A parametric evaluation of the discharge conditions which affect the quality of radiofrequency glow discharge optical emission spectroscopy (rf-GD-OES) depth profiles of Ni-P plated aluminium hard disks is described. This technique has been shown previously to provide good depth resolution for metallic and oxide layers, also being able to examine contaminants at the layer interfaces. A range of discharge parameters is investigated relative to their contributions to analyte responses and resultant depth profile characteristics. The optimal discharge operating parameters for this application were determined to be an rf power of 40 W and an argon discharge gas pressure of 6 Torr. The depth-resolved analysis of the Ni-P layer plated on the Al-Mg alloy substrate reflects the microscopic non-uniformity of the surface of the Al alloy base material. Diamond stylus profilometry is employed to extract crater profiles and sputtering rates obtained over a range of discharge conditions of rf power and argon discharge gas pressure. SEM, TEM and EDX images of specimen cross sections are used to examine the physical structure of the layer interfaces on a microscopic scale. For each of the aluminium hard disks investigated in this study, the interface breadths (Δz) obtained at the Ni-P/Al-Mg interface is ultimately limited by the roughness of the aluminium disk substrate to which the overlayer is applied. Optimized discharge conditions are employed to profile hard disks extracted from two commercial drives of different technological generations. Distinct compositional differences are observed that correlate with improvements in the base technology over the years 1992–1998.

Introduction

Nickel–phosphorous plated aluminium disks have been widely used as support matrices for magnetic data storage elements in computer hard drives. With the development of new thin film technologies,1,2 all rigid-disk drives are made by depositing magnetic thin films using vacuum-deposition technology. This technology provides metal films having higher magnetization than particulate thin films, which had been the prevalent method until the last decade. This higher magnetization allows the use of thinner films (as low as 20 nm) on the rigid substrate. Very thin layers are necessary to write very narrow transitions. Thin metal films can also be endowed with much higher coercivity (the magnetic field intensity needed to decrease the magnetization of a ferromagnetic material to zero after it has reached saturation) values than particulate films. This quantity is critical to increasing the areal density (i.e., information storage capacity) of the disks.

Aluminium is typically used as a substrate in the fabrication of magnetic data storage hard disks because of its low density, moderate rigidity and low cost. Through the production process, an aluminium magnesium (Al-Mg) substrate is normally coated with five successive layers, Ni-P, an underlayer, magnetic film, carbon coat, and lubricant, successively. The smoothness of the magnetic film is of ultimate importance in obtaining high fidelity/high density storage. As such, a high degree of smoothness of the supporting material is paramount for these applications. The support must be created in this way, or some form of polishing must be applied to achieve the desired smoothness. Other important qualities of the support material include physical and chemical stability, low mass (density) and low cost. Aluminium alloys certainly meet these latter requirements. Due to the fact that aluminium, by itself, is quite soft and cannot be polished to a sufficiently smooth finish, a modification of the aluminium substrate is needed to provide a hard surface that can be polished for the magnetic film support. The electrodeless deposition of a Ni-P layer on to an aluminium base is the most common way to prepare this hard surface as it has an amorphous structure that can be polished to a finish with an average roughness of 1–2 nm relative standard deviation (RSD).

The three layers above the Ni-P (comprising the storage medium) are deposited by either vacuum deposition or physical-vapor deposition techniques in a single sputtering chamber using different primary targets. The chromium underlayer, approximately 50 nm thick, is put down to help nucleate and grow microstructures having appropriate magnetic properties. The magnetic material is a cobalt-based alloy, which is coated to 20–50 nm in thickness on the underlayer. The final hard layer consists of amorphous carbon, 10–20 nm thick, which is deposited to protect the disk from the mechanical wear of the recording head. The topmost coating is a 1–2 nm layer of lubricant to reduce friction and wear between the carbon coat and the recording head.1,2

Glow discharge optical emission spectroscopy (GD-OES) has been used for depth profiling analysis of very thin to thick films in various types of samples.3 The capabilities of the method have been extended to a wide variety of sample systems through the use of radiofrequency powering (i.e., rf-GD-OES).4 Shimizu et al. have demonstrated depth resolution capabilities that are comparable to or better than secondary ion mass spectrometry (SIMS) for the analysis of anodic alumina films.5 Studies by Hoffman and co-workers have also demonstrated excellent depth resolution for very thin (<50 nm) metallic multilayers.6 Advantages of rf-GD-OES depth profiling analysis include high sputtering rates with uniform film removal, no deleterious surface charging effects in the sputtering of insulating materials, and no requirement for ultra-high vacuum.4 To date, there have been a few studies demonstrating the basic approach to Al hard disk profiling using GD-OES as
the analytical method. Shimizu et al. illustrated the basic potential for rf-GD-OES analysis of aluminium hard disks. In their study, the latent elements from the treatment of aluminium substrate (Zn, Fe and N) were found at the Ni-P/Al interface. The depth profile revealed each of the different coating materials on top of the Ni-P layer, which was consistent with transmission electron microscopy (TEM) images. Studies to date have been more demonstrative in nature than developments of suitable analytical methodologies.

