at a rate which depends on the sample material and the discharge conditions. The Grimm type discharge chamber[30,35] (reported in 1968) provided an excellent design for depth profiling analysis, due to the possibility to generate flat-bottomed craters in the surface. When carrying out such depth profiling analysis, the following points should be considered:

○ **Crater shape.-** The shape of the crater produced in the sample by the sputtering process depends on the discharge conditions[93] and determines the depth resolution.[94,95] A flat bottom should be obtained with perpendicular crater walls, so the information detected at any moment corresponds to the atoms proceeding from the same atomic sample layer.

○ **Variation of the parameters controlling the discharge.-** It is frequent that during the analysis and due to sample matrix changes, the electrical conditions and/or the discharge pressure vary. Such variations produce sample sputtering rate variations and this can lead to important differences between the appearance of the qualitative and quantitative profiles.

○ **Impossibility of using a major element from the sample as internal standard for quantification.-** In the case of coatings the main composition may

vary considerably with the sampling depth which makes it impossible to use the major element as internal standard.

B.3.2.2. Quantitative in-depth analysis

The determination of the quantitative depth profile (material composition as a function of its distance to the external layer of the surface, see Fig. 18b) requires quantification methods to convert the emission intensity measurements to element concentration and the sputtering time to penetration depth into the material.[84,96,97] While in bulk analysis this conversion is straightforward, the analysis of layered samples encounters a series of difficulties, derived from the presence of various matrices in the same solid sample, giving rise to changes in sputtering rates during the analysis.[98]

The quantification method most widely used is based on the concept of constant emission yield, which can be defined as "*the measured emitted light per unit sputtered mass of an element*". Experimentally, it is easy to show that the emission intensity of an analytical line measured by GD is not just proportional to the concentration of the corresponding element in the sample. The observed light intensity depends also on the sputtering rate of the sample. This observation is easy to understand: photons are generated in the negative glow, therefore, the emission intensity should be proportional to the sample atom density in the plasma, which in turn is directly linked to the sputtering rate. It is important to keep the discharge parameters, such as voltage, current, pressure and power, constant to avoid irreproducible operation. As long as the excitation conditions in the plasma remain constant, the sputtering rate – intensity proportionality provides a satisfying solution to the quantification problem. The basic assumption is that the integrated intensity from one element and spectral line is exclusively proportional to the sputtered mass of that element. This implies that the emission yield is independent of the sample matrix. Thus, the "emission yield" is an atom- and instrument-dependent quantity, which must be determined (calibrated) independently for each spectral line and instrument. This basic assumption is, nowadays, accepted for the case of conductive samples, using dc glow discharges.[99]

Up to date different corrections have been developed for the quantification of depth profiles of conductors obtained through direct current discharges,[90,100] including corrections for the 'hydrogen effect', the dc bias, the density and the background signal.[101-103] Nevertheless, when applying radiofrequency discharges in the analysis of non-

conducting samples, similar as for bulk analysis, the precise control of the discharge parameters (current, voltage, power or pressure)[104] should be improved in order to develop accurate quantification methods. The knowledge of the real applied power, as well as the electrical current and the dc bias voltage developed on the surface of non-conductors, has allowed the development of quantification methods for rf-GD, in a similar way to those employed in the case of dc-GD analysis.[105] At that time, it was generally thought that rf-GD-OES was an interesting and necessary tool for non-conductive materials, but it could not be used for quantitative analysis. However, further work published[43] demonstrated that quantitative, bulk and surface, analysis is possible with rf-GD-OES.

The process to obtain a quantitative depth profile out of a qualitative depth profile requires the conversion of Intensity into Concentration and of Time into Depth. Due to the existence of different layers and therefore different matrices, equation (3) can be rewritten as follows:

$$I_{nmbs} = C_{nbs} \cdot Q_{bs} \cdot R_{nm} \qquad (5)$$

with C_{nbs} being the concentration of element n in layer b in sample s and Q_{bs} the sputtering rate of this layer b from sample s.

The qualitative depth profile offers information at first glance on the elements present in the sample. With this knowledge, a group of bulk certified reference materials (CRM), consisting of different matrices with varying certified element concentration, is selected. Once the CRMs are selected, the calibration can be carried out. Due to the use of such standards with varying matrices, a correction for the variation in sputtering rate should be taken in account. Therefore, the term Q_A (sputtering rate of the calibration standard A) is added on the abscise axis of the calibration curve. As the calibration function represents I_{nmA} in function of ($C_{nA} \bullet Q_A$), with C_{nA} the concentration of element n in standard A and I_{nmA} the intensity of the emission line m of element n in standard A, the emission yield of the analytical line of each element (R_{nm}) will be the slope of the calibration curve (eq. 5). This calibration is known as “Multi-matrix Calibration” and is employed in the quantification process of qualitative profiles obtained under the same fixed working conditions (voltage and current for dc, pressure and power for rf), following the next steps.

♦ Conversion Intensity to Concentration

The extracted mass of element n during a time unit Δt of sputtering is determined by

$$m_n(\Delta t) = I_{net} \cdot \Delta t \cdot R_n^{-1} \quad (6)$$

with R_n the emission yield of element n obtained from the respective calibration curve and I_{net} the net emission intensity measured for element n.

The total sputtered mass (M) in this time interval (Δt) will be the sum of all the elements (m_n) during this interval

$$M(\Delta t) = \sum_n m_n(\Delta t) \quad (7)$$

Finally, the concentration (C_n) of each element during each time interval can be calculated as a fraction of the above sum, as follows:

$$C_n(\Delta t) = \frac{m_n(\Delta t)}{M(\Delta t)} \cdot 100 \quad (8)$$

♦ Conversion Time to Depth

The conversion to depth from the sputtered mass requires a calculated estimate of the density of the material, which introduces a certain uncertainty. Various approximations exist to calculate the density of a sample from its elemental composition (given by the qualitative profile). There are four simple ways in which composition might be used to predict density: (a) if density varies with the density of the pure constituents according to their mass fractions; (b) if density varies with the density of the pure constituents according to their atomic fraction; (c) if the atomic volumes of the atoms are independent of the composition; and (d) if the densities of a large number of materials are listed in a table and the density is assumed to equal the one with the closest match in composition. Payling et al.[23] evaluated the best of the first three approaches and, overall, found the best approach to be when using constant volume, slightly

ahead of atomic fraction (mass fraction was unsatisfactory). In this case, the extracted volume in each time interval can be determined as

$$V(\Delta t) = \sum_n \frac{m_n(\Delta t)}{\rho_n} \tag{9}$$

with ρ_n the density of each element present in the time interval.

If the sputtered volume is assumed to have a cylindrical form, with a base equal to the one of a circle with radius (r) equal to that of the anode, obtaining in this way the height of this cylinder or, which is the same, the depth of the crater in each time interval, it follows that:

$$Depth(\Delta t) = \frac{V(\Delta t)}{(\pi r)^2} \tag{10}$$

So, the concentration of each element and depth is calculated for each time interval, obtaining the quantitative profile of the sample of interest.

B.4. Glow Discharge Applications

Nowadays, glow discharges are considered as well-established analytical techniques allowing the analysis of both homogeneous solid samples (bulk) and coated samples (depth profile) and this for a wide range of applications.

B.4.1. Bulk analysis

The field of applications of glow discharges related to the analysis of homogeneous bulk samples extends itself from the steel industry and its alloys to the analysis of semi-conductors or environmental samples.

○ **Steels and Alloys.-** Steel was one of the first materials[88,106] analysed by glow discharge. GDs are most appropriate for the analysis of steels[87, 107 , 108] and different alloys such as Cu-Zn, Al-Zn, Al-Si, etc.[109-111]

○ **Semi-conductors.-** Due to the increasing demand of such materials in the industry (electronics, solar cells, photovoltaic cells, etc.) the use of GD in this field experienced a progressive growth. Numerous applications are described on the analysis of impurities, trace and ultra-trace elements in different types of solid semi-conductors.[69,70,112,113]

○ **Glasses and Ceramics.-** During the 20th century the industrial production of silica glass began due to its outstanding and physical properties and research in the field of science and technology led to the development and use of specialised glasses such as in fiber optics, electro-optics etc. Their properties and technical parameters are greatly dependent on the presence of certain elements within tight concentration ranges and may be affected by impurities that are trapped inside.[114] Therefore, different applications of GD for the analysis of glass samples[71,115,116] and glass-ceramics or glass powders[117,118] have been widely reported.

○ **Polymers.-** Because of the extended use of inorganic and organic polymeric material today, more and more applications of their analysis using GDs (for example for polycarbonates, polytetrafluoroethylenes etc.[119]) are increasingly reported in literature.

○ **Bone.-** The analytical potential of GD has also been demonstrated in the biomedical field through the analysis of the elemental composition of bones by rf-GD-OES[120] and the determination of P/C and Ca/C ratios, which can directly be related with the diagnostic of osteoporosis.

○ **Environmental samples.-** The nature of this type of sample varies a lot, from dust and sediments to dried organic substances (from animals or plants). As GD spectroscopy is a relative method, the calibration required for the quantification is the main limitation (due to the lack of appropriate reference materials for this kind of samples). In any case, the high interest of this spectrochemical source as chromatographic detector for gas samples should be highlighted.[121]

B.4.2. Thin film analysis

The use of GD for the in-depth analysis of thin films and coatings extends within a wide range of applications, from metallic coatings in the steel industry[122,123] to more specific cases such as organic coatings[124,125] and prosthetic devices,[126] where the depth distribution of nitrogen is studied in Co-Cr-Mo alloys. Applications of in-depth analysis by glow discharge are described, using both optical emission and mass spectrometry detection. The latter one is mostly employed for the detection of trace and ultra-trace elements ,while GD-OES is highly developed for the analysis of thin films.[94,127]

In recent years, GD techniques have shown rapid growth in number of sold instruments, in the variety of applications and in improved quantification methods. This broad success in quantitative characterisation of coatings, from a few micrometers up to 100 μm, has prompted applications of GD-OES to depth profiling of thin films. Below, a brief selection is given of the analytical applications developed so far for GD-OES in the area of thin and ultra-thin film analysis, while the concluding Table 4 summarises more details of some of those applications.

○ **Steels and Alloys.-** The GD allows the analysis of a great variety of coatings deposited on such substrates, such as anti-corrosive Zn electroplated coatings[48,64], air-formed oxide films less than 5 nm thick on a stainless steel film[91], titania coatings as colour coded biocompatible coatings on biomedical implants,[128] metal nitrides on steels,[36] metal oxides on galvanized steels,[129] etc.

○ **Hard disks.-** Shimuzu et al.[91] proved the ability of rf-GD-OES for the in-depth analysis of hard disks used for magnetic data storage, which compromise conductive and non-conductive layers of different thickness: e.g. amorphous Ni-P layers of about 12 μm with Cr, Co/Cr and diamond like carbon layers (each of 20-30 nm) on top. Further, those disks contain numerous elements, as well as various process-related impurities or contaminants that are important to be monitored and controlled during the production process.

○ **Glasses and Ceramics.-** The characterization of thin films on glasses[39,94] and ceramics [130] is analytically challenging and benefits from recent basic developments in rf-GD-OES. Le Coustumer et al.[131] demonstrated the practical utility of the qualitative profiles obtained for several glasses (including a multi-

layered triple-coated glass, photo-reactive glasses and an acid-leached glass with an alternation) for the characterization of physical discontinuities and diffusion processes. Other applications consist on the investigation of possible element migration between the deposited coatings and glass substrate.[132]

○ **Ultra-thin films.-** To conclude this Introduction, various applications should be stressed related to the depth analysis of ultra-thin films by GD (less than 10 nm thickness) including: anodic alumina films of varying thickness, with delta function marker layers of about 2 nm width, located at various depths from the oxide surface films,[91,133] Cr marker layers of 2.5 and 5 nm thickness buried in a Ti matrix,[134] a sub-nanometer thick thiourea monolayer absorbed on a mirror-polished copper substrate,[135] the measurement of trace elements in ultra-thin titanium oxide layers,[21] etc. The different nature of the coatings described demonstrates the present great potential of the GD technique for depth profiling analysis.

Table 4. Examples of applications of GD for thin film analysis.

Substrate	Coating (s)	Film thickness	Reference
Stainless steel	Air-formed oxide film	< 5 nm	102
Steel	CrAlN/CrN	300 nm/300 nm	46
Glass	SiO_2/TiO_2 Si_3N_4/SiO_2	133 nm/76 nm 100 nm/100 nm	46
Aluminium	Hydrated alumina film	~4 nm	102
Galvanized steel	Al_2O_3	4 nm	143
Titanium alloy T6Al4V	TiO_2	60 nm	142
Glass	$SiO_2/TiO_2/SiO_2$-TiO_2	90 nm/120 nm/60 nm	105
Hard disk	Amorphous Ni-P layers Co-Cr	12 mm 20-30 nm	102
Glass	$SnO_2/SiO_2/TiO_2$	90 nm/120 nm/60 nm	145
Titanium	TiO2	~300 nm	147
Aluminium	Cr delta-marker layer	~2 nm	102, 150
Glass	TiO_2/SiO_2	42-75 nm/10 nm	146
Copper	Monolayer of thiourea	Sub-nm	152
Silicon	Cr/CrN	110-270-1000 nm	136

B.5. References

[1] R.W. Cahn, "The Coming of Materials Science", Elsevier, Oxford, UK, 2001.

[2] D.L. Smith, "Thin-film deposition: principles & practice", McGraw-Hill Inc., USA, 1995.

[3] J.M. Abella, "Laminas Delgadas y Recubrimientos: Preparacion, Propiedades y Aplicaciones", Consejo Superior de Investigaciones Cientificas, Madrid, 2003.

[4] T. Wagner, "Thin Film Science", Max-Planck-Institute für Metallforshung, www.mpg.de/pdf/.../wb_materials_196_200.pdf.

[5] D. Vollath, "Nanomaterials: An introduction to synthesis, properties and applications", Wiley-VCH, Germany, 2008.

[6] R.K. Marcus, 'Glow Discharge Spectroscopies', Plenum Press, New York, USA, 1993.

[7] H. Bubert, H. Jenett, 'Surface and Thin Film Analysis', Wiley-VCH, Weinheim, Germany, 2002.

[8] B. Fernández, J.M. Costa, R. Pereiro, A. Sanz-Medel, 'Inorganic mass spectrometry as a tool for characterisation at the nanoscale', *Anal. Bioanal. Chem.*, **396** (2010) 15.

[9] R.K. Marcus, J.A.C. Broekaert, "Glow Discharge Plasmas in Analytical Spectroscopy", John Wiley & Sons, Chichester, 2003.

[10] R.E. Russo, X.L. Mao, C. Liu, J. Gonzalez, 'Laser assisted plasma spectrochemistry: laser ablation', *J. Anal. At. Spectrom.*, **19** (2004) 1084.

[11] Y.F. Lu, X.K. Shen, H. Ling, 'Laser-induced breakdown spectroscopy combined with spatial confinement of plasmas and laser-induced fluorescence for trace-elements detection'**,** *Proceedings of the ASME Micro/Nanoscale Heat and Mass Transfer International Conference 2009, MNHMT2009*, **1** (2010) 697.

[12] IUPAC Compendium of Chemical Terminology. *PAC*, **55** (1983) 2024.

[13] N.H. Turner, J.A. Schreifels, 'Surface analysis: X-ray photoelectron spectroscopy and Auger lectron spectroscopy', *Anal. Chem.*, **70** (1998) 229R.

[14] S. Hofmann, 'Advances in sputter depth profiling using AES', *Surf. Interface Anal.*, **35** (2003) 556.

[15] J.G.M. Van Berkum, M.J.P. Hopstaken, J.H.M. Snijders, Y. Tamminga, F.N. Cubaynes, 'Quantitative depth profiling of SiOxNy layers on Si', *Appl. Surf. Sc.*, **203** (2003) 414

[16] S. Shuttleworth, D.T. Kremser, 'Assessment of laser ablation and sector field inductively coupled mass spectrometry for elemental analysis of solid samples', *J. Anal. At. Spectrom.*, **13** (1998) 697.

[17] J.R. Bacon, J.C. Greenwod, L.V. Vaeck, J.G. Williams, 'Atomic spectrometry update. Atomic mass spectrometry', *J. Anal. At. Spectrom.*, **19** (2004) 1020.

[18] S. Dreer, P. Wilhartitz, K Piplits, H. Hutter, M. Kopnarski, G. Friedbacher, 'Quantitative sputter depth profiling of silicon- and amuminium oxynitride films', *Mikrochim. Acta*, **133** (2000) 75.

[19] A. Thobor, C. Rousselot, S. Mikhailov, 'Depth profiles study of n(TiN+AlN) bilayers systems by GDOES and RBS technique', *Surf. Coat. Technol.*, **174** (2003) 351.

[20] V. Hoffmann, M. Kasik, P.K. Robinson, C. Venzago, 'Glow Discharge Mass Spectrometry', *Anal. Bioanal. Chem.*, **381** (2005) 173.

[21] M. Hohl, A. Kanzari, J. Michler, T. Nelis, K. Fuhrer, M. Gonin, 'Pulsed r.f.-glow discharge time-of-flight mass spectrometry for fast surface and interface analysis of conductive and non-conductive materials', *Surf. Interf. Anal.*, **38** (2006) 292.

[22] M. Betti, 'Isotope ratio measurements by secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS)', *J. Int. Mass Spectrom.*, **242** (2005) 169.

