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## TECHNICAL NOTE

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# GLOW DISCHARGE DEPTH PROFILING A POWERFUL ANALYTICAL TECHNIQUE IN SURFACE ENGINEERING

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**Abstract** A variety of analytical techniques have been developed and employed to characterise the surfaces, subsurfaces and interfaces of surface engineering systems. They provide important information for quality control, process optimisation and further development. Since the mid 1980's, glow discharge spectrometry (GDS) has emerged as an important and versatile technique for rapid depth profiling analysis of the chemical compositions of surface layers with thickness ranging from a few nanometres to several tens of micrometers. The basic principles of GDS are first discussed briefly in the present paper. Then applications of the technique to various surface engineering systems, including PVD coatings, ion implanted surfaces, diffusion layers and multi-layer coatings, are demonstrated to highlight the important role of this analytical technique in surface engineering.

**Key Words** Profile, Depth Profiling, Surface Engineering, Coatings

**چکیده** روشهای تحلیلی گوناگونی برای طبقه بندی سطوح، زیر سطح ها و سطوح مشترک سیستمهای مهندسی، ایجاد و به کار گرفته شده اند. این روشها اطلاعات مهمی برای کنترل کیفیت، بهینه سازی فرایند و توسعه بیشتر فراهم می آورند. از سالهای میانی دهه ۸۰ میلادی اسپکترومتري در خششی (GDS) به عنوان روشی مهم و چند منظوره برای تحلیل عمق پروفیل لایه های سطحی با ضخامت در گستره چند نانومتر تا چند ده میکرومتر ظهور کرده و به کار رفته است. در این مقاله ابتدا اصول مقدماتی GDS به اختصار تشریح می شود. سپس کاربردهای این روش برای سیستم سطحهای مهندسی مختلف از جمله پوششهای PVD، سطوح یون کاشته شده، لایه های نفوذی و پوششهای چند لایه ای نمایش داده می شود تا نقش مهم این روش تحلیلی در مهندسی سطح روشن شود.

## INTRODUCTION

Surface, subsurface and interface chemical analyses have played an important role in the development of modern surface engineering technologies. Characterisation of spatial distribution of chemical compositions provides useful information for process optimisation because the physical, chemical and mechanical properties of engineering coatings/layers are determined, to a large extent, by the chemical composition of the coatings. Many special analytical techniques have been developed for surface and

interface chemical analysis. Among the most frequently used techniques are the electron spectroscopes (e.g. AES and XPS) and ion spectroscopes (e.g. SIMS and RBS). However, although most of these techniques provide high spatial resolution information, they are very time-consuming: it can take hours or even days to analyse a single sample. Accordingly, despite the successful application of these techniques in research laboratories, they have only found limited applications in industrial environments where rapid analysis is required.

Since the mid 1980's, glow discharge optical

emission spectrometry (GDOES) has emerged as an important and versatile technique for rapid in-depth profiling of chemical compositions of surface layers [1,2]. The GDOES technique employs a Grimm-type glow discharge source (lamp), where cathode sputtering is created by applying a controlled voltage to the sample with a controlled argon pressure across the sample surface. Surface atoms removed by this sputtering process diffuse into the argon plasma where excitation and emission occur. Separation of atom removal and excitation provides spectra with a linear relationship between concentration and spectral intensity. When combined with deconvolution algorithms using modern powerful computational techniques, quantitative profiling analysis of surface layers with thickness less than one micron and upto several tens of microns can be achieved [1,3].