In this study, a detailed parametric evaluation of rf-GD-OES conditions was performed on Ni-P plated aluminium disks used as substrates for the fabrication of computer storage media. The evaluation included determination of the effects of discharge parameters (i.e., power and argon pressure) on the resultant profile characteristics, including temporal behavior and elemental response factors. An rf power of 40 W and an argon discharge gas pressure of 6 Torr provided relatively good depth resolution and analyte sensitivity. Diamond stylus profilometry of the resultant sputtered craters was used to better understand the temporal profiles obtained. Scanning electron microscopy (SEM) imaging of specimen cross sections revealed that the original roughness of the Al surface limits the obtained resolution. The coating materials on top of aluminium hard disks obtained from two commercial hard drives were investigated using the optimal conditions (40 W and 6 Torr Ar). The depth-resolved analyses of these disks revealed all of the different coating materials on top of the Ni-P layer. The resultant GD-OES profiles were in good agreement with combined scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) spatial images.

Experimental

Optical spectrometer

The instrument used in this study is the Jobin–Yvon (Longjumeau, France) 5000 rf spectrometer system, which has been described in detail previously. The spectrometer is a 0.5 m focal length Paschen–Runge mount with a 2400 grooves mm\(^{-1}\) concave holographic, ion etched diffraction grating, covering the range of 110–620 nm. The instrument’s 26 multimode fiber tubes are sampled at a rate of 2 kHz each, with a dynamic range of ~6 orders of magnitude. The detection of various elements was performed using the spectral wavelengths (nm) as follows: Ni (I) 341.48; P (I) 177.50; Al (I) 396.15; Mg (II) 280.27; Cr (I) 425.43; Co (I) 345.35; C (I) 156.14; Ca (II) 393.37; Fe (I) 371.99; Na (I) 589.59; Zn (I) 213.86; MgF\(_2\) optics and flushing of the polychromator of nitrogen facilitate the monitoring of transitions in the VUV spectral region. An SAES Pure Gas (San Louis Obispo, CA) Model GC-50 Zr alloy getter is used to further purify the argon gas (99.999% purity) and allow the analysis of non-metallic elements such as O and N without interference from air contaminants. For this study, a 4 mm id anode limiting orifice is used, thus producing an approximately 4 mm diameter sputtering area. The instrument is interfaced with a Pentium Pro PC running Quantum 2000 software, which controls all aspects of the operation and the data acquisition parameters.

Surface analysis

Sample sputtering rates and areal uniformity were assessed through crater profiles acquired with a Tencor (Mountain View, CA) P-10 profilometer following each analysis. A 10 mm scan length was employed for the data presented here, providing a horizontal (width) resolution of 2.0 μm and a vertical (depth) resolution of 25 Å. The optical micrographs of the resultant craters were obtained using a Stocker & Yale-aus JENA microscope equipped with a Sony DXC-960MD CCD Video camera.

The lateral (depth) uniformity of the layer sputtering was evaluated through cross-sectional scanning electron micrographs obtained using a Hitachi S-3500 N scanning electron microscope (SEM). The SEM was operated in the backscattering electron (BSE) mode at 20 kV with a working distance (the distance between a sample and the electron beam) of 15 mm. For the investigation of the coating materials on top of the Ni-P layer, the disk was cut into small pieces, coated with a thin carbon layer for electrical conductivity and a tungsten layer for protecting the disk surface from the beam damage, placed in the sample holder and milled to a thin section (less than 100 nm thick) using the focused ion beam (FIB) attachment (Hitachi FB-2000A). The thin sample was then examined using a scanning transmission electron microscope (STEM) in conjunction with energy dispersive X-ray (EDX, Hitachi HD-2000) analysis with an electron beam operating at 200 kV and 30 μA.