[23] R. Payling, D. Jones, A. Bengtson, 'Glow Discharge Optical Emission Spectroscopy', John Wiley & Sons Ltd., Chichester, 1997.

[24] P.C. Peng, H.M. Wang, J.Q. Li, H.Y. Han, X.Q. Xi, Y.N. Chu, 'Detection of metal residue in aqueous solutions by electrolyte cathode atmospheric glow discharge emission spectroscopy', *Spectrosc. Spectr. Anal.*, **30** (2010) 1948.

[25] W.C. Davis, F. Jin, M.A. Dempster, J.L. Robichaud, R.K. Markus, 'Development of a new liquid chromatography method for the separation and speciation of organic and inorganic selenium compounds via particle beam-hollow cathode glow discharge-optical emission spectroscopy', *J. Anal. At. Spectrom.*, **17** (2002) 99.

[26] J. Castro, M.V.B. Krishna, J.R. Choiniere, R.K. Markus, 'Analysis of caffeic acids derivatives in Echinacea extracts by liquid chromatography particle beam mass spectrometry (LC-PB/MS) employing electron impact and glow discharge ionization sources', *Anal. Bioanal. Chem.*, **397** (2010) 1259.

[27] J.P. Guzowksi Jr, G.M. Hieftje, 'Gas sampling glow discharge: A versatile ionization source for gas chromatography time-of-flight mass spectrometry', *Anal. Chem.*, **72** (2000) 3812.

[28] C.G. Gago, J. Pisonero, R. Pereiro, N. Bordel, P.M. Ramos, A. Sanz-Medel, 'Evaluation of a glow discharge chamber coupled to time of flight mass spectrometry for the analysis of small gas volumes and bubbles in glass', *J. Anal. At. Spectrom.*, **25** (2010) 1612.

[29] A. Solà-Vázquez, A. Lara-Gonzalo, J.M. Costa-Fernández, R. Pereiro, A. Sanz-Medel, 'Gas chromatography coupled to tunable pulsed glow discharge time-of-flight mass spectrometry for environmental analysis', *Analyst*, **135** (2010) 987.

[30] W. Grimm, 'Glimmentladungslampe für spektralanalytische Routinemessungen', *Naturwiss.*, **54** (1967) 586.

[31] S. Caroli, "Low-pressure discharges: fundamental and practical aspects. A review", *J. Anal. At. Spectrom.*, **2** (1987) 661.

[32] W.W. Harrison, F. Adams, R. Gijbels, R. Van Grieken, 'Inorganic Mass Spectrometry', John Wiley & Sons, New York, 1988.

[33] W.A. Mattson, B.L. Bentz, W.W. Harrison, 'Coaxial cathode ion source for solids mass spectrometry', *Anal. Chem.*, **48** (1976) 489.

[34] D. Fang, R.K. Marcus, 'Parametric evaluation of sputtering in a planar, diode glow discharge-1. sputtering of oxygen-free hard copper (OFHC)', *Spectrochim. Acta Part B*, **43** (1988) 1451.

[35] W. Grimm, 'Eine neue glimmentladungslampe für die optische emissionsspektralanalyse', *Spectrochim. Acta B*, **23** (1968) 443.

[36] V-D. Hodoroaba, W. E. S. Enger, H. Jenett, V. Hoffmann, B. Hagenhoff, S. Kayser, K. Wetzig, 'Depth profiling of electrically non-conductive layered samples by RF-GDOES and HFM plasma SNMS', *Appl. Surf. Sci.*, **179** (2001) 30.

[37] J. Reese Roth, 'Industrial Plasma Engineering, Volume 1, Principles', IOP Publishing Ltd., 1995.

[38] S. Caroli, A. Alimonti, K. Zimmer, 'Applicability of a hollow cathode emission source for determining trace elements in electrically non-conducting powders', *Spectrochim. Acta Part B*, **38** (1985) 625.

[39] B. Fernández, A. Martin, N. Bordel, R. Pereiro, A. Sanz-Medel, 'In-depth profile analysis of thin films deposited on non-conducting glasses by radiofrequency glow discharge-optical emission spectrometry', *Anal. Bioanal. Chem.*, **384** (2006) 876.

[40] A. Bengtson, S. Hänström, 'Emission yield for quantitative depth profile analysis by glow discharge optical emission-the influence of discharge parameters: Invited lecture', *J. Anal. At. Spectrom.*, **13** (1998) 437.

[41] L. Therese, Z. Ghalem, P. Guillot, P. Belenguer, 'Improved voltage transfer coefficients for nonconductive materials in radiofrequency glow discharge optical emission spectrometry', *Anal. Bioanal. Chem.*, **386** (2006) 163.

[42] B. Fernández, N. Bordel, R. Pereiro, A. Sanz-Medel, 'The effect of thin conductive layers on glass on the performance of radiofrequency glow discharge optical emission spectrometry', *J. Anal. At. Spectrom.*, **20** (2005) 462.

[43] M.R. Winchester, R. Payling, 'Radio-frequency glow discharge spectrometry: A critical review', *Spectrochim. Acta B*, **59** (2004) 607.

[44] R. Payling, J. Michler, M. Aeberhard, Y. Popov, 'New aspects of quantification in r.f. GDOES', *Surf. Interf. Anal.*, **35** (2003) 583.

[45] A. Sola Vazquez, J.M. Costa-Fernandez, J. Ruiz Encinar, R. Pereiro, A. Sanz-Medel, 'Quantification of bromine in flame- retardant coating by radiofrequency glow discharge-optical emission spectrometry', *Anal. Bioanal. Chem.*, **389** (2007) 683.

[46] R.K. Marcus, 'Operation principles and design considerations for radiofrequency powered glow discharge devices. A review', *J. Anal. At. Spectrom.*, **8** (1993) 935.

[47] M.J. Heintz, G.M. Hieftje, 'Effect of driving frequency on the operation of a radiofrequency glow discharge emission source', *Spectrochim. Acta Part B*, **50** (1995) 1125.

[48] C. Pérez, R. Pereiro, N. Bordel, A. Sanz-Medel, 'In-depth quantitative analysis of conducting coatings by radiofrequency glow discharge optical emission spectrometry: influence of the source operation methodology', *J. Anal. At. Spectrom.*, **15** (2000) 1247.

[49] Ph. Belenguer, M. Ganciu, Ph. Guillot, Th. Nelis, 'Pulsed glow discharges for analytical applications', *Spectrochim. Acta Part B*, **64** (2009) 623.

[50] Th. Nelis, M. Aeberhard, M. Hohl, L. Rohr, J. Michler, ,'Characterisation of pulsed rf-glow discharge in view of ist use in OES', *J.Anal. At. Spectrom.*, **12** (2006) 112.

[51] C. Yang, K. Ingeneri, M. Mohill, W.W. Harrison, 'Influence of discharge parameters on the resolution of depth profiling by pulsed glow discharge atomic emission spectrometry', *J. Anal. At. Spectrom.*, **15** (2000) 73.

[52] V. Majidi, M. Moser, C. Lewis, W. Hang, F.L. King, 'Explicit chemical speciation by microsecond pulsed glow discharge time-of-flight mass spectrometry: concurrent acquisition of structural, molecular and elemental information', *J. Anal. At. Spectrom.*, **15** (2000) 19.

[53] A. Solà-Vázquez, A. Martín, J.M. Costa-Fernández, R. Pererio, A. Sanz-Medel, 'Tuneable microsecond-pulsed glow discharge design for the simultaneous acquisition of elemental and molecular chemical information using a time-of-flight mass spectrometer', *Anal. Chem.*, **81** (2009) 2591.

[54] J.H. Barnes, O.A. Gron, G.M. Hieftje, 'Determination of Ca^+ and K^+ by pulsed glow discharge sector-field mass spectrometry', *J. Anal. At. Spectrom.*, **19** (2004) 1564.

[55] L. Li, C.M. Barshick, J.T. Millay, A.V. Welty, F.L. King, 'Determination of bromine in flame-retardant plastics using pulsed glow discharge mass spectrometry', *Anal. Chem.*, **75** (2003) 3953.

[56] R.E. Steiner, C.M. Barshick, A. Bogaerts, 'Encyclopedia of Analytical Chemistry', John Wiley & Sons Ltd., 2009.

[57] V. Hoffmann, V. V. Efimova, M. V. Voronov, P. Smid, E. B. M. Steers, J. Eckert, 'Measurement of voltage and current in continuous and pulsed rf and dc glow discharges', *J. Physics: Conference Series*, **133** (2008) 012017.

[58] A.C. Muñiz, J. Pisonero, L. Lobo, C. Gonzalez, N. Bordel, R. Pereiro, A. Tempez, P. Chapon, N. Tuccitto, A. Licciardello, A. Sanz-Medel, 'Pulsed radiofrequency glow discharge time of flight mass spectrometer for the direct analysis of bulk and thin coated glass', *J. Anal. At. Spectrom.*, **23** (2008) 1239.

[59] S. Canulescu, J. Whitby, K. Fuhrer, M. Hohl, M. Gonin, Th. Horvath, J. Michler, 'Potential analytical applications of negative ions from a pulsed radiofrequency glow discharge in argon', *J. Anal. At. Spectrom.*, **24** (2009) 178.

[60] L. Lobo, N. Tuccitto, N. Bordel, R. Pereiro, J. Pisonero, A. Licciardello, A. Tempez, P. Chapon, A. Sanz-Medel, 'Polymer screening by radiofrequency glow discharge time-of-flight mass spectrometry', *Anal. Bioanal. Chem.*, **396** (2010) 2863.

[61] R.E. Steiner, C.L. Lewis, V. Majidi, 'Consideration of a millisecond pulsed glow discharge time-of-flight mass spectrometer for concurrent elemental and molecular analysis', *J. Anal. At. Spectrom.*, **14** (1999) 1537.

[62] N.H. Bings, A. Bogaerts, J.A.C. Broekaert, 'Atomic Spectroscopy', *Anal. Chem.*, **76** (2004) 3313.

[63] N. Jakubowski, R. Dorka, E. Steers, A. Tempez, 'Trends in glow discharge spectroscopy', *J. Anal. At. Spectrom.*, **22** (2007) 722.

[64] M. Vázquez Peláez, J. Pisonero, J.M. Costa-Fernández, R. Pereiro, N. Bordel, A. Sanz-Medel, 'Analytical potential of a glow discharge chamber coupled to a time of flight mass spectometer for qualitative in-depth profile analysis', *J. Anal. At. Spectrom.*, **18** (2003) 612.

[65] C. González Gago, R. Pereiro, N. Bordel, P. Mazón Ramos, A. Tempez, A. Sanz-Medel, 'Analysis of small bubbles in glass by glow-discharge-Time-of-Flight mass spectrometry', *Anal. Chim. Acta*, **652** (2009) 272.

[66] H. Iams, B. Salzberg, 'The Secondary Emission Phototube', *Proc. IRE*, **23** (1935)55.

[67] A. Bengtson, 'Depth profiling of organic coatings with GD-OES – Investigation of molecular emission and interference', *J. Anal. At. Spectrom.*, **18** (2003) 1066.

[68] D. Bortoletto, 'Solid State Detectors', Nucl. Instr. and Meth. A, **623** (2010) 35.

[69] P. Sanchez, B. Fernández, A. Menendez, R. Pereiro and A. Sanz-Medel, 'Pulsed radiofrequency glow discharge optical emission spectrometry for the direct characterisation of photovoltaic thin film silicon solar cells', *J. Anal. At. Spectrom.*, **25** (2010) 370.

[70] A. Menéndez, N. Bordel, R. Pereiro, A. Sanz-Medel, 'Radiofrequency glow discharge-optical emission spectrometry for the analysis of metallurgical-grade silicon', *J. Anal. At. Spectrom.*, **20** (2005) 233.

[71] A.B. Anfone, R.K. Marcus, 'Radio frequency glow discharge optical emission spectrometry (rf-GD-OES) analysis of glass samples', *J. Anal. At. Spectrom.*, **16** (2001) 506.

[72] K. Wagatsuma, 'Emission spectroscopic study on gas-gas Interactions in glow discharge plasma using several Binary gas mixtures', *Anal. Sc.*, **26** (2010) 303.

[73] B. Lange, R. Matschat, H. Kipphardt, 'Enhancement of intensities in glow discharge mass spectrometry by using mixtures of argon and helium as plasma gasses', *Anal. Bioanal. Chem.*, **389** (2007) 2287.

[74] B. Fernández, N. Bordel, C. Pérez, R. Pereiro, A. Sanz-Medel, 'The influence of hydrogen, nitrogen or oxygen additions to radiofrequency argon glow discharges for optical emission spectrometry', *J. Anal. At. Spectrom.*, **17** (2002) 1549.

[75] A. Martin, A. Menéndez, R. Pereiro, N. Bordel, A. Sanz-Medel, 'Modifying argon glow discharges by hydrogen addition: Effects on analytical characteristics of optical emission and mass spectrometry detection modes', *Anal. Bioanal. Chem.*, **388** (2007) 1573.

[76] A.A. Lozovan, S.V. Frangulov, D.V. Chulkov, A.I. Rodin, 'Methods for cleaning the inner surface of small-diameter pipes with glow discharge prior to depositing coatings', *Weld Int.*, **24** (2010) 646.

[77] W.W. Harrison, C.M. Barshick, J.A. Klinger, P.H. Ratliff, Y. Mei, 'Glow discharge techniques in analytical chemistry', *Anal. Chem.*, **62** (1990) 943A.

[78] Th. Nelis, R. Payling, 'Glow Discharge Optical Emission Spectroscopy: a Practical Guide', RSC Analytical Spectroscopy Monographs, UK, 2003.

[79] J.M. Harnly, D.L. Styris, N.E. Ballou, 'Furnace Atomic Non-Thermal Excitation Spectrometry with the furnace as hollow cathode', *J. Anal. At. Spectrom.*, **5** (1990) 139.

[80] M. Tarik, D. Günther, 'A laser ablation millisecond-pulsed glow discharge time-of flight mass spectrometer (LA-GD-TOFMS) for quasi-simultaneous elemental and molecular analysis', *J. Anal. At. Spectrom.*, **25** (2010) 1416.

[81] Z. Weiss, 'Emission yields and the standard model in glow discharge optical emission spectroscopy: Links to the underlying physics and analytical interpretation of the experimental data', *Spectrochim. Acta Part B*, **61** (2006) 121.

[82] P.W.J.M. Boumans, 'Studies of sputtering in a glow discharge for spectrochemical analysis', *Anal. Chem.*, **44** (1972) 1219.

[83] L. Wilken, V. Hoffmann, K. Wetzig, 'Erosion rate measurements for GDOES', *J. Anal. At. Spectrom.*, **18** (2003) 1141.

[84] A. Bengtson, S. Hänström, E. Lo Piccolo, N. Zacchetti, R. Meilland, H. Hocquaux, 'Development of a standard method for quantitative depth profile analysis of zinc-based metallic coatings by direct current glow discharge optical emission spectroscopy', *Surf. Interf. Anal.*, **27** (1999) 743.

[85] R. Berneron, 'L'analyse des surfaces métalliques par spectrométrie d'émission à décharge luminscente', *Spectrochim. Acta Part B*, **33** (1978) 665.

[86] J.E. Green, J.M. Whelan, 'Glow discharge-optical emission spectroscopy for the analysis of thin films', *J. Appl. Phys.*, **44** (1973) 2509.

[87] R. Payling, 'Glow discharge optical emission spectroscopy', *Spectroscopy*, **13** (1998) 36.

[88] C.J. Belle, J.D. Johnson, 'In-depth compositional profile analysis of alloys using glow discharge optical emission spectrography', *Appl. Spectrosc.* **27** (1973) 118.

[89] S. Suzuki, K. Suzuki, K. Mizuno, 'Quantitative GDOS analysis of oxide films on steels', *Surf. Interface Anal.*, **22** (1994) 134.

[90] K. A. Marshall, 'A comparison of lamp control parameters in both bulk and depth profile analysis by glow discharge optical emission spectroscopy', *J. Anal. At. Spectrom.*, **14** (1999) 923.

[91] K. Shimizu, H. Habazaki, P. Skeldon, G. E. Thompson, 'Radiofrequency GDOES: a powerful technique for depth profiling analysis of thin films', *Surf. Interface Anal.*, **35** (2003) 564.

[92] T.K. Rout, 'Nanolayered oxide on a steel surface reduces surface reactivity: Evaluation by glow discharge optical emission spectroscopy (GDOES)', *Scripta Mater.* **56** (2007) 573.

[93] R.E. Galindo, E. Forniés, J.M. Albella, 'Interfacial effects during the analysis of multilayer metal coatings by radio-frequency glow discharge optical emission spectroscopy: Part 1. Crater shape and sputtering rate effects', *J. Anal. At. Spectrom.*, **20** (2005) 1108.

[94] V. Hoffmann, R. Dorka, L. Wilken, V. D. Hodoroaba, K.Wetzig, 'Present possibilities of thin-layer analysis by GDOES', *Surf. Interf. Anal.*, **35** (2003) 575.

[95] R.E. Galindo, E. Forniés, J.M. Albella, 'Interfacial effects during the analysis of multilayer metal coatings by radio-frequency glow discharge optical emission spectroscopy: Part 2. Evaluation of depth resolution function and application to thin multilayer coatings', *J. Anal. At. Spectrom.*, **20** (2005) 1116.