As compared with other analytical techniques, the GDOES has the advantages of a high sputtering rate, rapid analysis and simplicity of use. For a coating of several microns thick, typical time for the whole analytical procedure is a few minutes provided the machine is fully calibrated. The GDOES technique thus does not only fully complement the established sophisticated laboratory surface analytical techniques

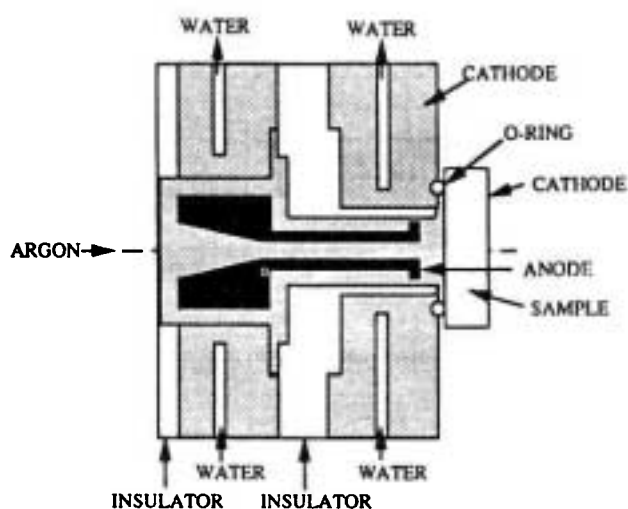
such as AES, EPMA and SIMS, but also provides an urgently needed quality control technique to the emerging surface engineering industry for the quantitative 'fingerprinting' of surface engineered materials [4].

The basic working principles of GDOES is discussed below. The applications of the GDOES technique in various sectors of surface engineering are presented to highlight the importance of GDOES in surface engineering quality control.

### BASIC PRINCIPLES OF GDOES DEPTH PROFILING ANALYSIS

Most commercial GDOES instruments use GD sources based on the design of Grimm [5]. Figure 1 schematically shows the analysis principles. The body of the Grimm lamp is normally at ground potential, and the water cooled isolated front plate is at negative potential during operation. The tubular-shaped anode fits tightly into the central opening of the front plate, and extends to approximately 0.2 mm distance from the front surface. The inner diameter of the anode is typically 8 mm, but anodes of 7, 5, 4, 2.5 and 1 mm diameter have also been used. The sample, which forms the cathode, is placed on the front plate, and sealed from the atmosphere by an O-ring. When operated, the lamp house is first evacuated for a few seconds by a rotary pump, then an argon flush valve is opened. After a few seconds, to stabilise the pressure, the discharge is initiated by applying a voltage of typically 500-1000 V. The sample surface is then continuously eroded by bombardment of ions and neutrals from the plasma due to cathode sputtering and the sputtered sample atoms diffuse into the plasma, where they are excited and emit element-characteristic optical emission [2,6].

The light emitted by the plasma enters the multichannel spectrometer via a window and a primary slit. A specific element corresponds to a characteristic



**Figure 1.** Schematic Diagram of Grimm-type Glow Discharge Source.

wavelength. Accordingly, from analysing the emissions from the plasma, elemental information of the sputtered material is obtained. Since the glow discharge lamp, operated by removing material from the sample surface layer by layer, is more or less parallel to the surface, depth profiles of elemental information can thus be obtained. With a relatively high current density of 50-500 mA/cm<sup>2</sup>, the sputtering rate is typically in the range of 1-10 μm/min [1]. The homogeneous electric field distribution in the active region ensures that the sample surface is sputtered rather evenly, resulting in a crater with a nearly flat bottom (Figure 2). Therefore, by recording the analytical signal (i.e. optical emission) as a function of sputtering time, an elemental depth profile is obtained. The high sputtering rate, combined with very high speed intensity measurement of analytical signals, has led to a very attractive technique capable of in-depth profiling of surface layers with thickness ranging from a few nanometers to several tens of micrometers.

The basic information obtained in a GD profile analysis is the relative intensity of each element as a function of the sputtering time. This qualitative analysis is often sufficient, particularly when comparisons are required. However, for quantitative depth profiling analysis, both the depth and concentration have to be properly calibrated [1,2].

If the sample is homogeneous, quantitative analysis is easy. The sputtered depth and chemical content can be determined with reference to the bulk composition.