Aluminium hard disk samples

A synthetic Ni-P/Al-Mg bi-layer test specimen of the same nominal composition as commercial storage disks was used as a surrogate sample in the evaluation of the role of discharge operating conditions on the rf-GD-OES profiles. The disk was provided by Professor Kenichi Shimizu (Keio University, Japan). The dimensions of the disk were 0.8 mm in thickness and 84 mm in diameter and coated with approximately 12 μm thick amorphous Ni-P layers. Hard disks extracted from two commercial hard drives fabricated in 1992 and 1998 were used as the practical test specimens. The dimensions of the disks were 0.8 mm in thickness and 95 mm in diameter and coated with approximately 13 and 9 μm thick amorphous Ni-P layers (determined ex post facto), respectively. The samples were cleaned with methanol-laden soft wipes and air-dried prior to analysis. The disks were analyzed using the Jobin–Yvon 5000 rf-GD-OES instrument in argon atmospheres of 2–10 Torr and at rf powers of 20–40 W.

Results and discussion

Effects of operating power on the depth profiles of Ni-P plated aluminium substrates

The applied rf power in a glow discharge source determines the dc-bias voltage essential to cause sputtering at a given pressure and the flux of incident argon ions (i.e., discharge current). Previous studies in this laboratory (on bulk specimens) have shown that rf power controls primarily the overall ablation rate, and by extension the analyte emission intensities, but has little effect on the shape of the resultant craters. Fig. 1(a) illustrates effects of rf power on signal transients for the nickel and aluminium matrix species at operating powers of 20, 30, and 40 W at an argon pressure of 6 Torr. Two primary consequences of increased power can be observed. The Ni (I) and Al (I) emission intensities (i.e., heights of the plateau regions of the transients) increase with the increases in power, while the appearance time for the onset of the Al (I) emission is reduced (reflective of higher sputtering rates). This would be expected because the dc-bias potential and discharge current increase with the power at a given pressure, thus increasing the ablation rate and the number of analyte atoms in the gas phase at a given instant in time. Of course, the presence of greater numbers of atoms is not a guarantee of higher analyte emission intensities. This can only occur if the efficiency of excitation is at least equivalent as power is increased. Based on the unreasonably long analysis time that results from 20 W rf power operation, only the 30 and 40 W data are reported in the remainder of this work.
During the course of a typical depth profiling experiment, multiple elements are sampled simultaneously along with the resultant d.c. bias potential, as measured by the system impedance matching circuitry. Table 1 presents the plateau (steady state within the given layer) intensities for the matrix elements in the overlayer (Ni and P) obtained across the range of discharge conditions investigated. The intensity of each element at a given point in time is a product of the number of atoms removed and the integrated emission intensities obtained for the matrix elements. Comparison of the integrated intensities (calculated from time zero to the time where they are reduced to 16% of maximum Ni intensity) for Ni suggests a difference in excitation conditions (3493 versus 3048 voltage units), while those for P are relatively equivalent (1983 and 1954 voltage units). In reality, the differences for Ni (1983 versus 1954 voltage units) are due to the differences in the transient shapes for the two conditions. This is supported by the much closer proximity of integrated values when lower threshold values (e.g. 5% of maximum) are employed for the integration. The equivalent excitation conditions are due to the consistency of the d.c.-bias potentials, which do not change appreciably (<5%) between the two power settings. Insensitivity of excitation conditions to changes in applied rf power have been known as a basic characteristics for rf-GD-OES devices.10

Effects of operating pressure on the depth profiles of Ni–P plated aluminium substrates

Operating pressure is an equally important (yet complementary in some respects) parameter to applied power in using glow discharges for spectrochemical analysis. It not only determines the discharge current under constant power/voltage conditions, but also the atomic mean free paths, the energy of ions bombarding the cathode surface and the extent of analyte redeposition, all of which may affect the sputtering rates, emission intensities, and depth resolution.13 Fig. 2 shows the effect of argon pressure on signal intensities and temporal

Table 1  Quantitative aspects of depth profiles as a function of discharge operation conditions

<table>
<thead>
<tr>
<th>Element</th>
<th>Power/ W</th>
<th>Pressure/ Torr</th>
<th>Ni (plateau)</th>
<th>Ni (integrated)</th>
<th>P (plateau)</th>
<th>P (integrated)</th>
<th>Ni transition width/μm</th>
<th>Al (plateau)</th>
<th>Mg (plateau)</th>
<th>Al transition width/μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6</td>
<td>304</td>
<td>5.6</td>
<td>3493</td>
<td>3.5</td>
<td>1983</td>
<td>6.1</td>
<td>3.3</td>
<td>0.5</td>
<td>1.9</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>452</td>
<td>6.8</td>
<td>5815</td>
<td>3.8</td>
<td>2983</td>
<td>5.3</td>
<td>6.6</td>
<td>0.8</td>
<td>4.9</td>
</tr>
<tr>
<td>40</td>
<td>6</td>
<td>217</td>
<td>6.8</td>
<td>3048</td>
<td>5.0</td>
<td>1954</td>
<td>6.4</td>
<td>4.1</td>
<td>0.7</td>
<td>1.3</td>
</tr>
<tr>
<td>40</td>
<td>10</td>
<td>311</td>
<td>7.2</td>
<td>4267</td>
<td>5.0</td>
<td>2715</td>
<td>4.6</td>
<td>7.5</td>
<td>1.3</td>
<td>4.3</td>
</tr>
</tbody>
</table>