[96] R. Payling, J. Michler, M. Aeberhard, Y. Popov, 'New aspects of quantification in r.f. GDOES', *Surf. Interf. Anal.*, **35** (2003) 583.

[97] Z. Weiss, 'Quantitative depth profile analysis by glow discharge optical emission spectroscopy: an alternative approach', *J. Anal. At. Spectrom.*, **10** (1995) 891.

[98] A. Bengtson, 'Quantitative depth profile analysis by glow discharge', *Spectrochim. Acta Part B*, **49** (1994) 411.

[99] A. Bengtson, Th. Nelis, 'The concept of constant emission yield in GDOES', *Anal. Bioanal. Chem.*, **385** (2006) 568.

[100] I. T. Spitsberg, K. Putyera, 'Depth profile and quantitative trace element of diffusion aluminided type layers on Ni-base superalloys using high-resolution glow discharge mass-spectrometry', *Surface and Coatings Technology*, **139** (2001) 35.

[101] R. Payling, M. Aeberhard, D. Delfosse, 'Improved quantitative analysis of hard coating by radiofrequency glow discharge optical emission spectrometry', *J. Anal. At. Spectrom.*, **16** (2001) 50.

[102] J. Michler, M. Aeberhard, D. Velten, S. Winter, R. Payling, J. Breme, 'Depth profiling by GDOES: application of hydrogen, d.c. bias voltage corrections to the analysis of thin oxide films', *Thin Solid Films*, **447-448** (2004) 278.

[103] R. Payling, T. Nelis, M. Aeberhard, J. Michler, P. Seris, 'Layer model approach to background correction in r.f.-GDOES', *Surf. Interface Anal.*, **36** (2004) 1384

[104] K.A. Marshall, T.J. Casper, K.R. Brushwyler, J.C. Mitchell, 'The analytical impact of power control in a radio frequency glow discharge optical emission plasma', *J. Anal. At. Spectrom.*, **18** (2003) 637.

[105] Report on Round Robin exercise with nonconductors "*Final General Meeting of the UE-GDS Network*", Wiener Neustadt, Austria, 2002.

[106] J. Durr, B. Vandorpe, 'A comparative, practical study of glow discharge lamp and spark source for routine analysis of steels and nickel alloys', *Spectrochim. Acta Part B*, **36** (1981) 139.

[107] W. B. Cho, Y. A. Woo, H. J. Kim, I. J. Kim, W. K. Kang, 'Comparison between direct-current and radio-frequency gas-jet-boosted glow discharge atomic emission spectrometry for the analysis of steel', *Appl. Spectrosc.*, **51** (1997) 1060.

[108] M. L. Hartenstein, R. K. Marcus, 'Practical aspects in the determination of gaseous elements by radiofrequency glow discharge optical emission spectrometry', *J. Anal. At. Spectrom.*, **12** (1997) 1027.

[109] M. R. Winchester, 'Development of a methods for the determination of phosphorus in Cu alloys using radiofrequency glow discharge optical emission spectrometry', *J. Anal. At. Spectrom.*, **13** (1998) 235.

[110] De Gendt, R. E. Van Grieken, S. K. Ohorodnik, W. W. Harrison, 'Parameter evaluation for the analysis of oxide-based samples with radiofrequency glow discharge mass spectrometry', *Anal. Chem.*, **67** (1995) 1026.

[111] A. Menéndez, R. Pereiro, N. Bordel, J. McDermid, J. Thomson, A. Sanz-Medel, 'Rf glow discharge optical emission spectrometry for cleaning process control of oil residues in low alloy steel', *J. Anal. At. Spectrom.*, **22** (2007) 411.

[112] F. Li, S. Anderson, 'Non-traditional spectroscopy for analysis of semi-conductor and photovoltaic thin film materials', *AIP Conference Proceedings*, **1173** (2009) 62.

[113] R. Jäger, A.I. Saprykin, J.S. Becker, H.-J. Dietze, J.A.C. Broekaert, 'Analysis of semiconducting materials by high-resolution radiofrequency glow discharge mass spectrometry', *Mikrochim. Acta*, **125** (1997) 41.

[114] J.E. Shelby, 'Introduction to glass science and technology', 2nd edition, Royal Society of Chemistry, Cambridge, 2005.

[115] B. Fernández, A. Martin, N. Bordel, R. Pereiro, A. Sanz-Medel, 'Application of radiofrequency glow discharge optical emission spectrometry for direct analysis of main components of glass samples', *J. Anal. At. Spectrom.*, **21** (2006) 1412.

[116] B. Fernández, N. Bordel, R. Pereiro, A. Sanz-Medel, 'Radio frequency glow discharge-optical emission spectrometry for direct quantitative analysis of glasses', *Anal. Chem.*, **76** (2004) 1039.

[117] X. Pan, R. K. Marcus, 'Direct analysis of glass powder samples by radio frequency glow discharge atomic emission spectrometry (rf-GD-AES)', *Mikrochim. Acta*, **129** (1998) 239.

[118] A. I. Saprykin, J. S. Becker, H. J. Dietze, 'Optimisation of an rf-powered magnetron glow discharge for the trace analysis of glasses and ceramics', *Fresenius J. Anal. Chem.*, **355** (1996) 831.

[119] R.K. Marcus, 'Direct polymer analysis by radio frequency glow discharge spectrometry', *J. Anal. At. Spectrom.*, **15** (2000) 1271.

[120] R. Martinez, C. Pérez, N. Bordel, R. Pereiro, A. Sanz-Medel, 'Exploratory investigations on the potential of radiofrequency glow discharge-optical emission spectrometry for the direct elemental analysis of bone', *J. Anal. At. Spectrom.*, **16** (2001) 250.

[121] S. Baude, J. A. C. Broekaert, D. Delfosse, N. Jakubowski, L. Fuechtjohann, N. G. Orellana-Velado, R. Pereiro, A. Sanz-Medel, 'Glow discharge atomic emission spectrometry for the analysis of environmental samples – a review', *J. Anal. At. Spectrom.*, **15** (2000) 1516.

[122] C. Xhoffer, H. Dillen, 'The versatility of GDOES: from bulk analysis to thin film and surface analysis', *B.H.M.*, **152** (2007) 18.

[123] K. Shimizu, H. Habazaki, P. Skeldon, G. E. Thompson, 'Impact of RF-GD-OES in practical surface analysis', *Spectrochim. Acta Part B*, **58** (2003) 1573.

[124] D. Klemm, V. Hoffmann, K. Wetzig, J. Eckert, 'Dc and rf-GD-OES measurements of adsorbed organic monolayers on copper', *Anal. Bioanal. Chem.*, **395** (2009) 1893.

[125] A. Bengtson, 'The impact of molecular emission in compositional depth profiling using glow discharge-optical emission spectrometry', *Spectrochim. Acta Part B*, **63** (2008) 917.

[126] M. L. Hartenstein, R. C. Compton, R. K. Marcus, 'Rapid depth-resolved analysis of nitride layers (> 50 micrometers) on prosthetic devices by radiofrequency glow discharge optical emission spectrometry', *Amer. Lab.*, (1997) 17C-17H.

[127] V.S. Hodoroaba, V. Hoffmann, E.B.M. Steers, M. Griepentrog, A. Dück, V. Beck, 'Round robin exercise: coated samples for glow discharge spectroscopy', *J. Anal. At. Spectrom.*, **21** (2006) 74.

[128] P. Kern, P. Schwaller, J. Michler, 'Electrolytic deposition of titania films as interference coatings on biomedical implants: Microstructure, chemistry and nano-mechanical properties', *Thin Solid Films*, **494** (2006) 279.

[129] R. Payling, M. Aeberhard, J. Michler, 'Quantitative analysis of conductive coatings by radiofrequency-powered glow discharge optical emission spectrometry: hydrogen, d.c. bias votage and density corrections', *Surf. Interface Anal.*, **33** (2002) 472.

[130] K. Shimizu, G. M. Brown, H. Habazaki, P. Skeldon, G. E. Thompson, G. C. Wood, 'Glow discharge optical emission spectrometry (GD-OES) depth profiling analysis of anodic alumina films – a depth resolution study', *Surf. Interface Anal.*, **27** (1999) 24.

[131] P. Le Coustumer, M. Montelica-Heino, P. Chapon, H. François, R. Payling, 'Surface characterization and depth profile analysis of glasses by r.f. GDOES', *Surf. Interface Anal.*, 35 (2003) 623.

[132] B. Yuksel, E.B. Sam, O.C. Aktas, M. Urgen, A.F. Cakir, 'Determination of sodium migration in sol-gel deposited titania films on soda-lime glass with r.f. glow discharge optical emission spectrometry', *Appl. Surf. Sci.*, **255** (2009) 4001.

[133] K. Shimizu, H. Habazaki, P. Skeldon, G.E. Thompson, R.K. Marcus, 'Influence of interfacial depth on depth resolution during GDOES depth profiling analysis of thin alumina films', *Surf. Interface Anal.*, **31** (2001) 869.

[134] R. Escobar Galindo, R. Gago, A. Lousa, J.M. Albella, 'Comparative depth-profiling analysis of nanometer-metal multi-layers by ion-probing techniques', *Trends Anal. Chem.*, **28** (2009) 494.

[135] K. Shimizu, R. Payling, H. Habazaki, P. Skeldon, G.E. Thompson, 'Rf-GDOES depth profiling analysis of a monolayer of thiourea adsorbed on copper', *J. Anal. At. Spectrom.*, **19** (2004) 692.

[136] R. Bayón, A. Igartua, X. Fernández, R. Martínez, R.J. Rodríguez, J.A. García, A. de Frutos, M.A. Arenas, J. de Damboronea, 'Corrosion-wear behaviour of PVD Cr/CrN multilayer coatings for gear applications', *Tribol. Intern.*, **42** (2009) 591.

EXPERIMENTAL

C.1. Rf-GD-OES Instrumentation

Two different commercial Glow Discharge instruments, coupled to Optical Emission Spectrometry instruments with radiofrequency sources, have been employed in the analyses carried out in present work. Both spectrometers are able to carry out both the direct elemental analysis of homogenous solid samples (conductors and non-conductors), and the in-depth analysis of coated samples. Next, the main characteristics of each of both are briefly described.

C.1.1. JY 5000 RF

This commercial rf-GD-OES instrument of Jobin Yvon Emission Horiba Group, (Longjumeau, France) is installed at both the University of Oviedo (Department of Physical and Analytical Chemistry, Oviedo, Spain) and Swiss Federal Laboratories for Materials Science and Technology, EMPA (Thun, Switzerland). Figure 19a shows the lateral view of the instrument with its different components and Fig. 19b its perspective view.

a) **b)**

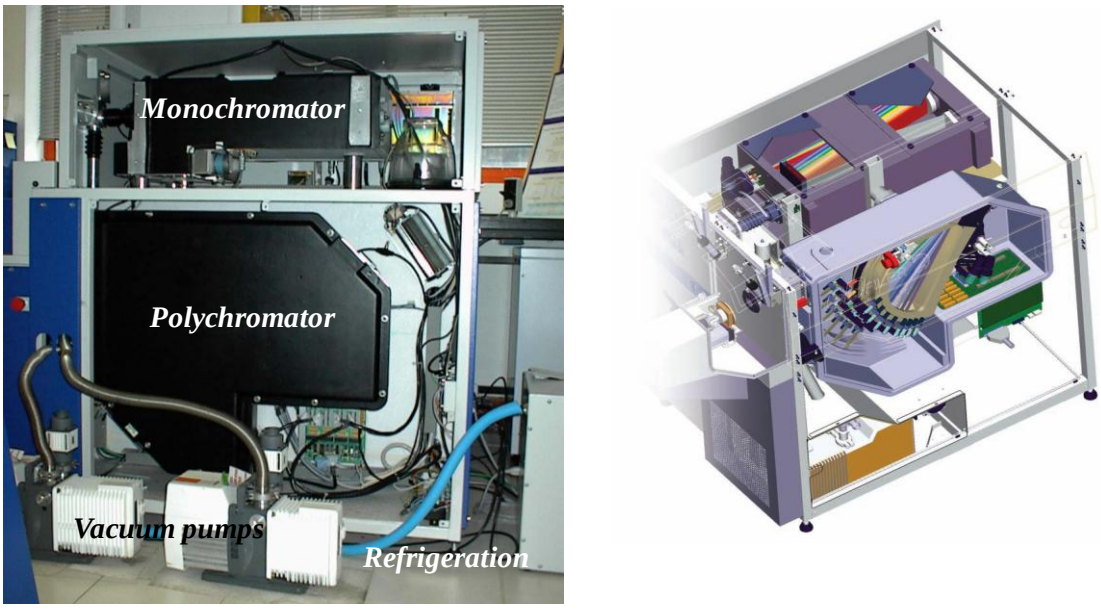


Figure 19. *The rf-GD-OES (JY 5000 RF) instrument. a) Lateral view, and b) perspective view.*

○ **Radiofrequency source.-** The discharge is generated through a 13.56 MHz radiofrequency generator (Hi Light™ 133, Dressler GmbH, Germany) with a maximum power of 150 W. This generator is capable of supplying constant real

power (understood as the difference between forward and reflected powers), constant applied rf-voltage or constant dc bias voltage and can be operated in both continuous and pulsed mode. The JY 5000 RF software allows the pulse repetition frequency to be varied from 0 to 20 kHz and the duty cycle from 6.25 to 50% in pre-determined steps.

○ **Polychromator.-** The spectrometer incorporated is a Paschen-Runge polychromator (see Part B.2.4.) with a focal path of 0.5 m and a concave grating of 2400 lines mm^{-1}. The maximum number of channels, or photomultiplier tubes (see Part B.2.4.) that can be installed is 47. The optical path is nitrogen purged to eliminate air traces inside the instrument covering this way a spectral range from 118.94 to 777.30 nm. In Table 5, the actually installed channels in the polychromator are summarised.

Table 5. Elements and their respective wavelengths measured by the polychromator in the JY 5000 RF instrument.

Element	Order	Wavelength (nm)
H	2	121.56
O	2	130.22
N	2	149.26
C	2	156.14
P	2	178.29
S	2	180.73
Pb	2	220.35
Cd	2	228.80
Se	2	241.35
Hg	2	253.65
Mn	2	257.60
Si	2	288.16
Si	1	288.16
Sn	1	317.51
Cu	1	324.75
Ag	1	328.07

Element	Order	Wavelength (nm)
Zn	1	334.50
Zr	1	339.20
Ni	1	341.47
Ti	1	365.35
Fe	1	371.99
Mg	1	383.83
Ca	1	393.37
Al	1	396.15
Ar	1	404.00
Sr	1	407.77
Nb	1	416.46
Cr	1	425.43
Na	1	589.59
Li	1	670.77
K	1	766.49

○ **Monochromator.-** Besides the polychromator, the instrument is also equipped with a Czerny-Turner monochromator (see Part B.2.4.) which allows the expansion of the instrument's capabilities to any wavelength of the spectral range. Its focal path is of 0.64 m and contains a blazed planar holographic

grating of 2400 lines mm^{-1}. Its spectral range is from 200 to 800 nm and the detector installed is a photomultiplier tube (Hamamatsu, model R955UH). Figure 20 represents schematically the optical system used in the instrument. As can be observed, part of the luminous beam coming out of the GD chamber will be reflected, after passing through a first MgF_2 lens, by a mirror to modify its propagation direction towards the monochromator, while the rest of the beam is focussed upon the entrance slit of the polychromator through a second lens.

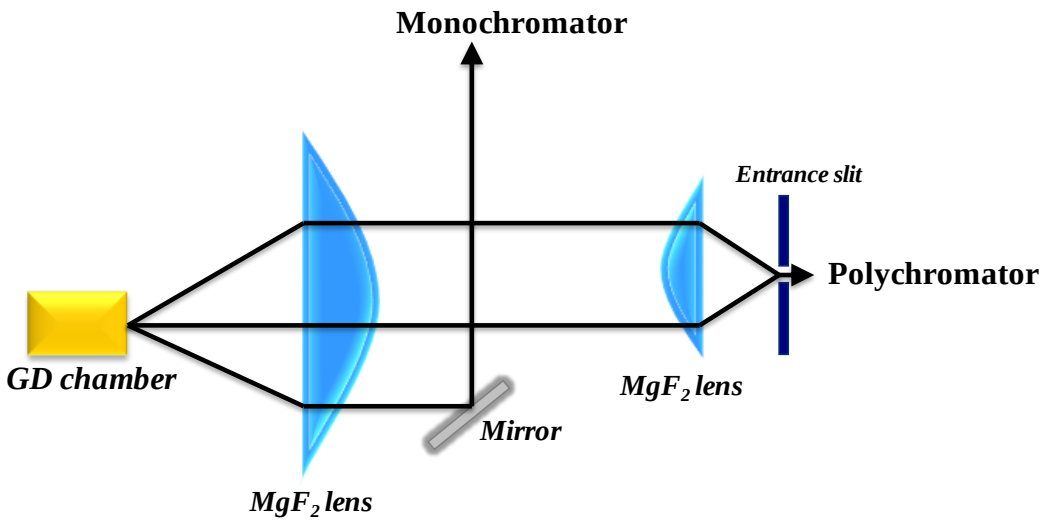


Figure 20. *Optical system of rf-GD-OES.*

○ **Vacuum.-** The vacuum inside the instrument is obtained through two rotary vane mechanical vacuum pumps, indicated in Fig. 19a (ALCATEL, models 2005 SD and 2015 SD with a flow of 4.8 and 12.5 $m^3 h^{-1}$, respectively).