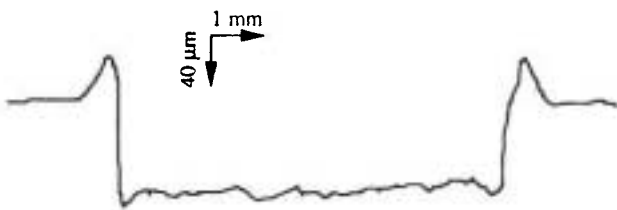


Figure 2. Two Dimensional Topography of Typical Sputtered Craters.

But in most surface engineering systems, the composition and structure of surface layer vary significantly within the layer and are different from the substrate. The burning voltage and sputtering rate are thus no longer constant and the problem of quantification becomes more complicated. In principle, sputtering rate is influenced by many factors, including composition and homogeneity of the sample, type of matrix, temperature and glow discharge process parameters. Both theoretical and experimental work have been carried out to correlate sputtering rate with all influencing factors, and quantitative expressions have been derived [1,2,3]. However, sputtering will roughen the surface of the sample, further, the bottom of the sputtered crater is never flat (Figure 2). These problems seriously limit the depth resolution of the glow discharge technique. Accordingly, GDOES is not particularly suitable for interfacial analysis.

For a full quantitative analysis, emission intensities have to be converted into concentrations. For layered surfaces, the concentration calibration procedure is rather complicated, since the element content is not proportional to profile intensity, and the spectral intensity-time profile is not proportional to depth. Considerable research effort has been directed towards the problem of quantification of GDOES depth profiles [3,6]. In the course of one depth profile analysis, several layers representing different matrices are often encountered. It is well established that the most important, matrix effect is the variation in sputtering rate. Based on this observation, quantitative techniques have been developed where the integrated intensity of a spectral line is assumed to be proportional to the sputtered weight of the corresponding element. Instruments with software based on this model are commercially available, and are used routinely for quantitative depth profiling analysis of surface engineered materials.

Table 1 summarises the analytical feature of GDOES, together with other sophisticated techniques [7]. The main advantages of GDOES over other techniques are [2]:

1. Almost all elements can be determined (including O,N, and H)
2. High vacuum is not required, so the technique is fast and easy to use,
3. Quantitative analysis in a homogeneous matrix is very easy because there are few effects of the matrix on the plasma and because calibration curves are commonly linear,
4. The initial and running costs are low, relative to other surface methods, and
5. The ability to produce depth profiles from layers a few nanometers to several tens of micrometers thick, in a short time.

It can be used in an industrial environment for quality assessment.

On the other hand, GDOES have some shortcomings some much follows:

1. Direct measurement of sputtered depth is not possible. The roughness of the surface increases during the course of sputtering and the shape of the

bottom of the crater depends on the operating parameters and on the structure of the sample. This fact limits the depth resolution in the interface region;

2. It has no lateral resolution. The sputtered area normally has a diameter of 1 to 8 mm. Accordingly, this technique is not suitable for microchemical analysis;

3. The technique does not give any direct information on chemical bonds;

4. The sample must be conductive or at least semiconductive. However, with the recent developments in the r.f glow discharge technique, it has become possible to analyze nonconductive materials as well [8].

#### APPLICATIONS OF GDOES IN SURFACE ENGINEERING

GDOES is particularly suitable for continuous depth profiling analysis of surface layers with thickness ranging from the nanometre scale to several tens of micrometers. This range covers most of the practical surface engineering systems. Accordingly, this technique has recently been successfully employed to