*a* Interface time = time to 50% of Ni (I) maximum. *b* Plateau = maximum intensity of each element. *c* Integrated = integration from zero time to time for 16% max of each element.
profiles of the nickel (Fig. 2(a)) and aluminium (Fig. 2(b)) matrix species over an argon gas pressure range of 2–10 Torr, at an rf power of 40 W. The quantitative data are presented in Table 1. The maximum Ni (I) emission intensities are seen to increase greatly between the pressures of 2–6 Torr, more or less levelling off beyond that point. The sputter rate for the 2 Torr argon plasma is sufficiently low that the bi-layer interface is not observed in this 10-min analysis time. The removal rates are observed to increase with pressure up to the 6–8 Torr range, and then reduce as the pressure is increased to 10 Torr. Interestingly, the temporal characteristics of profiles for the 6 and 8 Torr plasmas are nearly identical as the time required to reach the bi-layer interface is the same, and so the sputtering rates are equivalent.

As can be seen from Fig. 2, the temporal characteristics for the major elements of the disk layers are far more affected by the operating pressure than the applied rf power. Examination of the transient characteristics for the sputtering at 6 and 10 Torr reveals the subtle, yet important, differences that ultimately determine the obtained depth resolution. For example, the trailing edge of the Ni (I) and P (I) responses are very sharp at 6 Torr, with the complementary leading edge of the Al (I) and Mg (II) transients being sharp as well. In both cases, the last 20% of the transients appear to be drawn out. In the case of the 10 Torr discharge, somewhat opposite characteristics are observed. In this case, a very gradual initial decrease is observed for the Ni (I), with the end of the transient much more steeply approaching the detector background level. The onset of the Al (I) is very gradual here, increasing in slope toward the completion of the transition zone. Based on the differences in the shapes of the temporal responses, it is clear that the operating pressure more greatly affects the shape and quality of the sputter craters than the applied rf power, in agreement with the previous work in this group.10

The determination of depth resolution in any profiling technique is based on the assumption of the existence of an ideal, step-function interface between the two layers. As will be shown in subsequent paragraphs, this condition does not exist for the Ni–P/Al–Mg bi-layer system. In terms of deriving optimum analysis conditions, the working definition of depth resolution (based on the 84/16 criteria) is employed to calculate a practical “transition width” for the interface. These values are reported in Table 1 to put a quantitative perspective on the depth profiles. The obtained values reflect what might have been expected from the temporal traces. The most interesting point here is that, at both power settings, the best resolution values derived for the overlayer (Ni) and the substrate (Al) are obtained at different pressures. The transition width values are optimal at 8 Torr for the top coat and at 6 Torr for the substrate. These differences are not unexpected as the crater shape (concave or convex) would naturally lead to different analyte responses during the passage through the interface region. These will become more apparent in subsequent sections where crater shapes are presented.

One final aspect of the transition width/resolving powers presented in Table 1 is the general order of magnitude of the values, on the single-digit micron level. (Recall that a low value of depth resolution depicts the best resolution.) These values pale in comparison to recent work presented by Marcus and co-workers, where resolution values of the order of single nanometers were demonstrated. The disparity between the transition widths obtained for the test specimen and the previous resolution values can be explained by the SEM micrograph of a cross sectional portion of the aluminium disk, as shown in Fig. 3. Although this image does not provide as much detail as a cross-sectional TEM micrograph, it can be seen that the interface of Ni–P layer and Al–Mg substrate is not microscopically smooth. There is an apparent interdigitation of the two layers with each other. This ‘roughness’ can degrade the depth resolution because it causes non-uniform sputtering.14,15 Therefore, the transition width values obtained from this study are not impressive, but are indeed reflective of the bi-layer interface quality.