○ **Nitrogen purging method.-** A nitrogen generator (LABCRAFT, model NSC008C) purges the whole optical system, from the discharge chamber to the photomultiplier tubes, providing a constant N_2 flow to eliminate occluded air and to avoid photon absorption at wavelengths below 200 nm.

○ **Cooling system.-** A circulator (LABCRAFT, model CF2050) provides a constant flow of cold water circulating inside a disk placed in direct contact with the sample to analyse to avoid its overheating and consequently, thermal-related problems.

○ **Discharge chamber.-** The discharge chamber is a Grimm type design (see Part B.2.1., Fig. 8) and the different elements consisting the chamber are represented in Fig. 21. As can be observed, the anode is fixed inside the GD instrument. In order to carry out an analysis, the sample of interest has to be placed in the chamber. Therefore, the sample has to be supported upon the anode, together with the refrigerated disk (because of the circulation of water inside), through a pneumatic holder of stainless steel powered by compressed air. The radiofrequency generator is back coupled to the sample through a probe connected to the refrigerated disk.

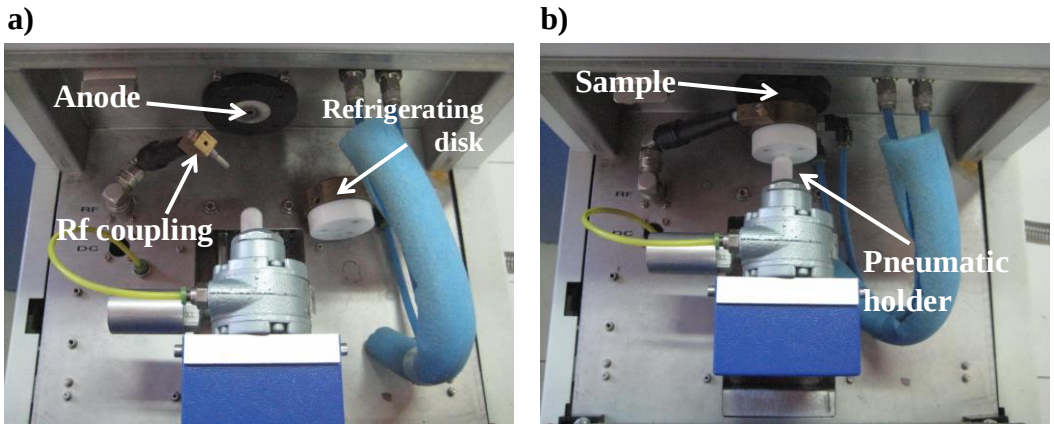


Figure 21. *The JY 5000 RF discharge chamber. a) Without sample, and b) with sample.*

○ **Discharge gas.-** High-purity argon (99.999% minimum purity) from Air Liquide (Oviedo, Spain) was employed as discharge gas.

C.1.2. LECO GDS 750 Grimm type

This commercial GD-OES instrument (LECO Corporation, St. Joseph, Michigan, USA) is installed at the Corrosion and Metals Research Institute SWEREA-KIMAB AB (Stockholm, Sweden) and the power source used can be direct current or radiofrequency. The instrument offers complete flexibility for the control of the operating parameters, including current, voltage and current. Figure 22 shows the LECO GDS 750 Grimm type instrument used.

Figure 22. *The LECO GDS 750 Grimm type instrument.*

○ **Radiofrequency power.-** In conjunction with this front coupling of the radiofrequency, LECO offers an exclusive treatment of the rf power to ensure that the lamp parameters are constant regardless the matrix and material thickness. The True Plasma Power (TPP), defined as the forward power from the rf generator subtracted by the reflected power and the "blind power" dissipated without plasma, is a power control in real-time which compensated for the various rf power losses occurring. The blind power is measured prior to the discharge with the sample in place, vacuum in the discharge chamber and the same rf voltage applied as during analysis. This represents the rf power dissipated in cables, connectors, lamp housing, sample etc. due to the finite impedance in these components. The blind power increases approximately as the square of the applied voltage, and can be even larger than the actual plasma power dissipated in the glow discharge.

○ **Polychromator.-** The instrument covers a spectral range from 120 to 800 nm and allows for custom configurations up to 58 channels equipped with photomultiplier detectors.

○ **Discharge chamber.-** The discharge chamber employed is a Grimm type design, as can be observed in Fig. 23. Important to stress is the LECO's patented rf front coupling, emphasized in the picture, contrary to the back coupling in the JY 5000 RF instrument. The copper anode has a cylindrical form and a diameter of 4 mm. A refrigerated disk is placed at the back of the sample and fixed by the

pneumatic holder which is also used as cleaning tool for the anode through the incorporation of a drill, perfectly aligned with the anode.

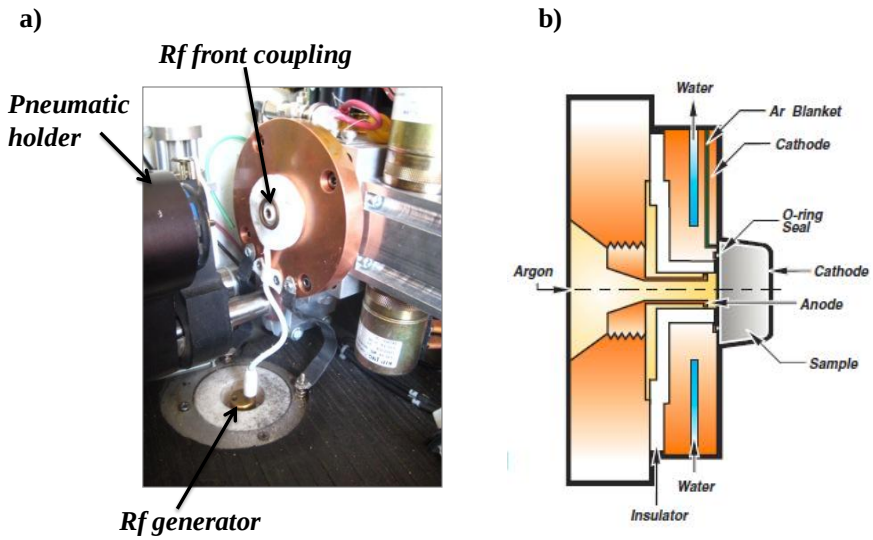


Figure 23. *The discharge chamber. a) Front view, and b) cross-section.*

○ **Discharge gas.-** High-purity argon (99.999% minimum purity) was employed as discharge gas.

C.2. Additional Instrumentation

Other instruments that have been employed during the experimental part of this dissertation are the following:

○ **Polisher/grinder.-** Model Metaserv 2000®, Buehler. This device is used to prepare adequately the material surface before the analysis. The solids are successively polished with a series of sandpapers. In this work, the commonly used ones were of silicon carbide. The polishing of the surface is carried out until obtaining a "mirror" effect. Next, the material surface is cleaned with ethanol (96% v/v) and dried with hot air. Of course, the use of the polisher is restricted to homogeneous samples and calibration standards.

○ **Profilometer.-** Model Perth-o-meter S5P, Mahr Perthen. The profilometer is employed for the measurement of the crater shapes obtained in the samples after analysis. The probe, with its thin diamond point, runs over the sample

topography following a longitudinal path across the crater diameter. This way the crater depth can be calculated and, as a consequence, the sputtering rate can be determined.

○ **Scanning Electron Microscope (SEM).-** Different SEM instruments have been employed in the present work: SUPRA™ FESEM, a HITACHI S-800 with a probe for EDX and a Quanta 400 instrument (FEI Company, Oregon, USA) coupled to an EDS analyzer (Oxford Instruments, UK). SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the sample atoms producing signals containing information about the sample's topography, composition and other properties such as electrical conductivity (see Part B.1.3.1.).

○ **Oscilloscope.-** A 350 MHz digital oscilloscope (LeCroy WaveJet Series 334, Chestnut Ridge, New York, USA) has been used, coupled to the monochromator photomultiplier detector output of the JY 5000 RF using a 2 m coaxial cable (~200 pF) and a 10 kΩ metal film type load resistor (0.25 W rated, 1% accuracy) on the oscilloscope input.

RESULTS AND DISCUSSION

I.

Time-resolved measurements of emission profiles in pulsed rf-GD-OES: investigation of the pre-peak

Glow discharges have been used in analytical chemistry, mainly as spectroscopic sources for mass spectrometry and optical emission spectrometry, for the bulk analysis and composition depth profiling of a wide variation of materials. With the advent of pulsed GD new possibilities of material analysis rose, due to the advantages offered by this operation mode, *e.g.* the creation of time regimes during which the background signal is suppressed while the analyte signal is enhanced, the alleviation of plasma instability arising from overheating the sample cathode, the lower average powers applied, etc. Most studies on PGDs have been made with direct current glow discharges. Nevertheless, the interest in radiofrequency PGDs, because of the possibility to analyse conductors, semi-conductors and insulators, led to pioneering studies from the 70's on the subject as an approach to increase the instantaneous power applied and to improve thermal stability. During the study of the emission characteristics of rf-PGDs, pre-peaks (and post-peaks) in the time-dependent emission profiles were observed, phenomena linked to different causes as the rf-power surge, sputtering effects, self-absorption, etc.

The effective use of pulsed glow discharges requires a more complete understanding of the temporal separation of various excitation and ionisation processes. Therefore, the main objective of this chapter is the study of rf-PGDs in view of the possible advantages for optical emission spectrometry. The existence of this pre-peak phenomenon will be investigated, together with the effect of the various discharge and pulse parameters on its behaviour.

D.I.1. Introduction

As stressed in the general Introduction of this Thesis, glow discharges are used nowadays for a wide variety of technological, physical and analytical applications. For analytical applications, GDs have a long and splendid history as sources for emission and mass spectrometry. GDs coupled to optical emission spectrometry and mass spectrometry are most commonly applied in materials sciences where they are routinely used for bulk[1-3] and depth profile analysis.[4-6] The GD source can be generated in two different modes: direct current and radiofrequency. Dc-GDs are better known due to the large amount of studies that have been devoted to them.[7-12] Moreover, the relation between the various working parameters, *i.e.* current, voltage and pressure, determining the discharge, are well-controlled. Also, the dc-GD is very convenient for the analysis of conductive samples due to its simplicity and stable operation conditions. Nevertheless, the need to analyse semi-conductive and non-conductive materials has led to the increasing interest in rf-GD.[13-15] Pulsed GDs, consisting on the application of a square wave power pulse followed by a power termination,[16] are gaining a lot of attention due to the advantages offered by this operation mode, compared to continuous operation. Among them can be cited the additional way of controlling the plasma by selecting the pulse parameters, and the instantaneous high powers that can be chosen nearly independent of the average power (responsible for thermal stress upon the sample) through the variation of the duty cycles of the applied pulses.[17] Moreover, different discharge processes take place at different times within the pulse, allowing to obtain quasi-simultaneous structural, molecular and elemental information,[18] in the case time-resolved detection is available. The important aspects of pulsed GDs and their applicability to analytical applications have recently been reviewed by Belenguer et al.[19]

Due to the limited application of dc-GDs, the development and study of pulsed rf-GD for analytical applications is more stressed.[15,19] Moreover, the relieved thermal stress upon the sample, due to the pulsing operation mode, will be of more benefit for non-conductive samples. Rf-PGDs have been investigated both in combination with OES[20-22] and MS.[23,24] Pioneering studies of the PGDs were carried out by Harrison and co-workers.[25]. They studied the pulsed power mode as an approach to enhance the plasma, obtaining more energetic sputtering species, greater efficiency of excitation and ionisation, and higher emission yields. More interesting was the temporal advantage

gained, during which certain interference species could be discriminated from the analyte species. Additionally, cathode sample overheating was avoided under pulsed measurement conditions. Winchester and Marcus [26] investigated the emission characteristics of rf-PGDs and observed emission at the beginning of the pulse for some Cu emission lines (*i.e.* a 'pre-peak'), enhanced emission at the end of the pulse for some other Cu emission lines (*i.e.* an 'after-peak') and no enhanced emission, for still some other Cu lines. This line-specific response under pulsing discharge conditions could mean that the optimum lines for pulsing may be different for those commonly used for continuous operation, *e.g.* the Cu I 324.7 nm atomic emission line is enhanced in the pre-peak, while the Cu II line at 213.8 nm is not. They noted the pre- and after-peak sizes varied with the plasma conditions, while their widths did not change with the pulse width applied. They attributed this phenomenon to the possibility of the easier sputtering of redeposited material from the previous pulse or temporal variations in the electron energy distribution function.

Later, as part of his engineering thesis, Vegiotti[27] studied rf-pulsing using a 30 W, 13.56 MHz rf power supply with a 1.25 ms pulse length (400 Hz pulse frequency and 50% duty cycle). Through the study of the intensity pulse shapes of sputtered atoms, he observed that many emission lines for different elements, such as Cu, Ni, Cr and Fe, showed enhanced emission during the first 100-150 μs, followed by a plateau region. This pre-peak was often twice the intensity of the plateau. Moreover, this effect was only detected for some atomic resonance lines, so he wondered if this phenomenon was related to a lack of self-absorption at the beginning of each pulse due to the absence of absorbers, since atoms from earlier pulses would have already been excited in the plasma and therefore will not reabsorb. However, plotting calibration curves, using either the pre-peak or plateau intensity, were non-linear, suggesting they were affected by self-absorption in the same way. Considering the plasma is approximately 3 mm long and the average particle speeds are approximately 500 m s^{-1}, the plasma should be filled in more or less 6 μs, much faster than the observed length of the pre-peak on that moment, suggesting other mechanisms are responsible (*e.g.* efficient excitation in the plasma during the early part of each pulse).

Nevertheless, the effective use of a PGD requires the understanding of the different plasma processes occurring. Nelis et al.[21] studied rf-PGDs in view of their use and possible advantages for optical emission spectrometry. During such work, a more

detailed study of this pre-peak was carried out through the measurement of a wide range of copper transitions between different excited states, trying this way to obtain a better insight into the GD's excitation processes. Pre-peaks were observed on the resonance lines and linked to a lack of self-absorption at the beginning of the plasma ignition. This would mean its presence depended on the lower transition state and its importance decreased with the wavelength of the involved transition. This could be due to two effects: (a) if short wavelengths are later excited they can cause radiation trapping, as the discharge volume will already be filled with a larger atom volume, and (b) the re-absorption cross-section increases as γ^3 for a Gaussian broadened line, reducing this way the effect of radiation trapping.[28] So, this reduced self-absorption at the pulse start, together with the slow diffusion processes, were clearly linked to the enhanced emission yields observed.

It is known that the GD source design is prone to self-absorption because the intensive negative glow, located near the sample surface, cools rapidly in the direction of the observation window. Self-absorption has been observed for resonance lines, even for analytes with elemental mass fractions in the solid sample as small as 3%.[29] In order to minimise the problem, the spectrometer should be located side-on to the negative glow. Moreover, self-absorption can be alleviated somewhat by reducing the sputtering rate, but the best solution, when possible, is to choose non-resonance emission lines. Unfortunately this is not always possible or convenient, and sometimes non-linear calibration curves must be used when significant self-absorption is present.

D.I.2. Objectives

According to the comments made above, it is indispensable to better understand the different processes occurring in the GD plasma to ensure an effective analytical use of pulsed glow discharges. Previous investigation on this subject demonstrated the existence of a characteristic pre-peak, which was observed during the study of the emission characteristics of pulsed rf discharges, and could be related to the temporal lack of self-absorption at the beginning of the pulse. Moreover, its presence would mainly depend on the lower state of transition. It is known that, due to self-absorption, non-linear calibration curves for elements with strongly self-absorbed emission lines (mostly these are the resonance ones) are obtained, leading to quantification problems. A lack of fundamental information on this phenomenon exists, as well as on the benefits it could offer for optical emission spectrometry.

Therefore, the main objective of this chapter has been a thorough study of time-resolved emission profiles obtained under pulsed discharge conditions. These studies have been realised through the next steps:

♦ The measurement of pulsed emission profiles for a wide range of copper transitions with an experimental set-up with shorter time-resolution, than that used in previously reported studies.

♦ The study of the influence of the analyte concentration on the pre-peak behaviour.

♦ The evaluation of the conventional discharge parameters, *i.e.* forward power and chamber pressure, on the pre-peak behaviour.

♦ The evaluation of the pulse parameters, *i.e.* pulse frequency, duty cycle and pulse width, on the pre-peak behaviour.

(Publication D.I.3.1.- *Spectrochimica Acta Part B: Atomic Spectroscopy*, 65 (2010) 533-541)

D.I.3. Results

D.I.3.1. Spectrochimica Acta Part B, 65 (2010) 533-541

D.I.4. Discussion of the Results

The measurement of pulsed emission profiles was carried out for a wide range of copper transitions, because of their use in previous model calculations.[30] The transitions studied were resonance transitions, transitions into the metastable states, transitions into high energy states and ionic transitions. As expected, for all resonance transitions the characteristic pre-peak was observed, and its relative importance decreased with the increasing energy of the respective excited level. However, the 324/327 nm pair did not show this behaviour, a fact already observed by Yan et al.[31] when measuring with a pulsed dc hollow cathode discharge on the same spectral line, where a stronger pre-peak for the 324 nm line was found instead for the 327 nm line. It is known that in the absence of self-absorption, the ratio of both emission lines should be close to 2, which is the case in our study, demonstrating the pre-peak dues its existence to the temporal absence of self-absorption. The transitions into the two metastable states showed small pre-peaks and only towards the lowest metastable level. The transitions into high energy states lying 30,000 cm^{-1} above the ground state showed a very small pre-peak, not resolved in previous studies.[21] And last, the ionic lines did not show any pre-peak. Through this study it was clear that the existence and importance of the pre-peak depends on the transition giving rise to the measured emission line.