**TABLE 1. Comparison of Surface Analysis Techniques.**

Parameter	Technique				
	AES	XPS	RBS	SIMS	GDOES
<b>Excitation</b>	electrons	X-rays	ions	ions	ions
<b>Emission</b>	electrons	electons	ions (E)	ions (m/e)	hv (optical)
<b>Typical Information Depth (nm)</b>	1	1	1-1000	0.6	10
<b>Lateral Resolution</b>	15 nm-30 μm	5 μm-10 mm	1mm	50 nm-10 mm	1mm-10 mm
<b>Detect Limit</b>	0.1 at%	0.1. at%	0.1 at%	1ppb-10 ppm	1ppm
<b>Detect Elements</b>	All except H	He	All except H	All	All
<b>Chemical Bond</b>	yes	yes	no	yes	no

characterise such surface layers as PVD coatings, ion implanted layers, diffusion layers and electroplatings. The quantitative evaluation of concentration profiles can be made with reference to bulk test samples such as nitrides, carbides and oxides. The sputtering rate and voltage of iron nitrides are identical to those of iron. Accordingly, iron nitrides,  $\gamma'$ -Fe<sub>4</sub>N, with a narrow homogeneity range for nitrogen, produced by nitriding of pure iron can be used as a reference samples to calibrate nitrogen [9]. This can produce a fairly good estimate of the nitrogen concentration profile in most nitride coatings. On the other hand, in surface layers containing a high oxygen content, the quantitative results are less precise since most oxides are nonconductive and thus it is difficult to find an appropriate reference sample for oxygen. For hydrogen, which is difficult to detect by most other analytical techniques, reference samples can be produced by solution treatment of such metals as titanium in a hydrogen atmosphere, where the amount of hydrogen dissolved in the metal can be calculated using thermodynamic data. A few examples of continuous depth profiling of surface engineered materials by GDOES are given below.

#### Nitrocarburised Compound Layers

Nitrocarburising treatments have long been used in industry to improve the tribological and corrosion properties of engineering steels. The treatments can be carried out using salt bath, gaseous, or plasma techniques. As a result, a compound layer containing predominantly  $\epsilon$ -Fe<sub>2-3</sub>(N,C,O) is produced on the surface. Inadequate process control can result in a poly-phased compound layer comprising  $\epsilon$ -Fe<sub>2-3</sub>N and  $\gamma'$ -Fe<sub>4</sub>N phases. Such elements as carbon and oxygen are frequently incorporated in the compound layer, not only to stabilise the  $\epsilon$ -phase, but also to further improve the tribological and corrosion properties of the layer. Accordingly, the nitrocarburised layer normally contains several

elements. The compound layer thickness normally ranges from 5  $\mu$ m to 20  $\mu$ m. This proved to be too thick for most other analytical techniques based on ion spectroscopy. However, EPMA has been frequently used to analyse the compositions of such compound layers. But, line scanning in EPMA only provides qualitative information. Quantitative results can be obtained by discontinuous point analysis, which is very time consuming and has poor depth resolution.

With the GDOES technique, it is now possible to obtain continuous composition depth profiles of nitrocarburised layers with various thicknesses, and thus provide more detailed information that could not be obtained previously. Figure 3 shows the GDOES profiles of salt bath and plasma nitrocarburised layers

