The Use of RF-GD-OES for the Characterisation of Thin Films

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Abstract

RF Glow Discharge Optical Emission Spectrometry (RF-GD-OES) is a technique to perform depth profile analysis of coatings and materials, conductive or non. Recently, the excellent surface sensitivity of RF-GD-OES has been applied to the analysis of thin films and to the characterization of the extreme surface of a variety of materials and the potential of the technique has been revealed with a depth resolution shown to be in the nm range. In this paper we will show first an application of great practical importance concerning the use of RF-GD-OES in the analysis of hard disks and we will also present a methodology developed in the Jobin Yvon (JY) Quantum IQ™ software to improve the accuracy of quantitative depth profiles on anodic alumina films.

1 Introduction

Glow Discharge Optical Emission Spectrometry (GD-OES) is a technique that relies on the controlled sputtering of atoms from a sample surface and the excitation of these sputtered atoms into an electric plasma to generate optical signals for analysis.

The use of a Radio Frequency source to power the GD-OES instruments – extending the range of applications to non conductive coatings and materials – has been developped by RENAULT and pioneered by Jobin Yvon (JY) for more than 10 years and is recognized by ISO for the analysis of thick coatings and bulk analysis.

The technique can analyse all elements (including the gases, O, N, H, Cl) and offers a depth profile sensitivity in the range of tens of ppm.

More recently, the excellent surface sensitivity of RF-GD-OES has been applied to the analysis of thin films and to the characterization of the extreme surface of a variety of materials and the potential of the technique has been revealed with a depth resolution shown to be in the nm range.

In these fields, RF-GD-OES has a lot to offer: it is not only extremely fast (with a sputtering rate of about 10 nm/s) and easy to use (as it requires only primary pumping and operates with a low flow of ultra high purity argon) but it also brings in an additional tool to characterize surfaces and a one that can be used for practical applications in surface technologies.

In this paper we will show first an application of great practical importance concerning the use of RF-GD-OES in the analysis of hard disks and we will also present a methodology developed in the JY Quantum IQ™ software to improve the accuracy of quantitative depth profiles on anodic alumina films.

2 GD-PROFILER

The GD-PROFILER instrument (Fig. 1) features a high resolution polychromator able to cover the full spectral range from 120 nm (for H) to 750 nm (for K). In addition, it includes an optional monochromator that gives to the instrument the flexibility to analyze any element in a depth profile.

Fig. 1 View of the GD-PROFILER Instrument

3 Application of RF-GD-OES to Hard Disks Manufacturing Process Control [1]

From estimates in 1996, some 750 million disks are produced world-wide each year, growing at around 20 % per annum. The extreme delicacy of the structures and the need for high quality means production losses of 60-70 % are common.

Most disks (called platters in the industry) are made from aluminium alloys, but some magnesium, ceramic, glass and silicon platters have been produced. The platters are coated on both sides with a magnetic material, newer drives having the magnetic material applied as thin metal films.

These multi-layer films contain numerous elements that are important to follow during production, as well as various potential contaminants, hence the double need that GD can fullfill both of a multi-elemental detection and of a high dynamic range of measurement as some elements can be traces in one layer and major components in a second layer.

Fig. 2 shows the RF-GD-OES depth profile of an amorphous Ni-P plated aluminium disk as used for the fabrication of computer hard disks. The disk was 1 mm thick and 3 in. (~75 mm) in diameter, from an Al- 4.5 % Mg alloy, polished to an average surface roughness of 5 nm. The Ni-P layer was about 12 µm thick : GD permits the analysis of such a thick film in a quick time (about 2 minutes to go through the NiP layer).