The previous paragraphs point out the dramatic effects of discharge gas pressure on sputtering characteristics, but in fact the effects on emission responses are even more substantial. Counterintuitively, while the sputtering rate at 10 Torr is the slowest of those excluding 2 Torr, the elemental responses are highest (or nearly so) for all four of the test elements. Given the fact that the number of atoms in the plasma is less at any given time at this pressure, this clearly reflects an increase in the efficiency of the excitation process. In glow discharge sources, the relevant parameter is termed the relative emission yield (REY).16 The REY is a useful quantity in terms of quantitative

Fig. 3 SEM micrograph of a cross sectional portion of the aluminium hard disk test specimen.
analysis as it provides a means of relating signal intensities and sputtering rates to elemental concentrations. Ideally, this quantity would be insensitive to changes in discharge conditions or sample matrix. Previous studies in this laboratory have shown that REYs are fairly invariant with changes in rf power, but are indeed sensitive to changes in source pressure. The effects of pressure are, of course, element/transition specific. This is easily seen in comparing the transients for the Ni (I) and Al (I) in Fig. 2, where the responses for Ni (I) are nearly the same for 6–10 Torr while they are very different at the same pressures for Al (I). The difference in the two transition responses points to differences in relative emission yields that are related to discharge pressure, which is not surprising based on previous optical emission and Langmuir probe studies reported by this laboratory.17,18 In the latter studies, electron energies (temperature and average energies) were found to be insensitive to changes in rf power, yet were very sensitive to changes in discharge gas pressure.18 The strong influence of discharge pressure is the reason why most rf-GD-OES sources are operated under constant pressure conditions.

As presented in Table 1, the plateau intensities for each element in the respective layers behave quite differently. Again, these values are the product of both the changes in sputtering rates and excitation efficiencies. The integrated intensities for the overlayer elements Ni and P are directly related to their REYs. As seen in the table, the excitation efficiencies steadily increase with discharge pressure, while their plateau values do not show continual increases. (The same is true for the Al and Mg substrate elements.) The integrated values for both elements nearly double from 4–10 Torr. Langmuir probe measurements suggest that the reason behind the increased efficiency is an increase in the electron number density in the plasma’s negative glow region.16

Sputtered crater shapes

The shape of the temporal responses in a depth profile is a direct reflection of the cross-sectional sputtering pattern. If sputtering across the crater face occurred with single-atom flatness, the observed optical response at the interface would be an ideal step-function in terms of the trailing edge of the topcoat and the lead edge of the substrate. This situation is not reality as variations in electric field potentials and redeposition patterns lead to inhomogeneous erosion.19 Fig. 4 illustrates the effect of the operating pressure on the sputtered crater depths and shapes at powers of 30 and 40 W for a sputtering time of 10 min. As can be seen, discharge pressure greatly influences the crater shape, as the power settings more directly affect the attained depth. High pressures tend to yield convex crater bottoms, in general becoming more flat to concave as the pressure is reduced. The apparent flatness of the 2 Torr craters is simply a reflection of the much-reduced sputtering rates at that pressure in comparison to the higher ones. Table 1 presents the average sputtering rates determined from the central regions of the respective crater profiles across the range of discharge conditions. As expected, the 40 W discharges sputter at higher rates for each of the pressure settings, with the removal rates showing maximum values at a pressure of 6 Torr. The fact that these are the flattest craters is also advantageous. The relative sputter rates correspond well with the interface times derived from the Ni (I) intensities presented in Table 1.

Fig. 5 presents a series of optical micrographs (10× magnification) of the resultant craters on the Ni-P plated Al disk samples sputtered under discharge conditions of 40 W rf power and 6 Torr argon gas pressure to illustrate the evolution of the craters over different sputtering times. The photograph shown in Fig. 5(a) is taken after 200 s of sputtering, which is equivalent to crater depth of approximately 11 μm. The exposed crater surface is still in the Ni-P overlayer as suggested by the same coloring within the crater as the bulk material (i.e., outside of the bright ring caused by reflection off of the angled crater edge). The photograph of Fig. 5(b) (taken after 220 s of sputtering) reveals a faintly lighter region near the center, indicating that the plasma has sputtered through to the more reflective Al-Mg substrate. Based on the analysis time, the sputtering depth is approximately at the point where the Ni (I) is decreased to one-half of its maximum intensity. The photograph suggests that the sputtering is non-uniform, though this does not correspond to the crater profiles of Fig. 4. This is not surprising since the degree of underlayer exposure that would reflect light is probably far less than might be detected via profilometry. This level of non-uniformity would also likely present itself in depth profiles. The Al-Mg substrate is increasingly exposed as the sputtering time increases to 250 and 300 s, as shown in Figs. 5(c) and 5(d), respectively. This is interesting because the apparent sputtering area increases with time. It illustrates the evolution of a concave crater where the central portion is being etched more quickly than the edges, as is reflected in the profilometer tracing in Fig. 4 for the 40 W, 6 Torr discharge condition.