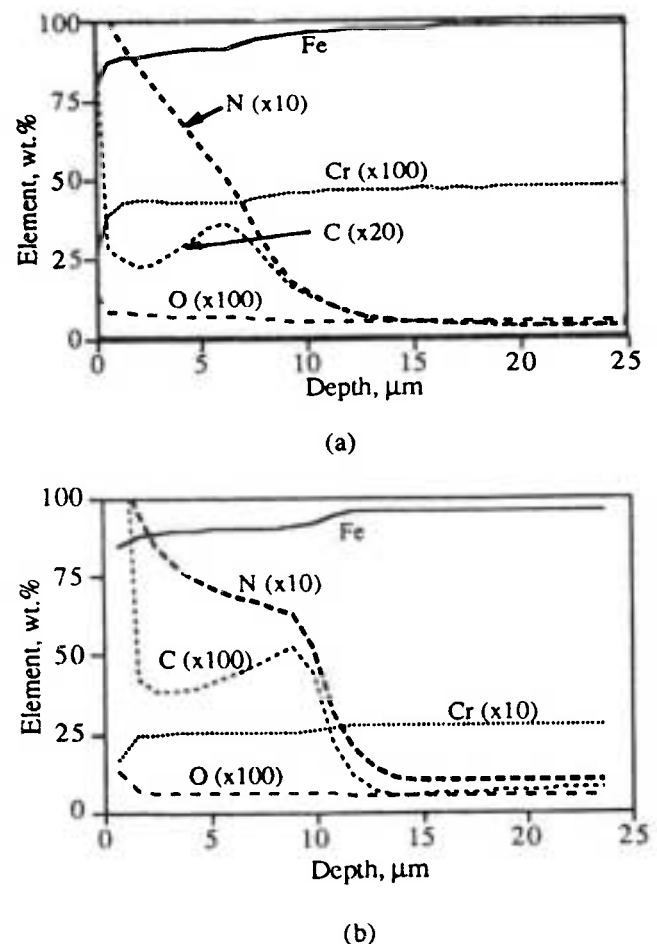


Figure 3. GDOES composition profiles of salt bath (a) and plasma (b) Nitrocarburised steel.

on En40B steel. Both treatments exhibit similar N, C, and O composition profiles. But the salt bath treated sample contains more C and O. A nitrogen content as high as 10% wt is detected in the near surface region, corresponding to the  $\epsilon$  phase. Further away from the surface, the nitrogen content decreases slowly, whilst the carbon content increases until a peak value is reached near the layer-substrate interface. This indicates that the  $\epsilon$  phase formed in the inner part of the layer is a low nitrogen high carbon phase. When the nitrogen and carbon contents at different depths composition can be obtained without detailed layer by layer X-ray diffraction analysis [11]. Curve 'a' in Figure 4 represents typical results of salt bath nitrocarburising, where all the nitrogen and carbon contents in the layer fall in the single  $\epsilon$  phase and dual  $\epsilon + \alpha$  phase fields, indicating that the compound layer is mono- $\epsilon$  phased without  $\gamma'$  phase formation. Whilst curve 'b' in Figure 4 represents typical results of plasma nitrocarburised layers, where the nitrogen and carbon contents not only fall in the  $\epsilon$  and  $\epsilon + \alpha$  fields, but also fall in the  $\gamma' + \alpha$  and  $\gamma + \epsilon$  fields, indicating that the compound layer is a poly phased ( $\epsilon + \gamma$ ) layer. These results have been confirmed by detailed X-ray diffraction analysis [10,11]. From Figure 4 it is clear that in order to produce a mono-

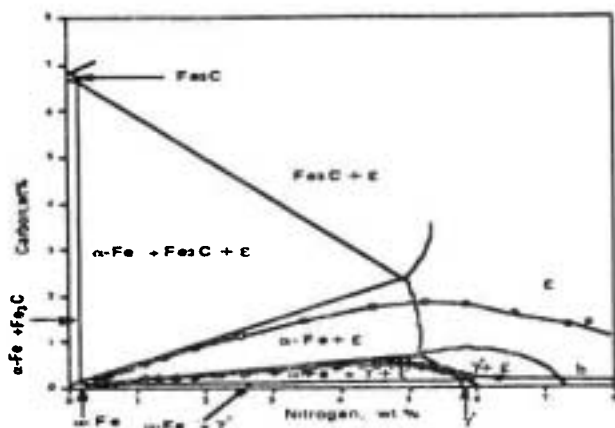


Figure 4. 57°C Isotherm of the Fe-C-N phase diagram with compositions of Nitrocarburised layers. curve 'a': Salt bath treated; Curve 'b': Plasma treated.

$\epsilon$ -phased compound layer in plasma nitrocarburising, it is necessary to increase the carbon level in the compound layer by proper process control.