Due to the nature of the pre-peak and its possible relation to self-absorption, it resulted necessary to look at the effect of varying analyte concentrations, in our case copper, on the pre-peak behaviour for a strong resonance line Cu I 324.75 nm. Pre-peak enhancement was observed with increasing copper concentration, as more atoms will be present in the discharge tube and thus, a stronger self-absorption effect is obtained. Calibration curves, based on the pre-peak and plateau emission intensities measured, showed a linear trend at low copper concentrations. In the case of the plateau-based curve, a deviation of this linearity is observed after 10% while the pre-peak-based curve maintains its linearity up to 50%. These results support the idea of the pre-peak being the consequence of the temporal lack of self-absorption at the pulse start. So, the optimal use of the pre-peak in pulsed discharges allows the improvement of the calibration linearity when measuring at strong resonance lines, prone to self-absorption.

As power and pressure are key parameters determining the analytical performance of GDs and influence the sputtered atom density, it is very probable they

will exert an influence on the pre-peak behaviour. Therefore, both the effect of varying power (at constant pressure) and varying the pressure (at constant power) have been studied measuring the characteristic pre-peak observed on two strong resonance lines, Cu I 324.75 and 327.40 nm. Increasing powers led to increasing pre-peak intensities, due to the larger amount of sputtered material in the discharge chamber and the enhanced excitation efficiency at high powers. Moreover, a delay in the time-scale was observed with decreasing powers probably due to the slow self-biasing of the sample. Pre-peak/plateau ratios showed an increasing trend with the applied power, while the pre-peak width decreased. These results are consistent with the higher sputtering rates (at high powers) because the steady state copper density will be increased and therefore self-absorption as well. The peaks will be narrower at high power because the same critical density is reached before. Similar results were obtained with increasing pressures.

As last step in the characterisation of the pulsed discharge, the evaluation of the influence of the different pulse parameters, *i.e.* pulse frequency, duty cycle and pulse width and off-time, on the pre-peak behaviour was carried out. First, the duty cycle was kept constant at 50%, while varying the pulse frequency from 2 to 20 kHz, obtaining pulse lengths between 250 and 25 μs, respectively. The pulsed time-resolved emission profiles were measured for the strong resonance lines Cu I 324.75 and 327.40 nm. Increasing frequency (decreasing pulse width and off-time) led to a pre-peak intensity decrease. It is obvious that the pre-peak shape cannot be affected by its own pulse length, but it can be affected by the preceding pulse's length and respective off-time. These two parameters affect the atom density remaining in the discharge chamber at the start of a new pulse. The pulse length determines the quantity of the sputtered material while during the off-time the remaining amount decreases due to diffusion and gas flow. So, this off-time is of great importance for short pulses and, as a consequence, short off-times (< 100 μs) will lead to decreasing pre-peak intensities. The pre-peak/plateau ratios increased with the pulse length (decreasing pulse frequency) until ~ 100 μs.

Because of these observations, the effect of power-off time on the pre-peak behaviour was studied, through the change of both pulse frequency and duty cycle in a way a constant pulse width (50, 100 and 250 μs) is maintained. The pulsed time-resolved emission profiles were measured for the strong resonance line Cu I 327.40 nm and a line corresponding to a transition into the metastable state Cu I 510.55 nm. When

analysing the pre-peak behaviour at each individual pulse width, it was observed that for a 250 μs pulse width the power-off time, within a range of 250 -1750 μs, did not influence neither on the pre-peak or plateau intensities. These results were expected as the previous measurements pointed out that power-off times longer than 100 μs would not affect the pre-peak. In the case of 100 μs long pulses, small intensity differences could be appreciated. However, in the case of 50 μs pulse widths, small pre-peaks were obtained at short power-off time, probably due to self-absorption. Moreover, it could be observed that in the case of the smallest pulse width, enhanced pre-peak intensities were observed compared to those obtained at 100 and 250 μs pulse width. So, this means the combination of high frequencies with small duty cycles (to obtain small pulse widths) will give rise to high emission intensities, only in the case the power-off time is long enough (> 100 μs) to ensure a minimum of self-absorption.

Finally, the influence of the duty cycle on the pre-peak behaviour was evaluated, maintaining the pulse frequency fixed at 5 kHz while varying the duty cycle from 6.25-50% (total pulse period of 200 μs). The pulsed time-resolved emission profiles were measured for the strong resonance line Cu I 324.75 nm and a line corresponding to a transition into the metastable state Cu I 510.55 nm. Through the increase of the duty cycle (decreasing power-off time) a decrease in pre-peak intensity was observed together with a displacement on the time-scale. This is due to self-absorption by atoms still present in the discharge tube because of the insufficient time to evacuate the discharge chamber under these conditions. These results proved the statement made above: small duty cycles are needed, together with high pulse frequencies, in combination with sufficiently long power-off times to obtain enhanced pre-peak intensities, of which analytical benefit can be obtained.

To conclude this discussion of the results obtained during the study of pulsed emission profiles and, consequently, the pre-peak observed, one should remember that to avoid self-absorption long enough off-times (> 100 μs) are required so the remaining amount of absorbing species in the discharge chamber is reduced through diffusion and gas flow processes. Moreover, enhanced emission intensities are obtained when measuring at high pulse frequencies and small duty cycles, resulting in small pulse widths, and sufficiently long off-times.

D.I.5. References

[1] R. Payling, 'Glow discharge optical emission spectroscopy', *Spectroscopy*, **13** (1998) 36.

[2] M. R. Winchester, 'Development of a methods for the determination of phosphorus in Cu alloys using radiofrequency glow discharge optical emission spectrometry', *J. Anal. At. Spectrom.*, **13** (1998) 235.

[3] F. Li, S. Anderson, 'Non-traditional spectroscopy for analysis of semi-conductor and photovoltaic thin film materials', *AIP Conference Proceedings*, **1173** (2009) 62.

[4] K. Shimizu, H. Habazaki, P. Skeldon, G. E. Thompson, 'Radiofrequency GDOES: a powerful technique for depth profiling analysis of thin films', *Surf. Interface Anal.*, **35** (2003) 564.

[5] M.R. Winchester, R. Payling, 'Radio-frequency glow discharge spectrometry: A critical review', *Spectrochim. Acta Part B*, **59** (2004) 607.

[6] N. Jakubowski, R. Dorka, E. Steers, A. Tempez, 'Trends in glow discharge spectroscopy', *J. Anal. At. Spectrom.*, **22** (2007) 722.

[7] A. Martin, R. Pereiro, N. Bordel, A. Sanz-Medel, 'Microsecond pulsed versus direct current glow discharges as ion sources for analytical glow discharge-time of flight mass spectrometry', *J. Anal. At. Spectrom.*, **22** (2007) 1179.

[8] A. Bogaerts, R. Gijbels, 'Behaviour of sputtered copper atoms, ions and excited species in a radio-frequency and direct current glow discharge', *Spectrochim. Acta Part B*, **55** (2000) 279.

[9] A.A. Garamoon, A. Samir, F.F. Elakshar, E.F. Kotp, 'Electrical characteristics of a DC glow discharge', *Plasma Sources Sci. Technol.*, **12** (2003) 417.

[10] R.H. Stark, K.H. Schoenbach, 'Direct current glow discharges in atmospheric air', *Appl. Phys. Lett.*, **74** (1999) 3770.

[11] G. Holland, "Recent advances in plasma source mass spectrometry", BPC Wheatons Ltd., Exeter, UK, 1995.

[12] A. Bogaerts, R. Gijbels, 'Modelling of the role of metastable argons in a direct current glow discharge', *Phys. Rev. A*, **52** (1995) 3743.

[13] R.E. Galindo, E. Forniés, J.M. Albella, 'Compositional depth profiling analysis of thin and ultrathin multilayer coating by radio-frequency glow discharge optical emission spectroscopy', *Surf. Coat. Technol.*, **200** (2006) 6185.

[14] A.B. Anfone, R.K. Marcus, 'Radio frequency glow discharge optical emission spectrometry (rf-GD-OES) analysis of glass samples', *J. Anal. At. Spectrom.*, **16** (2001) 506.

[15] M.R. Winchester, R. Payling, 'Radio-frequency glow discharge spectrometry: A critical review', *Spectrochim. Acta Part B*, **59** (2004) 607.

[16] V. Hoffmann, V.V. Efimova, M.V. Voronov, P. Smid, E.B.M. Steers, J. Eckert, 'Measurement of voltage and current in continuous and pulsed rf and dc glow discharges', *J. Phys. Conf. Ser.*, **133** (2008) 012017.

[17] C. Yang, K. Ingeneri, M. Mohill and W. W. Harrison, 'Influence of discharge parameters on the resolution of depth profiling by pulsed glow discharge atomic emission spectrometry', *J. Anal. At. Spectrom.*, **15** (2000) 73.

[18] C.L. Lewis, L. Li, T. Millay, S. Downey, J. Warrick, F.L. King, 'Temporal emission characteristics of millisecond pulsed radiofrequency and direct current glow discharges', *J. Anal. At. Spectrom.*, **18** (2003) 527.

[19] Ph. Belenguer, M. Ganciu, Ph. Guillot, Th. Nelis, 'Pulsed glow discharges for analytical applications', *Spectrochim. Acta Part B*, **64** (2009) 623.

[20] P. Sanchez, B. Fernández, A. Menendez, R. Pereiro and A. Sanz-Medel, 'Pulsed radiofrequency glow discharge optical emission spectrometry for the direct characterisation of photovoltaic thin film silicon solar cells', *J. Anal. At. Spectrom.*, **25** (2010) 370.

[21] Th. Nelis, M. Aeberhard, M. Hohl, L. Rohr, J. Michler, ,'Characterisation of pulsed rf-glow discharge in view of ist use in OES', *J. Anal. At. Spectrom.*, **12** (2006) 112.

[22] G. Gamez, S.J. Ray, F.J. Andrade, M.R. Webb, G.M. Hieftje, 'Development of a pulsed radio frequency glow discharge for three-dimensional elemental surface imaging. 1. Application to biopolymer analysis', *Anal. Chem.*, **79** (2009) 1317.

[23] C. González Gago, R. Pereiro, N. Bordel, P. Mazón Ramos, A. Tempez, A. Sanz-Medel, 'Analysis of small bubbles in glass by glow-discharge-time-of-flight mass spectrometry', *Anal. Chim. Acta*, **652** (2009) 272.

[24] M. Hohl, A. Kanzari, J. Michler, T. Nelis, K. Fuhrer, M. Gonin, 'Pulsed r.f.-glow discharge time-of-flight mass spectrometry for fast surface and interface analysis of conductive and non-conductive materials', *Surf. Interf. Anal.*, **38** (2006) 292.

[25] W.W. Harrison, W. Hang, 'Powering the analytical glow discharge', *Fresenius J. Anal. Chem*, 35 (1996) 803.

[26] M.R. Winchester, R.K. Marcus, 'Emission characteristics of a pulsed, radiofrequency glow discharge atomic emission device', *Anal. Chem.*, **64** (1992) 2067.

[27] J-P Vegiotti, *Engineering thesis*, Conservatoire National des Arts et Metiers, Paris, 1997.

[28] Th. Nelis, R. Payling, "A Guidebook to Glow Discharge Optical Emission Spectroscopy", RSC, Cambridge, 2004.

[29] M.R. Winchester, R.K. Marcus, 'Investigations of self-absorption in a radio-frequency glow discharge device', *Spectrochim. Acta Part B*, **51** (1996) 839.

[30] A. Bogaerts, R. Gijbels, 'Argon and copper optical emission spectra in a Grimm glow discharge source: mathematical simulations and comparison with experiment', *J. Anal. At. Spectrom*., **13** (1998) 721.

[31] X. Yan, W. Hang, B.W. Smith, J.D. Winefordner, W.W. Harrison, 'Primary studies of the microsecond pulsed glow discharge as an emission source using a conventional hollow cathode lamp', *J. Anal. At. Spectrom.*, **13** (1998) 1033.

II.

Investigation of continuous and pulsed rf-GD-OES for the depth profile analysis of coated materials

Coating materials deposited on different substrates (conductive, semi-conductive and insulating) are widely used in the automobile, aerospace, petrochemical, glass, food industry, etc. The need to improve the performance of coated components by diversifying both the chemical composition and the number of coating layers (from single up to multi-layers) leads to the necessity of new tools for quality control of these final coated components. The selected technique should be fast, easy and cheap while providing reliable and chemical lateral and in-depth characterisation of the material of interest.

Great part of these coated materials consist, partially or as a whole, of semi-conductive or non-conductive materials. Moreover, the deposited coatings on these substrates can be very fragile as well as heat-sensitive, properties which difficult or even impede the analysis. It has been described that rf-GD-OES applied in pulsed mode can overcome these problems due to the lower average powers applied, compared to these applied in continuous mode, without losing sensitivity.

Therefore the main objective of this chapter is the study of the potential of rf-GD-OES, applied both in continuous and pulsed operation mode, for the characterisation and direct solids analysis of, both homogeneous and coated, conducting and insulating samples. Moreover, the effect of coated non-conductive samples on the electrical parameters of rf-GD-OES is also evaluated.

D.II.1. Introduction

Radiofrequency glow discharges coupled to optical emission spectrometry or to mass spectrometry have become during the last years important analytical tools for the rapid and sensitive in-depth characterisation of a wide range of coated materials.[1-8] The nature of the cathodic sputtering mechanism of rf-GD, during which the solid sample undergoes sputtering of its sample atoms through the bombardment with low energy Ar^+ ions (< 50 keV) at high velocity (100 mA cm^{-2}) in a stable and reproducible way, is one of the main characteristics of the technique which is exploited in the analysis of coated samples. Moreover, the low energy of the Ar^+ ions ensures that the sputtering process happens without any significant alteration of the layers, a requirement needed for the successful depth profile analysis of thin and ultra-thin layered samples with high spatial resolution.[3,9]

Rf-GD-OES has been widely employed for the depth profile analysis of coatings of different nature deposited on conductive matrices, including organic coatings[10,11], hard disks[9], nitride layers on steel alloys[12], Zn-Ni alloys[13], nitride layers on prosthetic devices (Co/Cr alloys),[14] etc. Moreover, lately an increasing trend has been observed related to the depth analysis of samples with non-conducting substrates[4,5, 15] by radiofrequency glow discharge, demonstrating its potential for such applications. The characteristics rf-GD provides for the analysis of non-conducting samples broadens significantly its application field, allowing for example, the possibility to control the quality of industrial coatings depositing processes as well as to discover fast problems during their development and production processes (*e.g.* multi-layered glasses for solar control, thermal isolation and anti-reflective coatings are commercially used).

In addition, Le Coustumer et al.[16] demonstrated the practical utility of qualitative profiles obtained for a multi-layered glass and photo-reactive glasses (with potential chemical diffusion gradients), showing it is a valuable tool for the characterisation of physical discontinuities. Within the same area, the glow discharge also allows the analysis of ultra-thin films, *i.e.* films with thicknesses less than 10 nm. Various applications have been published on the subject: the analysis of a multi-layer system compromising six 5 nm thick layers of Cr buried between Ti layers of variable thickness with a total coating thickness of 3 μm[17,18], the determination of anodic alumina films of

varying thickness with delta function marker layers of about 2 nm width[9] and the depth profiling of a sub-nanometer thick thiourea monolayer adsorbed on copper are some examples.[19]

The advent of rf-GDs has given greater diversity to the use of GD techniques as they can be applied in the analysis of conductors, semi-conductors and non-conductors, advantages compared to the direct current GD and other analytical techniques where the effect of charge accumulation should be compensated. However, important limits of rf-GD still exist during the analysis of insulators, such as the lack of commercial instruments able to measure the electrical parameters of the discharge (including the generated dc bias and the electrical current), and the complication of the adequate development due to the sample nature and thickness effect.[20]

Thérèse et al.[21] demonstrated the important influence a thin layer deposited on a non-conductor substrate can exhibit on the different electrical parameters of the discharge. A thin conductive top layer can increase the "voltage transfer coefficient", defined as the ratio voltage facing the gas and voltage applied to the back of the sample, to increase this way the power deposited into the plasma. This approach was successfully tested by Fernández et al.[22] with real-life samples, obtaining enhanced emission intensities for the coated non-conductive substrates. This effect should be taken in account during the development of quantification methods for the in-depth analysis of insulating samples with thin conductive top coatings.

Other limitations of rf-GDs are related to the analysis of thermally unstable and fragile samples (glasses, polymers), originating possible sample breakdown and degradation during the sputtering process. Therefore, although both dc and rf-GDs are most commonly powered in continuous mode, the analytical interest in pulsed GDs is steadily increasing because of the advantages offered, commented in Part D.I. However, most of the studies of PGDs have been focussed on dc and studies on pulsed rf-GD are still lacking, even if increasing efforts are made to better understand and develop[23,24] analytically useful rf-PGD sources as some specific applications already showed their promising performance.[5,25-27] Anyhow, few systematic studies exist on the analytical effects produced by pulsed rf-GD, particularly using OES detection.