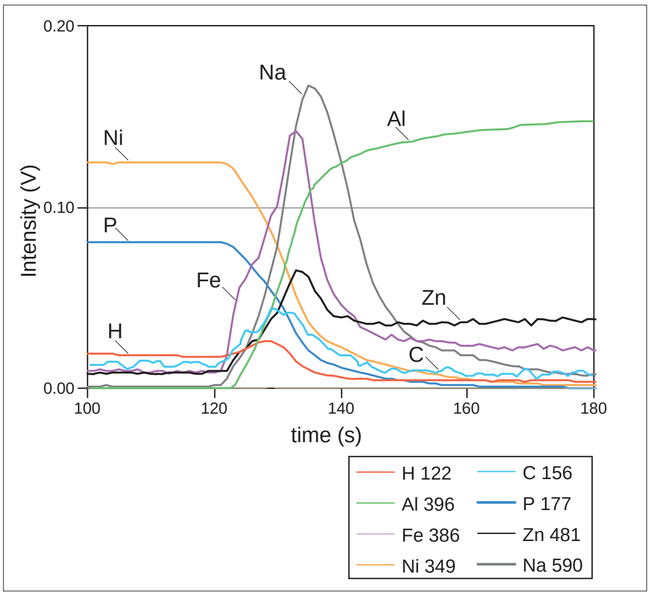

Fig. 2 Depth Profile Analysis of a Hard Disk (Focus on the NiP/Al Interface)

In this experiment the GD acquisition rate was set at 0.01s for the surface and 0.1 s for the rest of the experiment. The surface data will be described further.

There is considerable interest in plating industries in the composition of electro-deposited Ni-P layers, as the performance of hard disks depends critically on the thermal stability, flatness, and presence of micro-defects, in the Ni-P layers. These qualities of the layers depend on the uniformity of the composition through the film and the presence of process-related impurities especially at interfaces.

The major elements present – Ni, P, Al, and Mg – are shown in Fig.2. The Ni and P signals are almost constant indicating that the composition of the Ni-P layer was uniform, though closer examination shows the P signal increases slightly towards the surface. Pb and N are also present and uniform in the coating, and C and H are present but not constant. All these elements are from the chemicals used in the plating bath.

GD is also capable of analysing Hydrogen and in Fig.2 the GD analysis reveals that the H signal is enhanced at the interface between the Ni-P coating and Al substrate, of concern because H is implicated in blistering of the coating.

Prior to plating the Al substrate was degreased and etched and then given an alkaline zincate treatment containing ferric chloride which explain the Fe signal observed at the interface.

A closer examination of the interface also reveals high levels of Na and Zn together with Fe at the interface. The GD-OES analysis therefore proves that the zincate treatment remains at the interface.

The quantitative analysis is shown in Fig. 3. Only some elements have been displayed. The TEM (Transmission Electron Microscope) view of the sample is used to correlate the obtained data.

The extreme surface of the sample has been investigated within the same analysis and also compared with the TEM view of the sample surface. It is a complex multilayer system of about 30 nm thick.

The results obtained are presented in Fig. 4 which gives a zoom of the GD result on the first 2 seconds of measurement (recorded with a fast acquisition rate) and the TEM result of the first 30 nm on the sample where the active surface is.

The depth profiles of C, Co and Cr on this zoom fit neatly with the TEM observation and reveal that GD is capable of an exact determination of the surface. This experiment also confirms the excellent depth resolution attainable with GD.

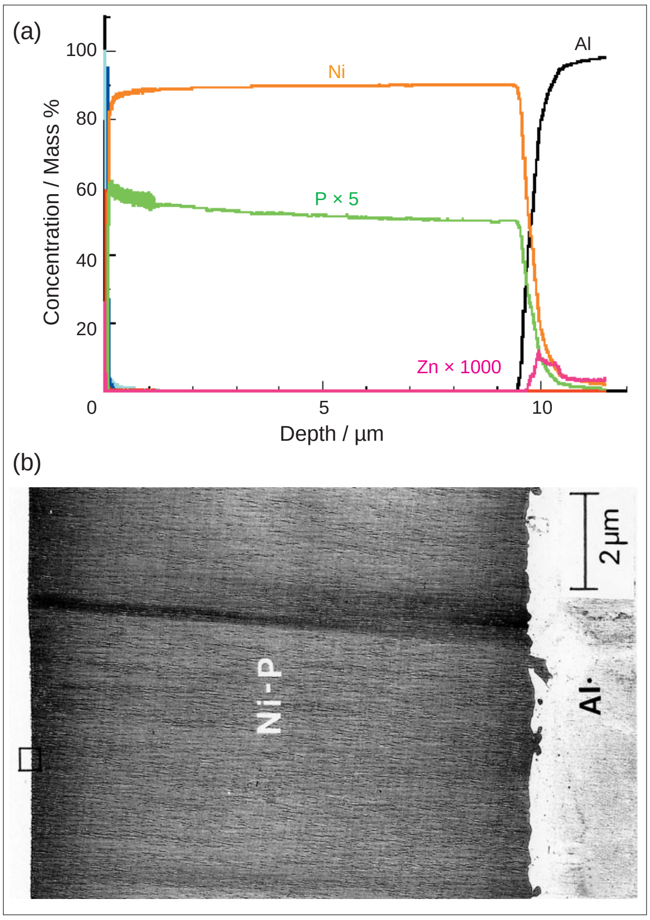

Fig. 3 Quantitative Analysis of Depth Profile for a Hard Disk
(a) Analysis by RF-GD-OES
(b) TEM Image