### Plasma Nitrided Steels

Plasma nitriding of steels normally produces a  $\gamma'$ -Fe<sub>4</sub>N compound layer of several micrometers thick on the surface and a thick nitrided diffusion zone. The thickness of the diffusion zone ranges from 100  $\mu\text{m}$  to 500  $\mu\text{m}$ , which is too thick to be continuously analysed by the GDOES technique. But GDOES can be used to obtain depth profiles for the compound layer. Figure 5 shows typical composition depth profiles of the compound layer produced on En40B steel ( $\sim 3\% \text{Cr}$ ,  $0.25\% \text{C}$ ). The compound layer has a nitrogen content of about 6% wt, which decreases very slowly with distance from the surface, so that a nitrogen plateau is obtained. This corresponds to a single  $\gamma'$  phased compound layer. More importantly, GDOES profile analysis reveals that the carbon content in the compound layer and in the diffusion region near the compound layer is very low, significantly lower than the base carbon level of the steel, indicating that carbon redistribution (i.e. decarburisation) occurred during the nitriding process in the near surface region. This phenomenon has a significant influence on the nitriding kinetics and hardening response of the nitrided case [12].

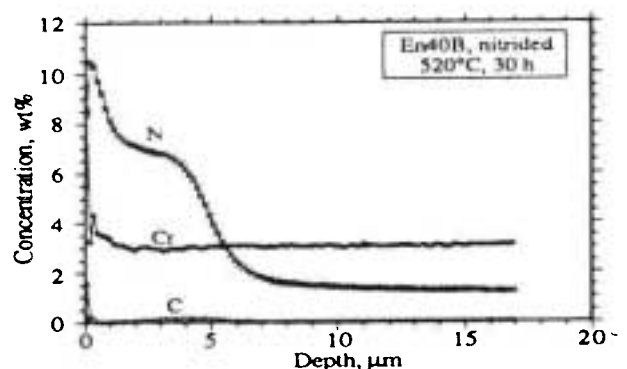


Figure 5. GDOES composition profiles of plasma Nitrided en40 B Steel.

Furthermore, the content of chromium in the compound layer is similar to that in the substrate, suggesting that at the nitriding temperature (520 °C) diffusion of chromium is negligible. Mechanical property measurements using the continuous load-depth recording nanoindentation technique revealed that the  $\gamma'$ -phased compound layers on alloy steels are harder than those on non-alloyed materials [13]. Although the GDOES results do not give any direct information on chemical bonds, in conjunction with the nanoindentation test results, it suggests that the chromium in the compound layer may be in the form of nitride precipitates, resulting precipitation hardening and thus the increase in observed hardness [13].

#### PVD TiN Coatings

The thickness of most PVD coatings is several micrometers. GDOES is the ideal technique to obtain composition profile rapidly (in a few minutes) for process control and optimisation. Since the  $\gamma'$ -Fe<sub>4</sub>N reference sample for nitrogen has a much lower nitrogen content than TiN coatings, in order to obtain more reliable quantitative results, it is necessary to use a reference sample with a nitrogen content similar to that of TiN Coatings. CVD TiN coating with nominal atomic ratio of N/Ti=1 can be used as a reference sample for most PVD TiN coatings.

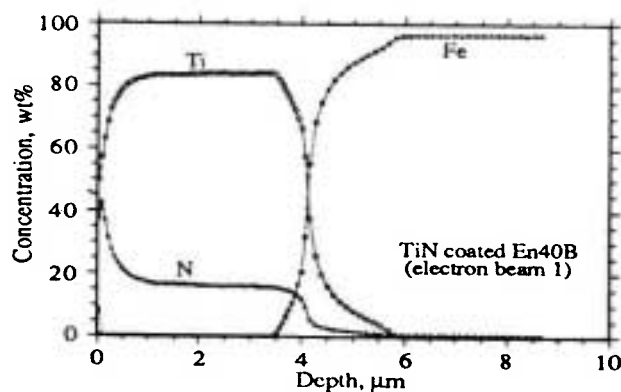


Figure 6. GDOES composition profiles of PVD TiN coated steel.