D.II.2. Objectives

According to the comments made, studies related to continuous and pulsed radiofrequency glow discharges, especially regarding non-conducting materials are still needed. Nevertheless, the variety of materials and layers electrically insulating developed is very large and every day growing as new materials of unique chemical and physical properties are being developed, calling for new analytical methodologies. Despite the increasing analytical interest in rf-GD, the devices are less developed than those for dc-GD and consist an important actual investigation field since the control of the different working parameters (voltage difference over electrodes, applied and dissipated power, etc.) is difficult, and therefore, complicate the development of quantification methods for in-depth analysis.

On the other hand, great part of the new materials and coatings being developed nowadays, besides their insulating character, are heat-sensitive and fragile; properties which can lead to sample breakdown and degradation. Therefore, due to the advantages offered, pulsed powered rf-GD-OES should be investigated for such samples to overcome these problems.

So, the main objective of this chapter has been the investigation of the analytical performance of both continuous and pulsed rf-GD-OES for direct solids analysis of conductive and non-conductive materials. Due to the complexity of the subject, different studies have been carried out, including the comparison of the analytical performance of continuous and pulsed operation modes on different analytical parameters (emission intensities, sputtering rates, emission yields and crater shapes) for bulk materials, as well as the evaluation of both power modes for the in-depth analysis of thin deposited conductive layers. Besides, as has been demonstrated by Thérèse et al.[21] that thin conductive top layers on insulating samples exert their influence on the electrical discharge parameters, it resulted necessary to carry out a detailed study of this influence for a range of insulators with varying thickness and diameter, as well as a study of the effect produced by a magnetic field added to the set-up which could result in enhanced emission intensities.[28]

These studies have been realised through the next steps:

♦ The study to improve the analytical performance of rf-GD-OES for electrically insulating materials through the deposition of thin golden top layers and the addition of an axial magnetic field to the set-up by means of optical and electrical measurements.

(Publication D.II.3.1.- *Journal of Analytical Atomic Spectrometry*, **25** (2010) 1247-1252.)

♣ The study of the effect of the pulsed power mode on the detection limits for non-conductive bulk materials and the evaluation of crater shapes obtained in thermally unstable polymer coatings.

♣ The evaluation of the potential of pulsed rf-GD-OES for the in-depth analysis of a thin conductive gold layer deposited on a glass substrate and an industrial glass with various nanometer-thick layers.

(Publication D.II.3.2.- *Mondragon Unibertsitateko Zerbitzu Editoriala*, ISBN: 978-84-608-0770-4, (2008) 1009-1011.)

◘ The investigation of the analytical performance of pulsed rf-GD-OES, compared to its continuous counterpart, for various analytical parameters (sputtering rates, crater shapes, emission intensities and emission yields) measured in both conductive and non-conductive bulk materials.

◘ The evaluation of the potential of pulsed rf-GD-OES, compared to its continuous counterpart, for the in-depth analysis of thin conductive and insulating layers deposited on conductive and non-conductive bulk materials.

(Publication D.II.3.3.- *Journal of Analytical Atomic Spectrometry*, (2010) doi: 10.1039/c0ja00094a)

D.II.3. Results

D.II.3.1. Journal of Analytical Atomic Spectrometry, 25 (2010) 1247-1252.

D.II.3.2. *Mondragon Unibertsitateko Zerbitzu Editoriala*, ISBN: 978-84-608-0770-4, (2008) 1009-1011.

D.II.3.3. *Journal of Analytical Atomic Spectrometry*, (2010) doi: 10.1039/c0ja00094a

D.II.4. Discussion of the Results

The first part of this chapter described the improvement of the analytical performance of continuous rf-GD-OES for the analysis of non-conductive samples through the deposition of thin top coatings and/or the addition of a magnetic field. This improvement was evaluated through electrical and optical measurements of Al_2O_3 samples, of varying thickness and diameter, with 30 nm golden top layers. On one hand, the electrical measurements demonstrated an improvement of the "voltage transfer coefficient" (defined as the ratio voltage facing the gas and voltage applied to the back of the sample) for all the coated samples in comparison with the non-coated samples: an increase of voltage transfer coefficient of 35-90% was observed for the coated samples with varying thickness and of 35-80% for these of varying diameter. So, electrically, it was possible to increment the voltage facing the gas 3 to 5 times, and therefore the amount of power deposited in the plasma, through the deposition of thin conductive films on the sample surface.

On the other hand, an optical parametric study was carried out to evaluate the influence of these thin conductive layers upon the emission intensities measured by rf-GD-OES in "constant pressure-constant forward power" operation mode. Therefore, the Al emission intensities of the Al_2O_3 samples of varying thickness and diameter, coated and non-coated, were measured at increasing forward powers (10-70 W). As expected, enhanced emission intensities were detected at increasing forward power. Moreover, in case of increasing sample thickness, enhanced emission intensities with a factor 2-4 are observed for the coated samples compared to the non-coated ones. In the case of the varying diameters, the results are more complicated: for sample diameters smaller than the ceramic piece surrounding the copper anode and isolating the sample from the aluminium discharge chamber wall, enhanced emission intensities are obtained for the coated samples. However, when the sample diameters exceeds the ceramic piece's size, a sudden decrease in emission intensity can be observed due to the generation of a "parasitic capacitance", developed between the sample and this aluminium ground plate. This effect was observed for both the coated and non-coated samples. In order to avoid this parasitic capacitance, a better isolation between sample and ground plate is necessary by, for example, increasing the ceramic piece its diameter or removing this piece.[29]

As last step to improve the measurement of insulating samples, the addition of an axial magnetic field was evaluated. This field was placed to the back of the coated and non-coated Al_2O_3 samples of varying thickness and optical measurements were carried out in function of increasing forward power. Intensity enhancements of a factor of 1.5 were observed for the non-coated samples due to this magnetic field, but a considerable gain was noticed when combining the effects produced by both thin conductive layers and magnetic field, obtaining this way enhancement factors of 2-6, as a function of the applied forward power. This approach demonstrates a possible way to overcome the problems related to the analysis of non-conductive samples, being of great interest for rf-GD-OES analysis.

A first attempt to investigate the potential of pulsed rf-GD-OES for the surface and depth profiling analysis of thin coated samples was carried out on homogeneous glass samples covered by a 30 nm thick gold layer and an industrial glass with nanometer-thick layers. Also, the advantage of the pulsed mode for thermally unstable samples was tested in terms of crater shapes, as well as its influence on the limits of detection (LOD) for different elements constituting the homogeneous glass samples. In order to evaluate the benefit of pulsed rf-GD-OES for thermal sensitive samples, a 10 μm thick polymeric coating (polyurethane) on a glass substrate was measured in both continuous and pulsed mode and the crater shapes were evaluated by SEM. The craters obtained under pulsed working conditions were not burned, probably due to the lower average powers applied, avoiding this way thermal degradation. The analytical interest of pulsed rf-GD-OES for the analysis of non-conductive samples was evaluated through emission intensity measurements and the calculated limits of detection obtained for elements constituting the 2 mm thick homogeneous glass sample, analysed under different discharge conditions. It could be observed that for most elements the highest emission intensities were obtained in continuous rf-GD-OES, as well as the lowest LODs. However, here, the differences between those in continuous and pulsed mode are less than in the case of the emission intensities (sometimes one order of magnitude) due to the improved plasma stability.

The potential of pulsed rf-GD-OES for thin layer (and even ultra-thin layer) analysis was evaluated for a glass substrate covered by a 30 nm thick gold layer, demonstrating high depth resolution together with a short analysis time. Also, a commercial glass sample with nanometer-thick layers was analysed and all the layers

were perfectly resolved within 40 sec., demonstrating the capability of pulsed rf-GD-OES for the qualitative in-depth analysis of coated non-conductive samples.

These preliminary results proved the interest of rf-PGD-OES for the in-depth analysis for a limited variety of samples. Therefore, it seemed necessary to investigate in detail the analytical performance of pulsed rf-GD-OES for a wide range of bulk and coated materials, both conducting and insulating, compared to the continuous rf-GD-OES performance. This study was carried out in terms of crater shapes, sputtering rates, emission intensities, emission yields and in-depth resolution, important analytical parameters for the development of adequate quantification methods.

As the analyte emission intensity depends on sputtering rate and excitation efficiency, or emission yield, it was of interest to study the effect of pulsed powering upon these two important factors. For the three different conducting matrices (Al, Cu, Fe) and the three homogeneous glasses of varying thickness (1, 1.8, 2.9 mm), the sputtering rates decreased with the duty cycle, because the average power applied to the sample was lower under these conditions. For the three conducting bulk materials, enhanced sputtering rates were observed in pulsed mode, compared to the continuous mode, when applying high pulse frequencies (*i.e.* 10 kHz). Moreover, when comparing the rates in pulsed mode at 40 W forward power and 50% duty cycle (average power of 20 W), it can be observed they were higher than those obtained in continuous mode at 20 W forward power. This trend was described by Jackson and King[30] and could be caused through a discharge current increase and a contraction of the plasma sheath.[31] Concerning the glass samples, the highest sputtering rates were no longer observed at 10 kHz (as for the conductive materials) but at 5 kHz and at lower frequencies when increasing the glass thickness. Again, the trend of enhanced rates in pulsed mode at 40 W and 50% duty cycle, compared to those at 20 W in continuous mode, could be observed.

The emission yields (ratio of the emission intensity and the sputtering rate) of the conducting samples were higher in pulsed than in continuous mode, obtaining a maximum at 10 kHz pulse frequency and 25% duty cycle (pulse width of 25 μs). These results were in agreement with previous experiments[23] concerning time-resolved measurements of emission profiles by pulsed rf-GD-OES, commented in Part D.I.4. This observed enhancement for the emission yield in pulsed mode could be attributed to

the presence of a pre-peak, observed on such time-resolved pulsed profiles, due to the temporal absence of self-absorption at the beginning of the power pulse. It has been demonstrated that at long pulse widths and short evacuation times, more atoms are present in the discharge tube, and as a consequence the effect of self-absorption is stronger. The observation of a pre-peak depends on the emission line under study (especially strong for resonance lines) and although no time-gated detection is available in this study, enhanced emission intensities and, as a consequence, emission yields were observed with decreasing pulse width, demonstrating the importance of the pulse parameters. The trend for the non-conductive glasses was not so clear. In any case, an increasing trend for the emission yields was observed with decreasing duty cycle and the thinnest glass sample showed a behaviour similar to that of the conductive matrices.

The advantage of pulsed rf-GD-OES was very clear in the case of the crater shapes obtained for the non-conductive glasses. In the case of applying 20 and 40 W forward powers the measured crater shapes were inadequate, showing deformations due to thermal-related effects. Moreover, thin glass samples broke under high forward powers. Nevertheless, in the same samples, under pulsed discharge conditions, good crater shapes were obtained with a flat bottom and without any deformation.

As good crater shapes were obtained, even after long sputtering times (> 30 min), pulsed rf-GD-OES demonstrated to be a promising tool for depth profiling analysis. To prove its potential, the depth resolution was calculated, using the slope of the intensity-time profiles at the layer interface, of a 30 nm thick gold coating deposited on the conductive and insulating samples. For both types of substrate, the depth resolution was found to be better when changing from continuous to pulsed discharge conditions and with increasing power. It should be highlighted that, when working with pulsed rf-GD, it was possible to measure the coated glass samples at powers up to 80 W without any risk of breakdown. Besides the better depth resolution, improved emission intensities were measured at lower average powers (in pulsed mode) than the forward powers applied in continuous mode, even without time-gate detection. These results have demonstrated the real advantages offered by rf-PGD-OES and so its future potential for thin film depth profiling.

Finally, after demonstrating the potential of rf-PGD-OES through the measurement of different analytical parameters, this technique was applied to the depth

profiling analysis of real-life samples, *i.e.* a tinplate and a multi-layer glass with thermal and antireflective properties. In the case of the tinplate, the pulsed mode offered the possibility of a better discrimination of the first outer thin layers together with enhanced emission intensities (up to a factor of 2 for the same working power of 20 W), compared with the results in continuous mode. In the analysis in pulsed mode of the multi-layered glass sample, enhanced emission intensities were observed, as well as less noisy signals. Therefore, the presence of contaminants in the coating layers could be easier detected, demonstrating the rf-PGD-OES potential for the quality control and optimisation of the deposition processes during which fast in-depth profile information is necessary to ensure the optimal performance of the coating.

D.II.5. References

[1] R.K. Marcus, J.A.C. Broekaert, "Glow Discharge Plasmas in Analytical Spectroscopy", John Wiley & Sons, Chichester, 2003.

[2] R. Payling, Th. Nelis, "Glow Discharge Optical Emission Spectroscopy: A Practical Guide", RSC Analytical Spectroscopy Monographs, Cambridge, 2003.

[3] J. Pisonero, B. Fernandez, R. Pereiro, N. Bordel, A. Sanz-Medel, 'Glow-discharge spectrometry for direct analysis of thin and ultra-thin solid films', *Trends in Anal. Chem.*, **25 (**2006) 11.

[4] B. Fernández, A. Martin, N. Bordel, R. Pereiro, A. Sanz-Medel, 'In-depth profile analysis of thin films deposited on non-conducting glasses by radiofrequency glow discharge-optical emission spectrometry', *Anal. Bioanal. Chem.*, **384** (2006) 876.

[5] A.C. Muñiz, J. Pisonero, L. Lobo, C. Gonzalez, N. Bordel, R. Pereiro, A. Tempez, P. Chapon, N. Tuccitto, A. Licciardello, A. Sanz-Medel, 'Pulsed radiofrequency glow discharge time of flight mass spectrometer for the direct analysis of bulk and thin coated glass', *J. Anal. At. Spectrom.*, **23** (2008) 1239.

[6] M.R. Winchester, R. Payling, 'Radio-frequency glow discharge spectrometry: A critical review', *Spectrochim. Acta Part B*, **59** (2004) 607.

[7] F. Li, S. Anderson, 'Non-traditional spectroscopy for analysis of semi-conductor and photovoltaic thin film materials', *AIP Conference Proceedings*, **1173** (2009) 62.

[8] N. Jakubowski, R. Dorka, E. Steers, A. Tempez, 'Trends in glow discharge spectroscopy', *J. Anal. At. Spectrom.*, **22** (2007) 722.

[9] K. Shimizu, H. Habazaki, P. Skeldon, G. E. Thompson, 'Radiofrequency GDOES: a powerful technique for depth profiling analysis of thin films', *Surf. Interface Anal.*, **35** (2003) 564.

[10] D. Klemm, V. Hoffmann, K. Wetzig, J. Eckert, 'Dc and rf-GD-OES measurements of adsorbed organic monolayers on copper', *Anal. Bioanal. Chem.*, **395** (2009) 1893.

[11] A. Bengtson, 'The impact of molecular emission in compositional depth profiling using Glow Discharge-Optical Emission Spectroscopy', *Spectrochim. Acta Part B*, **63** (2008) 917.

[12] S. Sato, K. Omori, S. Araki, Y. Takahashi, K. Wagatsuma, 'Surface analysis of nitride layers on Fe-based alloys through plasma nitride processes', *Surf. Interf. Anal.*, **41** (2009) 496.

[13] W. Tian, F.Q. Xie, X.Q. Wu, Z.Z. Yang, 'Study on corrosion resistance of electroplating zinc-nickel alloy coatings', *Surf. Interf. Anal.*, **41** (2009) 251.

[14] M. L. Hartenstein, R. C. Compton, R. K. Marcus, 'Rapid depth-resolved analysis of nitride layers (> 50 micrometers) on prosthetic devices by radiofrequency glow discharge optical emission spectrometry', *Amer. Lab.*, (1997) 17C-17H.

[15] B. Yuksel, E.B. Sam, O.C. Aktas, M. Urgen, A.F. Cakir, 'Determination of sodium migration in sol-gel deposited titania films on soda-lime glass with r.f. glow discharge optical emission spectrometry', *Appl. Surf. Sci.*, **255** (2009) 4001.

[16] P. Le Coustumer, M. Montelica-Heino, P. Chapon, H. François, R. Payling, 'Surface characterization and depth profile analysis of glasses by r.f. GDOES', *Surf. Interface Anal.*, 35 (2003) 623.

[17] R. Escobar Galindo, R. Gago, A. Lousa, J.M. Albella, 'Comparative depth-profiling analysis of nanometer-metal multi-layers by ion-probing techniques', *Trends in Anal. Chem.*, **28** (2009) 494.

[18] R. Escobar Galindo, J.M. Albella, 'Modelling of Glow Discharge Optical Emission Spectroscopy depth profiles of metal (Cr, Ti) multilayer coatings', *Spectrochim. Acta Part B*, **63** (2008) 422.

[19] K. Shimizu, R. Payling, H. Habazaki, P. Skeldon, G.E. Thompson, 'Rf-GDOES depth profiling analysis of a monolayer of thiourea adsorbed on copper', *J. Anal. At. Spectrom.*, **19** (2004) 692.

[20] M. Parker, R.K. Marcus, 'Investigation of a dielectric sample atomization and electrical characteristics in a radiofrequency glow discharge source', *Spectrochim. Acta Part B*, **50** (1995) 617.

[21] L. Therese, Z. Ghalem, P. Guillot, P. Belenguer, 'Improved voltage transfer coefficients for nonconductive materials in radiofrequency glow discharge optical emission spectrometry', *Anal. Bioanal. Chem.*, **386** (2006) 163.