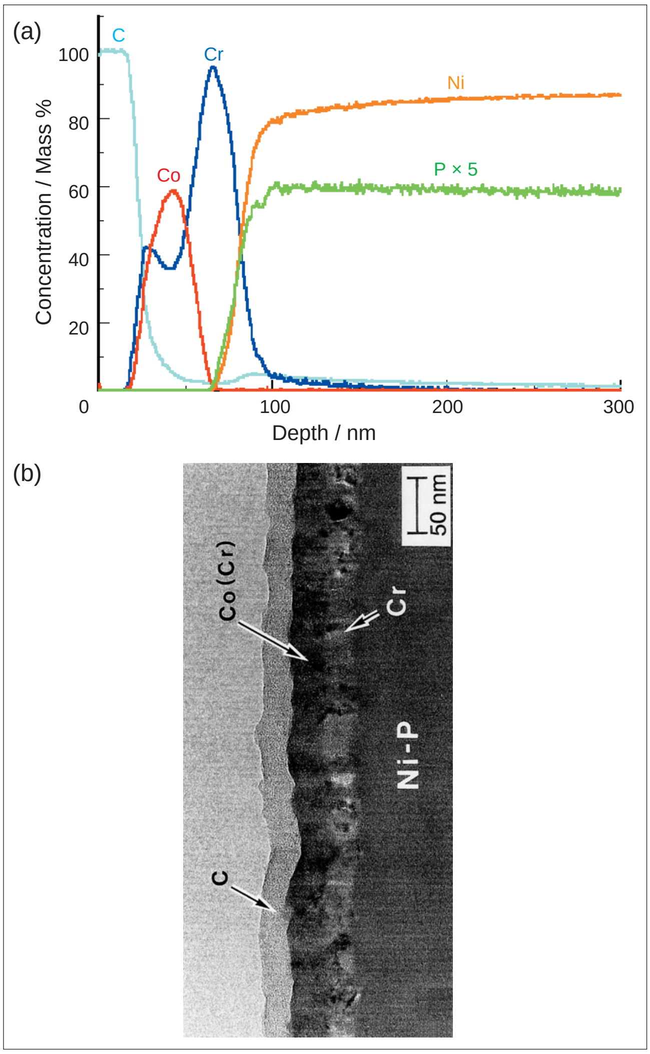

Fig. 4 Quantitative Analysis of Depth Profile on the Surface of Hard Disk
(a) Analysis by RF-GD-OES
(b) TEM Image

4 Quantification of Anodic Alumina Films

The ability of RF- GD-OES to analyse anodic oxide thin films qualitatively is well established with intensity vs. time profiles [2]. However the classical quantification algorithms often fail to provide accurate results on these materials. This is essentially due to the absence of appropriate certified reference materials for calibration and to the assumptions and approximations used in these algorithms [3].

To quantify anodic oxide film depth profiles successfully, calibration standards should first be produced and the JY software has been updated in a first step to permit simultaneously the use of well-characterised in-house coated materials (with constant distribution of the species in the film) and non-anodic oxide matrices such as metallic alloys in a multi-matrix calibration mode.

In addition all information known independently on the samples is introduced in a new mode of the software (called layer mode, Fig. 5) which overcomes the limitations of the classical algorithms.