This technique has been used to characterise the composition profiles of TiN coatings. This technique has been used to characterise the composition profiles of TiN coatings produced by various commercial sources and research institutions in a nanoindentation Round-Robin test [14]. Figure 6 shows typical GDOES composition profiles. Due to the fact that intensive sputtering roughens the sample surface, GDOES does not have enough depth resolution to give precise information at the interface region. However, in the outer part of the coating, the nitrogen profile exhibits a plateau, and the N/Ti ratio of the coating can thus be derived from the plateau. Analysis of TiN coatings from different sources revealed that most of the TiN coatings have similar N/Ti atomic ratio around 0.9. But structural and properties measurements showed that the investigated TiN coatings have quite different grain structures and properties [14], indicating that the N/Ti ratio is not the only factor that influences the mechanical properties of the coating.

#### Multi Layer Coatings

Multi layer coatings usually contain many layer about 50 nm thick. Although the GDOES technique does not have sufficient depth resolution to give precise chemical composition information for each

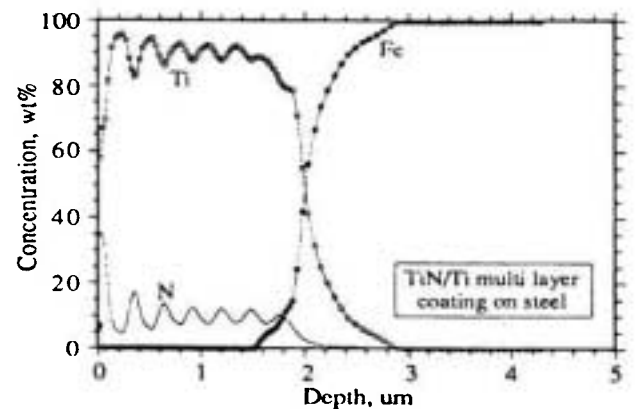


Figure 7. GDOES composition profiles of multi layer TiN/Ti coating on steel.

layer, it can give useful information about the number of layers, layer thicknesses and relative concentration profiles. Figure 7 shows the GDOES profile of a multi TiN/Ti layer system produced by magnetron sputtering [15]. It can be seen that the coating has a total thickness of about 2  $\mu\text{m}$ , and contains 14 layers in sequence of TiN/Ti from the surface. The nitrogen content in the TiN layers gradually increases towards the surface, such that a graded functional coating is actually obtained. This information can be used for process control to adjust the layer thickness, number of layers and nitrogen content in the TiN layers.

### Ion Implanted Surfaces

Ion implantation of steels with nitrogen ions normally produces a modified layer of about 200 nm thick. With the novel hybrid techniques, i.e. plasma immersion ion implantation (PI<sup>3</sup>) or plasma source ion implantation (PSI<sup>2</sup>), modified surface layers up to several micrometers can be produced [16]. Nuclear analysis using the resonant reaction  $^{15}\text{N}(\text{P}, \alpha\gamma)^{12}\text{C}$ , which is a very difficult technique has been frequently used to characterise such composition profiles. Accordingly, GDOES has recently become a very useful analytical tool for ion implantation. The GDOES results are in excellent correlation with those obtained by nuclear analysis, i.e. the nitrogen concentration at the implanted surface is very low, which increases further away from the surface and then a peak value is reached at some distance below the surface before it starts decreasing.

### SUMMARY

As a versatile analytical technique, glow discharge spectrometry, particularly glow discharge optical emission spectrometry has found increasing applications in surface engineering, both in research institutions and in industry for quality control. The

working principle of the technique is simpler, the use is easier and the analysis is much more rapid than most other analytical techniques. The presented application examples have clearly demonstrated the ability of the technique to provide quantitative continuous depth profile of surface engineered materials with varying thicknesses in a short time. However, the GDOES technique has certain shortcomings, such as poor depth resolution and no lateral resolution. In many aspects, improvements are possible. New lamps (sources) will appear so as to increase sensitivity and analyse nonconductive materials. Other carrier gases may also improve the sensitivity. The depth and concentration calibration technique can be improved to cover a wide range of elements and increase the accuracy. It is anticipated that with further development and improvement of the technique, GDOES will become a powerful analytical tool in surface engineering practice.

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