[22] B. Fernández, N. Bordel, R. Pereiro, A. Sanz-Medel, 'The effect of thin conductive layers on glass on the performance of radiofrequency glow discharge optical emission spectrometry', *J. Anal. At. Spectrom.*, **20** (2005) 462.

[23] Th. Nelis, M. Aeberhard, M. Hohl, L. Rohr, J. Michler, 'Characterisation of pulsed rf-glow discharge in view of ist use in OES', *J. Anal. At. Spectrom.*, **12** (2006) 112.

[24] Ph. Belenguer, M. Ganciu, Ph. Guillot, Th. Nelis, 'Pulsed glow discharges for analytical applications', *Spectrochim. Acta Part B*, **64** (2009) 623.

[25] J. Pisonero, L. Lobo, N. Bordel, A. Tempez, A. Bensaoula, N. Badi, A. Sanz-Medel, 'Quantitative depth profile analysis of boron implanted silicon by pulsed radiofrequency glow discharge time-of-flight mass spectrometry', *Sol. Energy Mater. Sol. Cells*, **94** (2010) 1352.

[26] P. Sanchez, B. Fernández, A. Menendez, R. Pereiro and A. Sanz-Medel, 'Pulsed radiofrequency glow discharge optical emission spectrometry for the direct characterisation of photovoltaic thin film silicon solar cells', *J. Anal. At. Spectrom.*, **25** (2010) 370.

[27] I.S. Molchan, G.E. Thompson, P. Skeldon, N. Trigoulet, A. Tempez, P. Chapon, 'Analysis of thin impurity doped layers in anodic alumina and anodic tantala films by glow discharge time-of-flight mass spectrometry', *Trans. Inst. Met. Finish.*, **88** (2010) 154.

[28] A.I. Saprykin, J.S. Becker, H.-J. Dietze, 'Trace analysis of glasses by magnetically enhanced rf GDMS', *Fresenius J. Anal. Chem.*, **359** (1997) 449.

[29] L. Thérèse, Ph. Guillot, D. Alberts, R. Pereiro, A. Sanz-Medel, Ph. Belenguer, 'Strategies for improving the analysis for non-conducting samples', poster Plasma Winter Conference, Zaragoza, 2011.

[30] G.P. Jackson, F.L. King, 'Probing excitation/ionization processes in millisecond-pulsed glow discharges in argon through the addition of nitrogen', *Spectrochim. Acta Part B*, **58** (2003) 185.

[31] L. Thérèse, Ph.D. Thesis, "Plasmas radiofrequence pour l'analyse de materieaux: Etudes experimentale, analytique et numerique", University of Toulouse III, 2005.

III.

Development of new applications of continuous and pulsed rf-GD-OES for the direct analysis of nanostructured and nanocomposite materials

Nowadays, nanostructured and nanocomposite materials constitute an important material group in present industry due to their interesting possible applications. As these materials depend on their chemical composition and structure, the use of reliable characterisation analytical techniques is of critical importance today to assist the optimisation of their synthesis procedures as well as to assess their quality as a final product. Up to date, a great variety of such nanostructured materials and nanocomposites exists, each with its specific properties. In particular, metallic nanowires are among the most attractive nanometer-sized materials used in a great variety of applications. On the other hand, Zn-based nanocomposite materials with occluded nanoparticles are widely used due to the improved corrosion protection they offer, together with enhanced mechanical properties. Especially, the use of TiO_2 nanosized particles is of great interest because of their behaviour as photocatalysts, being excellent candidates for environmental purification processes.

Therefore, the main objective of this chapter will be the development of new applications of radiofrequency glow discharge coupled to optical emission spectrometry, both in continuous and pulsed power mode, for the direct analysis of oxide nanostructured templates filled with metallic nanowires and metal-matrix films with TiO_2 nanoparticles deposited upon conductive substrates.

D.III.1. Introduction

The progress in the development of advanced materials, electronics, information storing devices and new analytical sensors, strongly depends on the continuous improvement obtained related to nanotechnology and nanoscience. During the last years a great variety of such materials have been designed and developed. Here, a material is considered to be a nanomaterial when the sizes of the individual building blocks are less than 100 nm, at least in one dimension. Metallic nanowires, for example, differ from their corresponding bulk material through the increased surface area, the very high density of electronic states and joint densities of states near the energies of their van Hove singularities, the enhanced excitation binding energy, the diameter-dependent bandgap, the increased surface scattering for electrons and photons, etc. These differences convert them into a very attractive nanometer-sized materials, leading to new unique properties (*e.g.* superior opto-electronic properties, reduced thermal conductivity, enhanced infrared thermal emission [1]) used in applications as interconnecters in nanoelectronic, magnetic, chemical or biological sensors, electrochemical batteries and as biotechnological labels.[2,3] The existence of two-dimensional nanostructured materials such as nanotubes and nanorods, consisting of metals, polymers, carbon or semi-conductors, with special properties converts them into materials with increasing impact in the industrial and technological sector.[4]

On the other hand, a great variety of nanocomposite materials exists, which are as multiphase solid materials where one of the phases has one, two or three dimensions of less than 100 nm, or structures having nanoscale repeated distances between the different phases that make up the material. In the broadest sense, this definition can include porous media, colloids, gels, etc., but usually it means the combination of a bulk matrix with one or more nano-dimensional phases differing in properties due to dissimilarities in structure and chemistry. So, the mechanical, electrical, chemical, optical, electrochemical and catalytic properties of this nanocomposite materials will differ from those of the components materials. In mechanical terms, nanocomposites differ from conventional composite materials (where a thin layer is deposited upon a bulk substrate) because of the exceptionally high surface to volume ratio of the reinforcing phase, which can be made up of particles, sheets or fibers, typically of one order of magnitude greater than for the conventional composite materials. Nowadays,

electrodeposition techniques provide a route to many new composite coatings with a metallic matrix having a variety of spherical shaped nanosized particles occluded, including silicon dioxide,[5] titanium dioxide[6,7] and aluminium dioxide.[8,9] TiO_2 nanosized particles are of most interest due to their increasing availability, low cost, high chemical stability, and their behaviour as almost ideal photocatalyst. Therefore, they are considered to be excellent candidates for environmental purification, particularly in the treatment of polluted water.[10]

Important properties of nanostructured and nanocomposite materials depend on their chemical composition and structure and, therefore, the use of reliable characterisation techniques is indispensable during both the optimisation steps of the synthesis procedures and the quality control of the final products to guarantee their optimal performance. The increasing interest in this field of materials created the need for novel or advanced techniques capable of the characterisation of both the new nanostructures and the fabricated functionalised nanostructured materials. Moreover, to obtain a deeper understanding, adequate analytical tools providing spatial and in-depth resolution at the nanometer scale are demanded. The analytical performance of available techniques, based on both optical emission and mass spectrometry, for such analysis demands have recently been overviewed and compared by Fernández et al.[11] and Galindo et al.[12].

The glow discharge analytical plasma is widely used as atomisation, excitation and ionisation source, both for optical emission spectrometry and mass spectrometry, due to the generation of atoms and ions directly sputtered from the solid sample of interest, following an atomic “layer-by-layer” approach.[13] Radiofrequency GD have attracted great interest because of the possibility to analyse, whether bulk or coated, conductive, semi-conductive and insulating materials, contrary to the better-known counterpart direct current GD. This crucial advantage broadened the application field widely.[14] As mentioned previously (Part D.I.), pulsed GDs are gaining a lot of attention due to the advantages this operation mode offers, compared to continuous operation. The important aspects of pulsed GDs and their applicability in analytical applications have recently been reviewed by Belenguer et al.[15]

D.III.2. Objectives

Due to the increasing interest in new nanostructured and nanocomposite materials for their application in the industrial and technological field, adequate analytical characterisation techniques are needed, providing fast and reliable information, both with lateral and in-depth resolution. GD proved by now to be a powerful and versatile technique for depth profiling analysis of a wide range of materials. The GD ensures a high sputtering rate due to the high flux of energetic species. Additionally, these species are of low energy, resulting in low penetration depths and limiting the surface damage to a very shallow layer with a thickness of 2 nm more or less, and so providing high depth resolution.[16] Both GD-OES and GD-MS demonstrated their capability for the qualitative analysis of such materials, recently reviewed by Fernández et al.[17]

Therefore, the main objective of this chapter will be the investigation of new applications of radiofrequency glow discharge optical emission spectrometry, operated in both continuous and pulsed mode, for the quantitative in-depth analysis of such nanostructured and nanocomposite materials.

♦ Highly ordered and self-assembled magnetic nanowires, obtained through the filling of nanoporous anodic alumina templates or titanium dioxide nanotube arrays by electrodeposition techniques, will be analysed by continuous rf-GD-OES.

(Publication D.III.3.1.- *Analytical and Bioanalytical Chemistry*, 396 (2010) 2833-2840)

♣ Metal-matrix titanium dioxide nanocomposite films deposited upon titanium or steel substrates will be characterised by pulsed rf-GD-OES (because of the advantages offered in this pulsed mode to analyse heat-sensitive and fragile samples).

(Publication D.III.3.2.- *Talanta*, submitted November 2010)

D.III.3. Results

D.III.3.1. Analytical and Bioanalytical Chemistry, 396 (2010) 2833-2840

D.III.3.2. Talanta, submitted November 2010

D.III.4. Discussion of the Results

The first part describes the qualitative and quantitative depth profiling analysis of highly ordered and self-assembled magnetic nanowires, obtained through the filling of nanoporous anodic alumina templates (NAATs) or titanium dioxide nanotube arrays by electrodeposition techniques. The nanoporous alumina membranes were grown at the "Scientific-Technical Research Services" of the University of Oviedo in such a way that different pore lengths could be obtained: 5, 2.5 and 1.2 μm. By SEM pictures the hexagonal symmetry of the nanoporous arrays was clear, as well as the alignment of the nanopores along the membrane thickness, forming a columnar-type nanoporous structure. For the titania nanotube arrays, the SEM pictures showed the tubular structure of the template, with average inner pore diameters of 100 nm and a nearly uniform wall thickness above 40 nm mean size. The resulting average outer diameter of the titania nanotubes was in the range of 140-150 nm. The nanotube arrays were synthesised in order to obtain 500 nm long tubes. Through pulsed electrochemical deposition and potentiostatic electrodeposition processes, metallic nanowires were grown filling the NAATs and titania nanotube arrays, respectively. Different metals have been used including Ni, Au and FeNi alloys. Additionally, EDX measurements have been carried out to confirm the chemical composition of the samples. A residual S signal was detected for the titania samples, probably due to the use of a Watts-type electrolyte during the Ni deposition process.

Rf-GD-OES in continuous mode has been used for the compositional depth profile characterisation of the samples. The measurement conditions (an effective output voltage of 500 V and a true plasma power of 12 W) have been chosen so good depth resolution should be obtained without thermal-related problems. Through this power – voltage rf control mode all plasma parameters are held constant except the pressure. The emission yield is held constant as well, even when measuring a wide variety of matrices, and linear calibration curves are obtained. Moreover, as the structures of interest consists of nanometer-thick features, the voltage drop formed above the insulating samples (commented in Part D.II.3.1.) will be negligible (coupling capacitance about 0.5 nF), and voltage losses are insignificant. The multi-matrix calibration carried out under these conditions gave linear calibration curves for all elements of interest, including oxygen through "matrix-matching" by an aluminium oxide sample.

The qualitative depth profiles provided elemental information on the respective samples while the quantitative depth profiles provided information on the nanowire length, their composition and on the homogeneity of the electrodeposition processes carried out to fill the templates. For all the samples, the profiles were in good agreement with the estimated pore or tube lengths. Moreover, in the cases the nanowires consisted of different elements, good layer discrimination was possible, in good agreement with the results obtained by SEM and EDX. However, it could be noted that for the filled NAATs lower oxygen concentrations were measured than the weight percent 1:1 ratio expected, a fact that could be due to recombination processes of oxygen with hydrogen and hydroxide groups formed during the electrodeposition processes. It should be noted that, for the cases where samples consisting of longer empty pores or tubes are measured, the sample porosity should be included in the quantification process. However, in our case, through an appropriate multi-matrix calibration procedure, rf-GD-OES proved to be able to characterise the composition and depth profiles of these nanostructured materials, providing information regarding the quality of the electrochemical deposition processes, for future optimisation processes.

The second part describes the qualitative and quantitative depth profiling analysis of metal-matrix titania nanocomposite coatings deposited on titanium and steel substrates by pulsed rf-GD-OES. These nanocomposite coatings were prepared at the Dpt. of Chemistry and Biochemistry of the University of Lisbon (Portugal) by pulsed-reverse current techniques, obtaining this way micrometer-thick Zn-matrix composite coatings with occluded TiO_2 nanoparticles, deposited on titanium and steel substrates. This structure is clearly observable in SEM pictures published by Frade et al.[7]

The analyte emission intensity in GD-OES depends upon two important factors: the sputtering rate (determining the final density of analyte atoms in the plasma) and the excitation efficiency of these atoms (emission yield). Previous work carried out in our laboratory (see Part B.II) demonstrated that enhanced emission intensities and emission yields (calculated as the ratio of the measured emission intensity and the sputtering rate) can be obtained in pulsed power mode, by applying high pulse frequency and small duty cycles, in comparison with those obtained by using the GD continuous mode counterpart. Moreover, it was found that less thermal-related problems and good crater shapes, in the interface region and in the substrate, are obtained by using such pulse conditions.

One of the potential advantages of pulsed rf-GD sources arises from the creation of certain time regimes in which the background signal may be virtually suppressed while the analyte signal is enhanced. In previous work (see Part D.I) it has been observed that the intensity observed in the so-called pre-peak, at the beginning of the pulse, is enhanced in comparison to the plateau intensity. The existence of this pre-peak has been linked to the temporal absence of self-absorption at the beginning of the pulse. Moreover, the use of this effect has been able to improve analytical calibration curves, so increasing the sensitivity, important during the detection of possible contamination of the Zn-TiO_2 nanocomposite films. To evaluate the interest of pulsed rf-GD-OES for these analyses, a critical comparison with the continuous mode has been carried out in terms of emission intensities, penetration rates and emission yield ratios. Five CRMS with O and varying Ti concentration have been measured under continuous and pulsed conditions. The penetration rates measured in pulsed mode were always lower, probably due to the lower average power deposited in the plasma. Also, significant differences were observed for the emission intensities and for the ratio intensity and penetration rate. For Ti, a noticeable increase can be observed in pulsed mode: an 1.5-factor improvement in the 4 cases for the emission intensities, independently of the sample matrix and a 2.5-factor improvement for the emission yield ratios. In the case of O, only slight variations were observed for the emission intensities together with a lower sputtering rate, leading to a very small increase of the emission yield. Nevertheless, the interest of power pulsing has been proven for the analysis of Zn-TiO_2 nanocomposite films.

Finally, rf-PGD-OES has been investigated for the depth profile characterisation of Zn-TiO_2 nanocomposite films. The qualitative depth profiles demonstrated less than 100 s was needed to sputter the film before reaching the titanium or steel substrate and were perfectly distinguishable with good depth resolution. Moreover, contamination signals of C,O and S, due to the synthesis procedures, were clearly visible and also identified by semi-quantitative SEM/EDS measurements. A pulsed multi-matrix calibration has been carried out to convert the qualitative into quantitative depth profiles. Calibration curves, demonstrating good linearity, were obtained plotting the normalised intensity signals as a function of the product of the mass content of each element in the CRM and the sputtering rate of the standard (in $\mu g\ s^{-1}$). The quantitative depth profiles calculated through this multi-matrix calibration showed a sharp interface with good

depth resolution of the Zn-TiO_2 nanocomposite film and the substrate. Moreover, a rather homogeneous distribution of the TiO_2 particles, occluded in the Zn-matrix, was observed, especially in the case of the steel substrate.

Both the thickness and element concentrations measured were validated by comparison with other techniques such as SEM with EDS and ICP-MS. The rf-PGD-OES quantitative profiles demonstrated that the thickness of the Zn-TiO_2 nanocomposite films was found to be around 35 ± 2.1 μm and 28 ± 1.6 μm for the Ti and steel substrates, respectively. These values were in well agreement, within the given uncertainties, with the values obtained by SEM measurements. Additionally, the Ti concentrations in the films, obtained by GD-OES (0.3-0.4%), have also been measured by wet-chemical analysis with ICP-MS obtaining a value of 0.35 ± 0.04%, demonstrating that pulsed rf-GD-OES offers the possibility of accurate and precise depth profiling analysis of Zn-TiO_2 nanocomposite films deposited on different substrates, showing comparable or better results than those obtained by more “traditional” techniques used for the characterisation of such samples.

D.III.5. References

[1] L.J. Klein, H.K. Hamann, Y.-Y. Au, S. Ingvarrson, 'Coherence properties of infrared thermal emission from heated metallic nanowires', *Appl. Phys. Lett.*, **92** (2008) 213102.

[2] S.A. Dayeh, C. Soci, X.Y. Bao, D. Wang, 'Advances in the synthesis of InAs and GaAs nanowires for electronic applications', *Nano Today*, **4** (2009) 347.

[3] P.R. Bandaru, P. Pichanusakorn, 'An outline of the synthesis and properties of Si nanowires', *Semicond. Sci. Technol.*, **25** (2010) 024003.

[4] Mitura S, "Nanotechnology in materials science", Elsevier Science, Amsterdam, Netherlands, 2000.