As illustrated in Fig. 3, scanning electron micrographs can be quite informative in terms of revealing the physical structure of the Ni/P/Al-Mg bi-layer. Fig. 6(a) is an SEM micrograph of a cross sectional portion of the aluminium hard disk after sputtering at 40 W and 6 Torr for 10 min. While profilometry suggests that the center region is relatively smooth and flat, the thin disk is seen in the SEM micrograph to have been slightly bent during the cutting procedure. Fig. 6(b) illustrates a magnified view of the right edge portion of the specimen in

![Fig. 4](image-url)  
Fig. 4 Diamond stylus profilometer traces of the resultant craters in the Ni-P plated aluminium disks sputtered under different combinations of rf power and discharge gas pressure. Sputter time = 10 min.

![Fig. 5](image-url)  
Fig. 5 Optical micrographs of the sputtered crater in the Ni-P plated aluminium disks after sputtering times of (a) 200, (b) 220, (c) 250, and (d) 300 s. Rf power = 40 W, Ar pressure = 6 Torr.
the micrograph of Fig. 6(a) to view the details. In this figure, the Ni–P layer is completely removed toward the center of the crater as the Al–Mg substrate is exposed. The curved nature of the crater bottom is very clearly seen as a beveled slope extends to the exposed Ni–P layer near the crater edge. The dark, small conical structures near the periphery of the crater that appear to sit within micro-craters seem to reflect the existence of inclusions within the interface region, that themselves have low sputtering rates. The remnants of these inclusions appear in the center of the crater as shallow dimples, as can be seen in Fig. 6(c), which is the top-view micrograph of the central region. The combination of GD sputtering and SEM imaging is a powerful combination of tools for applications in chemical and physical metallurgy.

Distribution of impurities in Ni–P plated aluminium substrates

Based on the results presented in the previous figures and the obtained transition widths, it can be concluded that the optimal conditions for analysis of the aluminium hard disk are an rf power of 40 W and a discharge gas pressure of 6 Torr Ar. There are other elements present in the simple bi-layer system that in and of themselves could affect the performance of a storage disk. Contaminants on the surface of the Ni–P layer can influence the adhesion of the uppermost storage-functioning layers, as would species present between the Ni–P and Al–Mg with the adhesion of the Ni–P. In addition, contaminants within each layer will potentially affect the longevity of the device (e.g., via oxidation chemistry) as well as the magnetic properties of the device.

Fig. 7 is the rf-GD-OES depth profile previously depicted in Fig. 1(b) (40 W, 6 Torr), expanded so that the distribution profiles of various ‘minor’ elements are easily observed. Very prominent at the initiation of the plasma is the signal of C (I). That the signal continues for upwards of 100 s is evidence that the carbon is incorporated into the overlayer and is not simply surface contamination. Any sort of redeposition of surface contamination would not exist for more than a second or so at the sputtering rates observed here. There is also evidence of carbon contamination on the substrate as the C (I) response shows a slight increase in the region of the interface. Zinc is a common surface contaminant in aluminium alloy systems and so might be expected to appear at the interface of the Ni–P/Al–Mg interface. Fig. 7(a) reveals, however, that Zn is present at the beginning of the analysis, taking the same temporal form as the Ni matrix element. Differently though, the Zn distribution appears to pass deeper into the Al substrate, which may be an artifact of the suggested zinc contamination of the primary aluminium surface. Based on the O (I) temporal profile, the presence of oxygen can be attributed to the processing of the Ni–P overlayer.

The profiles of cobalt, chromium, iron, lead, sodium, nitrogen, and silicon are shown in Fig. 7(b). The signal intensities of Pb and Na evolve in the same fashion as those of nickel and phosphorus. Cobalt, on the other hand, appears much like Zn, as it is surely in the overlay, extending some depth into the substrate. The signals of Fe, Si, and Cr increase in parallel with those of aluminium and magnesium. The presence of Pb and Na is likely due to the additives used in the electroless-deposition process, while nitrogen comes from ammonia added to adjust pH of the plating bath. The presence of Fe in the interface region is quite clear from the profile. Shimizu et al. described that the presence of iron at the interface results from small amounts of ferric chloride which are used in the zincate process.2 However, zinc and sodium are not observed at elevated levels at the interface here as shown in their study. In general, the high spectral resolution of this instrument and the coincidence of the transients of “related” elements give support for the fact that the low signal levels for these trace species are indeed valid and not due to background interference.