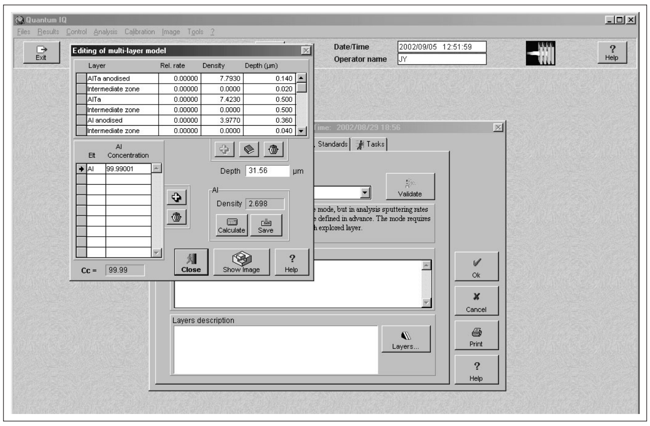

Fig. 5 Layer Mode Edit Screen of JY Quantum IQ Software

Fig. 6 shows the calibration curve for oxygen obtained from 10 samples - anodic alumina films grown at different densities and one high purity (99.99 %) aluminium disk. These samples were prepared by Prof. G. Thompson at the University of Manchester Institute of Science and Technology (UMIST). The resulting curve is linear with a good correlation coefficient of 0.994. The RSD and standard error of estimate of oxygen are also good.

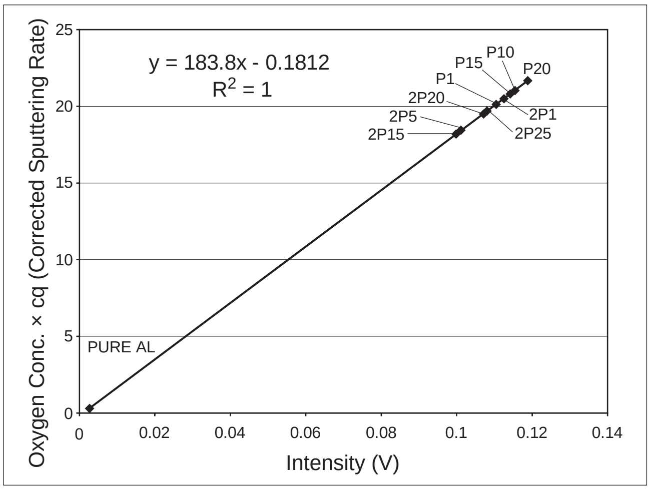

Fig. 6 Calibration Curve of Oxygen Concentration by Coating Membrane as Reference Material

In this way, emission yield variations that appeared when different matrices were employed in multi-matrix calibration, were reduced to near zero. An excellent agreement to the known stoichiometric composition of anodic alumina (40 at % Al and 60 at % O in Al_2O_3) was thus obtained.

In addition, as the samples were also analyzed by TEM, the film thickness and hence the sputtering rates of the films were known and entered in the model.

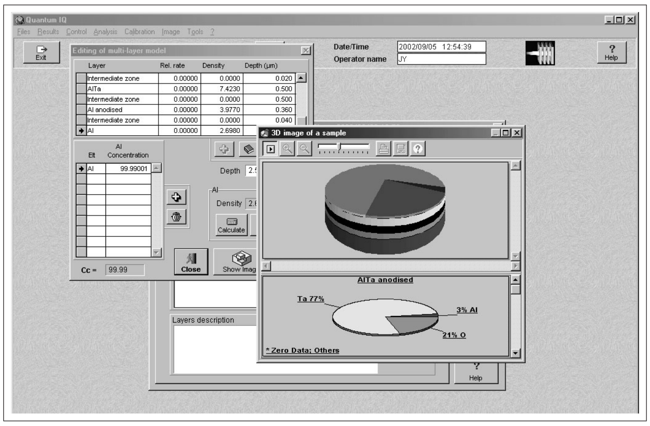

Fig. 7 Patented 3D View of Quantified Sample using Layer Mode

5 Conclusion

In November 2002, the first symposium on Surface Analysis by Glow Discharge Emission Spectrometry was held in Japan at Keio University. This event organised by Professor Shimizu – a recognized scientist in the field of Surface Analysis – and sponsored by JY HORIBA marks the recognition of the GD technique as an attractive tool to characterise thin films and do practical surface analysis.

A special edition of SIA (Surface and Interface Analysis – the reference journal in this field) to be released in July 2003 is dedicated to GD and will present the proceedings of the symposium, including theoretical work on the RF-GD plasma and practical applications on surfaces and thin films.

References

[1] K. Shimizu et al., GDOES depth profiling analysis of amorphous Ni-P aluminium hard disks, Surface and Interface Analysis 29, 151 - 154 (2000)

[2] In Glow Discharge Plasmas edited by K. Marcus (Wiley 2002)

[3] In Practical Guide to Glow Discharge OES by T. Nelis and R. Payling (RSC 2003)

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