[5] K. Kondo, A. Ohgishi, Z. Tanaka, 'Elecytodeposition of Zinc-SiO2 Composite', *J. Electrochem. Soc.*, **147** (2000) 2611.

[6] T. Deguchi, K. Imai, H. Matsui, M. Iwasaki, H. Tada, S. Ito,' Rapid electroplating of photocatalytically highly active TiO_2-Zn nanocomposite films on steel', *J. Mat. Sci.*, **36** (2001) 4723.

[7] T. Frade, V. Bouzon, A. Gomes, M.I. da Silva Pereira, 'Pulsed-reverse current electrodeposition of Zn and Zn-TiO_2 nanocomposite films', *Surf. Coat. Techn.*, **204** (2010) 3592.

[8] M. Tavoosi, F. Karimzadeh, M.H. Enayati, A. Heidarpour, 'Bulk Al-Zn/Al_2O_3 nanocomposite prepared by reactive milling and hot pressing methods', *J. Alloys. Comp*. **475** (2009) 198.

[9] S. Oue S, H. Nakano, S. Kobayashi, T. Akiyama, H. Fukushima, K. Okumura, 'Electrodeposition of Zn-Al2O3 Composite from non-suspended solution containing quaternary ammonium salt', *J. Surf. Finish. Soc. Japan*, **53** (2002) 920.

[10] A. Fujishima, T.N. Rao, D.A. Tryk, 'Titanium dioxide photocatalysis', *J. Photochem. Photobiol. C*, **1** (2000) 1.

[11] B. Fernández, J.M. Costa, R. Pereiro, A. Sanz-Medel, 'Inorganic mass spectrometry as a tool for the characterisation at nanoscale', *Anal. Bioanal. Chem.*, **396** (2010) 15.

[12] R. Escobar-Galindo, R. Gago, D. Duday, C. Palacio, 'Towards nanometric resolution in multilayer depth profiling: a comparative study of RBS, SIMS, XPS and GDOES', *Anal. Bioanal. Chem.*, **396** (2010) 2725.

[13] R.E. Steiner, C.M. Barshick, A. Bogaerts, in: R.A. Meyers (Ed.), "Encyclopedia of Analytical Chemistry", John Wiley & Sons Ltd., Chichester, UK, 2009.

[14] M.R. Winchester, R. Payling, 'Radio-frequency glow discharge spectrometry: A critical review', *Spectrochim. Acta Part B*, **59** (2004) 607.

[15] Ph. Belenguer, M. Ganciu, Ph. Guillot, Th. Nelis, 'Pulsed glow discharges for analytical applications', *Spectrochim. Acta Part B*, **64** (2009) 623.

[16] N. Trigoulet, H. Hashimoto, I.S. Molchan, P. Skeldon, G.E. Thomson, A. Tempez, P. Chapon, 'Surface topography effects on glow discharge depth profiling analysis', *Surf. Interface Anal.*, **42** (2010) 328.

[17] B. Fernández, R. Pereiro, A. Sanz-Medel, 'Glow discharge analysis of nanostructured materials and nanolayers – A review', *Anal. Chim. Acta*, **679** (2010) 7.

CONCLUSIONS/CONCLUSIONES

The main conclusions of this Thesis Work can be summarised in the following points:

1. Time-resolved measurements of emission profiles in pulsed rf-GD have been studied in view of possible advantages for OES and in order to get a better insight in the different plasma processes taking place under pulsed conditions. Pulsed emission profiles were measured for a wide range of copper transition, observing a characteristic pre-peak with enhanced emission intensities for some emission lines which could be linked to a lack of self-absorption at the beginning of the pulse. Calibration curves showing improved linearity using pre-peak intensities were obtained, even at high analyte concentrations and for resonance lines. Both discharge parameters (power and pressure) and pulse parameters (pulse length, pulse frequency and duty cycle) exerted an influence on the pre-peak behaviour. It has been demonstrated that the pre-peak can be exploited advantageously for analytical purposes when measuring at high pulse frequency combined with a small duty cycle (obtaining small pulse widths). Moreover, self-absorption can be minimised using long evacuation times (> 100 μs).

2. The analytical performance of a continuous rf-GD-OES system for non-conductor analysis has been improved through the deposition of thin conductive layers and/or the addition of an axial magnetic field to the set-up. Electrical measurements of "model" coated and non-coated insulating samples, with varying dimensions, demonstrated a "voltage transfer coefficient" increase (defined as the ratio of voltage facing the gas and voltage applied to the back of the sample) and so more power will be deposited into the GD plasma. Optical emission measurements showed enhanced emission intensities for the coated samples. With the addition of an axial magnetic field (to the back of the sample), increased emission intensities were obtained as well and a considerable gain was observed implementing the combination of thin conductive layers and a magnetic field. This study demonstrated a viable approach to overcome the drawbacks related to the analysis of non-conductors by rf-GD-OES.

3. The analytical performance of pulsed rf-GD-OES for the analysis of homogenous and thin layered samples, both conducting and non-conducting, has been studied, compared to its steady-state counterpart. Enhanced sputtering rates

were obtained in pulsed mode (when the average power applied is the same as the continuous forward power), especially at high pulse frequencies for the conductors. Enhanced emission yields were obtained for all samples using the pulsed mode at high pulse frequency and small duty cycle, related to the presence of the "pre-peak" under such conditions. Moreover, the advantage of decreased thermal stress, on heat-sensible samples, was shown through crater shape measurements. Finally, pulsed rf-GD-OES has demonstrated its potential for depth profiling analysis of thin and ultra-thin multi-layered coated samples, offering improved depth resolution, enhanced emission intensities, less noisy signals and good layer discrimination.

4. The viability of continuous rf-GD-OES has been studied for the direct analysis of "model" solid nanostructured materials; in particular for metallic nanowires grown inside alumina nanopores and titania nanotubes. The results, both qualitative and quantitative, have demonstrated the great potential of rf-GD-OES to characterise those nanostructures. Faster detection, without any form of previous sample treatment and without any requirement of high vacuum, together with decreased overall costs and analysis time have been achieved. The growth and composition of metallic nanowires grown inside the nanostructures, as well as the homogeneity of their distribution inside the porous templates can be monitored. Moreover, the elemental composition and nanopore or nanotube length results were in good agreement with those obtained by SEM and EDX.

5. Similarly, the potential of pulsed rf-GD-OES has been evaluated for the direct analysis of solid metal-based titania nanocomposite films deposited on titanium and steel substrates. The GD pulsed measurement conditions were chosen according to previous studies. Under such conditions, good crater shapes were obtained in the interface region, free from any thermal-related problems, and useful linear curves through a multi-matrix calibration. The observed Ti and O concentrations were in good agreement with those obtained by ICP-MS and the nanocomposite film thicknesses were satisfactorily checked by SEM. Moreover, a rather homogeneous distribution of the TiO_2 particles in the Zn-matrix was observed, especially for the steel substrate.

Las principales conclusiones derivadas de esta Tesis Doctoral pueden resumirse en los siguientes puntos:

1. Se ha estudiado a fondo la rf-GD pulsada mediante medidas con resolución temporal de los perfiles de emisión. Estos perfiles de emisión en el tiempo se han medido para un amplio intervalo de transiciones de cobre, observándose para algunas líneas de emisión un "pre-peak" característico y de gran intensidad, que se podría relacionar con la ausencia de auto-absorción al principio del pulso. Las líneas de calibración obtenidas a partir de las intensidades medidas en dicho "pre-peak" muestran buena linealidad, incluso a altas concentraciones del analito y utilizando lineas resonantes. Por otro lado, se ha comprobado que el comportamiento de esta señal analítica ("pre-peak") está claramente influido por los parámetros tanto de la descarga (presión y potencia) como del pulso (anchura, frecuencia y factor de ocupación o "duty cycle"). El empleo del "pre-peak" como señal analítica ha demostrado ser muy ventajoso si se trabaja a altas frecuencias combinadas con duty cycles pequeños (anchuras de pulso muy cortas) y tiempos de evacuación > 100 μs.

2. La deposición de capas delgadas conductoras sobre la muestra y/o la presencia de un campo magnético, axial al dispositivo experimental, han logrado mejorar el rendimiento analítico de rf-GD-OES en modo continuo para el análisis de muestras no-conductoras. Medidas eléctricas realizadas sobre muestras no-conductoras de diferentes dimensiones (con o sin capa conductora) han demostrado que el "coeficiente de transferencia de voltaje" (definido como la relación voltaje frente al gas y el aplicado a la muestra) se ve favorecido por la presencia de capas conductoras. Además, se ha observado que para las muestras con capa conductora se obtienen mayores intensidades de emisión. Por otro lado, la aplicación del campo magnético axial también da lugar a un incremento de las intensidades de emisión y resulta especialmente beneficioso si se aplica en combinación con las capas conductoras. Este estudio muestra, por tanto, una posible vía para superar muchas dificultades relacionadas con el análisis de no-conductores por rf-GD-OES.

3. Se ha estudiado el potencial analítico de rf-GD-OES en modo pulsado en el análisis directo de materiales, tanto conductores como aislantes, homogéneos y con capas delgadas, comparado los resultados con los observados con el modo continuo. En modo pulsado, se han obtenido mayores velocidades de arrancado, especialmente a altas frecuencias, en el caso de los conductores. Por otro lado, las mayores eficiencias de emisión se han obtenido, tanto para conductores como no-conductores, en modo pulsado (debido a que la presencia del "pre-peak" da lugar a mayores intensidades de emisión, especialmente a altas frecuencias con duty cycles pequeños). Además, se ha comprobado observando los perfiles de los cráteres obtenidos, que en modo pulsado los problemas derivados de los efectos térmicos se reducen considerablemente. Por último, se ha demostrado que la técnica rf-GD-OES en modo pulsado para el análisis de perfiles en profundidad de muestras con capas delgadas o ultra-delgadas, ofrece mejor resolución en profundidad, mayores intensidades de emisión, menor ruido y mejor discriminación de las capas delgadas que en modo continuo.

4. Hemos estudiado la viabilidad de la técnica rf-GD-OES para el análisis directo de materiales nanoestructurados; concretamento nanohilos metálicos en nanoporos de alúmina (Al_2O_3) y en nanotubos de titania (TiO_2). Los resultados, tanto cualitativos como cuantitativos, han demostrado la capacidad de rf-GD-OES para caracterizar estas nanoestructuras, consiguiendo una detección rápida, sin ningún tratamiento previo de la muestra y sin necesidad de utilizar condiciones de alto vacío. Todo ello hace esta técnica mas atractiva al disminuir el tiempo y el coste del análisis. Los resultados (*e.g.* composición elemental y la longitud de los poros o tubos) se han comparado favorablemente con los obtenidos por otras técnicas mas comunes para ello (SEM y EDX).
En conclusión, ha sido posible medir el crecimiento de los nanohilos metálicos en el interior de las nanoestructuras con muy buena resolución e identificar las varias capas que los constituyen permitiendo así controlar la homogeneidad de estos procesos de deposición en las membranas porosas.

5. Se ha evaluado el potencial de rf-GD-OES en modo pulsado para el análisis directo de películas nanocomposites dopadas con partículas de óxido de titanio depositadas en sustratos de titanio y acero. Las condiciones de medida han sido seleccionadas para garantizar mayores eficiencias de emisión de los

componentes mayoritarios de la muestra en tiempos de análisis mas cortos. Además, en dichas condiciones, en la región de la interfase, se han obtenido buenas formas de crater (sin problemas relacionados con efectos térmicos). Por otro lado, mediante una calibración multi-matriz se han obtenido curvas con buena linealidad que han permitido cuantificar las concentraciones de Ti y O en las capas nanocomposites, así como determinar espesores de las películas con buena exactitud ya que los resultados obtenidos concuerdan con los de ICP-MS y SEM. Por último, reseñar que se ha observado que la distribución de las partículas de titania ocluidas en la matriz de Zn parece bastante homogénea (especialmente para el sustrato de acero).

-

SUGGESTIONS FOR FUTURE RESEARCH

Science, in the very act of solving problems, creates more of them.
Abraham Flexner, 1930

In this last section, as customary in our Research Group, I would like to point out some paths, opened by the results obtained in this Ph.D. Thesis, which could be of interest to pursue in further research work.

1. The conclusions obtained during this Ph.D. Thesis firmly demonstrated the advantages offered by pulsed radiofrequency glow discharge optical emission spectrometry, especially those related to enhanced emission intensities and emission yields, using the pre-peak signals observed at the beginning of the pulse. These advantages could be even better exploited when using adequate time-gated detection, making it possible to measure the emission intensity only during the pre-peak instead of the signal average during the whole pulse (as it was in our case for most of the experiments). In particular, time-resolved measurements of pulsed emission profiles by radiofrequency glow discharge optical emission spectrometry should be particularly interesting for other elements known to have strong self-absorbed emission lines (*e.g.* Al 396.40 nm and Cr 425.43 nm.).

2. The coupling of pulsed radiofrequency glow discharges to solid state detectors (*e.g.* intensified charge-coupled devices) is envisaged also as a highly powerful combination, because it would allow time-gated detection providing very useful spectral information (of particular interest if organic materials are being sputtered). Besides, such detectors offer the possibility to measure two-dimensional emission images from the glow discharge, obtaining spatial information necessary for the understanding of the various excitation processes, known to take place sequentially when pulsing the rf discharge.

3. Although the analytical performance of rf-GD-OES for non-conductor analysis could be improved through the deposition of thin conductive top layers, with or without the addition of an axial magnetic field to the set-up, our results are qualitative and information on crater shapes or on emission yields is still missing. This will be of crucial importance for future quantification studies. Moreover, the effect of different magnetic fields (perpendicular, circular, etc.)

and their placement (embedded in the anode, behind or lateral to the sample) should also be electrically and optically investigated. As last, a better understanding of the problems occurring when measuring large samples (leading to the generation of a parasitic capacitance between the sample and the grounded part of the instrument) could be obtained through simulations with electrical circuit software. A potential solution for many of those problems could be a better isolation of the sample from the instrument through the increase of the ceramic piece's diameter or its removal.

4. We have studied rf-GD-OES, both in continuous and pulsed mode, for the compositional depth profile analysis of specific advanced materials (*e.g.* metallic nanowires grown inside nanoporous alumina and nanotubular titania templates, and metal-matrix composite films containing occluded TiO_2 nanoparticles). The proven application of rf-GD-OES in direct solids analysis could be extended towards new materials of present importance, such as energy related materials like thin film solar cells, materials for thermal power plants, Li-ion batteries, etc.

PUBLICATIONS

PUBLICATIONS DERIVED FROM THE PH.D. THESIS

1. D. Alberts, R. Pereiro, V. Vega, V. Prida, N. Bordel, A. Sanz-Medel, "In-depth profile analysis of thin films by radiofrequency glow discharge optical emission spectrometry", ISSBN: 978-84-608-0770-4, Mondragon Unibertsitateko Zerbitzu Editoriala, Spain (2008) 1009-1011.

2. D. Alberts, V. Vega, R. Pereiro, N. Bordel, V. M. Prida, A. Bengtson, A. Sanz-Medel, "In-depth profile analysis of alumina and titania nanostructured templates by radiofrequency glow discharge coupled to optical emission spectrometry", *Anal. Bioanal. Chem.* 396 (2010) 2833-2840

3. D. Alberts, L. Therese, Ph. Guillot, R. Pereiro, A. Sanz-Medel, Ph. Belenguer, M. Ganciu, "Electrical properties of non-conductive samples, with and without thin conductive layers, and the presence of a magnetic field to enhance their optical emission in RF-GD-OES", *J. Anal. At. Spectrom.* 25 (2010) 1247-1252

4. D. Alberts, P. Horvath, Th. Nelis, R. Pereiro, N. Bordel, J. Michler, A. Sanz-Medel, "Time-resolved measurement of emission profiles in pulsed radiofrequency glow discharge optical emission spectroscopy: investigation of the pre-peak", *Spectrochim. Acta Part B* 65 (7) (2010) 533-541.

5. D. Alberts, B. Fernández, R. Pereiro, A. Sanz-Medel, "Investigation of the analytical performance of pulsed radiofrequency glow discharge coupled to optical emission spectrometry for bulk and in-depth profile analysis of conductors and insulators", *J. Anal. At. Spectrom.* (2010), doi: 10.1039/c0ja00094a.

6. D. Alberts, B. Fernández, T. Frade, A. Gomes, M.I. da Silva Pereira, R. Pereiro, A. Sanz-Medel, "Depth Profile Characterization of Zn-TiO_2 Nanocomposite Films through Pulsed Radiofrequency Glow Discharge - Optical Emission Spectrometry", submitted to *Compos. Sci. Technol.* (November 2010)

PUBLICATIONS RELATED TO THE PH.D. THESIS

1. V. Vega, M.A. Cerdeira, V.M. Prida, D. Alberts, N. Bordel, R. Pereiro, F. Mera, S. García, M. Hernández-Vélez, M. Vázquez, "Electrolyte influence on the anodic synthesis of TiO_2 nanotube arrays", *Journal of Non-Crystalline Solids* 354 (2009) 5233-5235.

2. T. Frade, A. Gomes, M.I. da Silva Pereira, D. Alberts, R. Pereiro, B. Fernandez, "Studies on the Stability of Zn and Zn-TiO_2 Nanocomposite Coatings Prepared by Pulse Reverse Current", submitted to *J. Electrochem. Soc.*(September 2010)