Investigation of coating layers and distribution of impurities in commercial hard disks

Having determined the optimum conditions for profiling the Ni–P/Al–Mg system, and demonstrated the ability to detect the most likely of important and contaminant elements, two commercial hard disks of different technological generations (1992 and 1998) were profiled. The coating layers, the chromium support, the cobalt magnetic material, the amorphous carbon coating, and the carbon lubricant layer, are revealed successfully from the temporal profiles of both disks. Fig. 8(a) shows a very intense Cr (I) signal transient at the onset of the discharge, followed by a rapid increase in the Ni and P disk components for the disk fabricated in 1992. There is no evidence of Cr in the Ni–P layer. It is easy to see that the
profiles for each of the major elements of the hard disk substrate are similar to those of the Ni–P plated aluminium disk used in the method development studies. The Ni (I) and P (I) are quite stable until the onset of the transition region after approximately 210 s of sputtering. Based on the Ni (I) response and profilometer tracings, the interface with the Al substrate is reached in 230 s with an effective depth of 13.4 μm. The effective breadths of the interface based on the major elements’ responses (Ni 7.6, P 7.4, Al 2.1, and Mg 4.0 μm) are slightly greater than those in test matrix. These values imply that the interface of Ni–P layer and Al–Mg substrate in this disk is not as smooth as the simple metallic disk.

Figs. 8(b) and (c) present the distribution of trace elements in the overlayers and in the aluminium substrate. In the expanded scale of Fig. 8(b), the cobalt magnetic medium layer is easily seen. Different from the Cr overlayer, there is evidence of Co in the Ni–P layer. The profile of zinc shows the same basic form as the Ni and P matrix elements, though perhaps penetrating deeper into the Al substrate, as was seen in the test disk. Further scale expansion in Fig. 8(c) shows the same minor elements that were seen in the test matrix, with the signal intensities of cobalt and lead dropping off after passage through the Ni–P layer. Interestingly, the Cr (I) response increases gradually after passing the interface due to the fact that it is the impurity in the Al–Mg alloy. Apprecciable amounts of Na and Ca are seen as well in the substrate. Finally, as in the test disk, there is a pronounced signal for Fe located at the Ni–P/Al–Mg interface.

Fig. 9 is an expansion of the time axis of the depth profile of the 1992 hard disk presented in Fig. 8 to highlight the near-surface region. The data acquisition was tailored in this early time frame such that a sampling interval of 0.01 s was employed for the first 15 s of the analysis. (A sampling time of 0.1 s was used for the remainder of each profile.) The assignment of a depth scale is based on ex post facto profilometry measurements of the crater. The profile reveals the existence of at least three distinct layers on top of the Ni–P film. At the onset of the discharge, only carbon (of the list of analytes) exists to an appreciable extent. This is likely the primary lubricant layer. The second layer (which does not appear to be entirely discrete) is seen to consist of carbon and calcium and extends into the cobalt–chromium magnetic layer. This is the amorphous carbon layer that protects the magnetic medium. The cobalt–chromium magnetization layer is quite well defined. On the other hand, the chromium layer is not well defined, showing its presence in the cobalt layer. The trailing edge of the Cr (I) response shows much more definition at the interface with the Ni–P layer. If it is assumed that the sputtering rates for top coat layers are close to that of the Ni–P layer, i.e. 3.5 μm min⁻¹, the thicknesses of the cobalt–chromium and chromium layers are approximately 55 and 90 nm, respectively. This estimation is based on the widths at half-height fo the cobalt and chromium profiles.

Fig. 10 presents the depth profile of the commercial hard disk fabrication in 1998. The basic characteristics seen here are the same as the older disk, with one major exception. Based on the reduction of the Ni (I) to one-half of its plateau value, the interface is reached in 160 s of sputtering, corresponding to a depth of 9.3 μm, thinner than the corresponding layer of the 1992 disk. The effective interface breadths values of each major element (Ni 5.2, P 4.5, Al 1.6, and Mg 3.0 μm) are less than those in other hard disk, reflecting a more uniform Al–Mg surface. The scale expansions of Figs. 10(b) and (c) reveal two other differences between the commercial hard disks that appear to be related to the Al substrate. First, there appears to

![Fig. 8](image8.png)  
**Fig. 8** rf-GD-OES profile of major and trace elements in commercial hard disk produced in 1992. rf power = 40 W, Ar pressure = 40 W and 6 Torr.

![Fig. 9](image9.png)  
**Fig. 9** Expansion of the time scale of Fig. 8 to reveal the near-surface structure of the commercial hard disk produced in 1992. Rf power = 40 W, Ar pressure = 40 W and 6 Torr.

![Fig. 10](image10.png)  
**Fig. 10** rf-GD-OES profile of major and trace elements in commercial hard disk produced in 1998. rf power = 40 W, Ar pressure = 40 W and 6 Torr.
be a far greater amount of residual iron located at the Ni–P/Al–Mg interface. Second, there is also a large amount of chromium present in the substrate alloy. The presence of a greater amount of chromium in the aluminium alloy is likely intended to add greater rigidity to the substrate.

The expansion of the time scale of the depth profile in Fig. 11 reveals the structure of the near-surface region of the 1998 hard disk. The basic structure is very similar to that of the 1992 hard disk depicted in Fig. 9. If it is assumed that the sputtering rates for the overlayers are close to that of the Ni–P layer, the thickness of the cobalt–chromium and chromium layers are approximately 35 and 55 nm, respectively. These values are approximately 50% of the thickness of the older disk. Another difference is seen in the relative concentration of the chromium layer. Simple comparison between the Co (I), Cr (I), and Ni (I) intensities suggests that the purity of the chromium layer is much greater in the newer disk. In general, the profiles presented here represent well the technical evolution in hard disk storage devices.

It is not unreasonable to question the validity of the assumptions used to assign the layer thickness values. Certainly, it would be fortuitous if the sputter rates for each of the layers would be the same. Cross-sectional transmission electron microscopy (TEM) imaging is a powerful tool for measuring the thickness of very thin layers and coatings. Fig. 12 is the TEM micrograph taken from a cross section of the 1998 hard disk. The fundamental processes of TEM are such that the transmission/scattering characteristics of each layer are different, based on their elemental composition. As can be seen, the depth assignments derived by correlating analysis times and sputtering rates agree very well with the thickness revealed in the TEM images. The composition can be confirmed as well by the use of energy dispersive X-ray (EDX) analysis in conjunction with the TEM imaging. Fig. 13 presents the resultant X-ray images of the disk cross section. The tungsten present in the image is an artifact of the sample preparation, as it is coated on the sample prior to cleaving and ion beam milling. The elemental maps reveal the structure of the overlayers. The Co distribution is seen to be very well defined, with the Cr appearing to diffuse in the upper portion of the band, and is finite at the Ni–P interface. Of course, X-ray emission is not capable of providing the distribution of the light elements such as carbon and oxygen and is much more time and cost

![Fig. 11](image1) Expansion of the time scale of Fig. 10 to reveal the near-surface structure of the commercial hard disk produced in 1998. rf power ~ 40 W, Ar pressure ~ 40 W and 6 Torr.

![Fig. 12](image2) TEM micrograph of a cross section of the commercial disk produced in 1998.

![Fig. 13](image3) X-ray emission images generated by tandem EDX analysis of a cross section of the commercial disk produced in 1998.
expensive than rf-GD-OES. On the other hand, the depth resolution and mapping capabilities are far superior to those of the glow discharge method. Given their complementary nature, the combination of rf-GD-OES profiling and TEM/EDX imaging is a very powerful pair of tools for advanced materials research.

Conclusions

The roles of discharge operating conditions (rf power and Ar pressure) have been evaluated toward applications of rf-GD-OES for the depth profiling of computer storage media (i.e., hard disks). These devices are typically composed of a number of metallic layers coated on Ni-P/Al-Mg bi-layer supports. The applied rf power controls the rate of sample erosion and thus the intensity of the analyte responses and analysis times. The discharge gas pressure is shown to affect the sputtering rate, resultant crater shape, and the relative emission yields (REYs) of the analyte elements. As such, the discharge gas pressure has a large influence on the shape of the depth profiles. Operating parameters of an rf power of 40 W and an Ar pressure of 6 Torr yield the most ideal crater shapes, as determined by diamond stylus profilometry. The depth profiles obtained under these conditions show the most narrow of transition widths. Depth resolution is not a practical figure of merit in the profiling of the Ni-P/Al-Mg bi-layer as the Al surface is quite rough. The lack of a finite interface is confirmed by scanning electron microscopy. Minor and trace element remnants from the production of the Ni-P overlay are easily observed, as are minor alloying elements in the Al-Mg base alloy. The depth profiles of disks extracted from commercial hard drives provide detailed information about the critical top coating layers containing the storage media. The profiles clearly reflect the technological advances taking place between 1992 and 1998 in the production of hard disk devices. Well-defined profiles of layers in the tens-of-nanometer thickness scales are obtained. The complementary use of transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis provides validation of the fidelity of the rf-GD-OES profiles in terms of elemental composition and depth assignments. It is believed that the combination of rf-GD-OES and the more elaborate microbeam analysis techniques provides an excellent set of tools for advanced materials analysis.

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