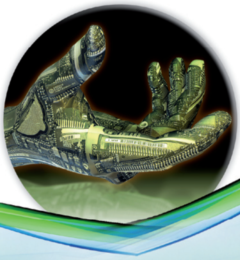
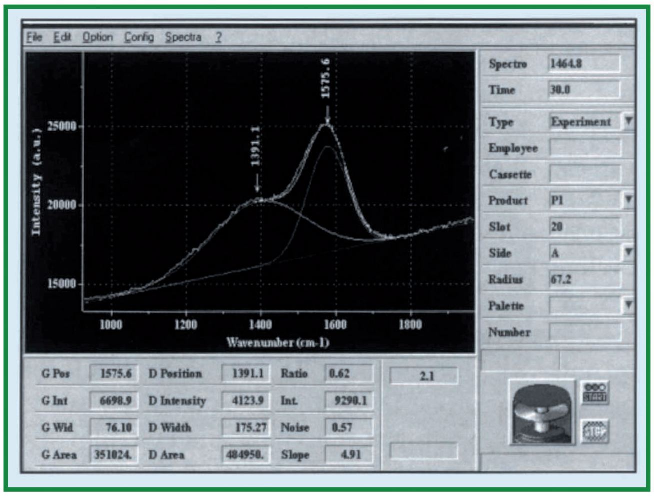


Derivation of Physical Parameters from Raman Spectra of Hard Carbon Films

The Raman spectra of elemental carbon materials are known to be sensitive to polymorphy1. For hard carbon films, the spectra of amorphous and diamond-like carbons can be band-fit to separate the contributions of the “graphitic carbon» (G band) from the «disordered carbon» (D band). Figure 1 shows a typical spectrum of a hard carbon film. The spectral behaviour of carbon films has been empirically correlated with thin film physical properties such as hardness, durability, optical transparency, electrical conductivity, thermal conductivity and corrosion resistance, and can be of use for prediction of these properties without extensive alternative testing. In recent years the computer hard disc manufacturing industry has implemented hard carbon coatings on all disc media as a means of protecting the magnetic media with hard, non-brittle films. The coatings provide wear protection against head sliders repeatedly dragging and slapping on the disk surface during the start and stop cycles of normal operation.

Usually the coatings contain some amount of hydrogen which is added to improve the corrosion protection of the underlying magnetic layer, to increase the film hardness for improved wear resistance, and to optimise interaction with the lubricants in order to eliminate friction problems. New films under development often contain nitrogen as well in order to reduce the surface resistivity and hence static charging without compromising film hardness. Combinations of hydrogen and nitrogen in the layers can improve the compatibility of the magnetic data storage media with different types of read/write heads.

The DiskRam has been engineered to facilitate and significantly accelerate the acquisition of the Raman spectra of hard carbon overcoats on disk media. Subsequent data reduction automates the derivation of the physical properties of interest. Curve-fitting the spectrum with two carbon bands (the D and G bands), additional nitrogen bands if required, and a baseline achieves these goals. The methodology used for the spectral reduction will be reviewed in this note.



Spectro 1464.8
Time 30.0
Type Experiment
Employee
Cassette
Product P1
Slot 20
Side A
Radius 67.2
Palette
Number

G Pos	1575.6	D Position	1391.1	Ratio	0.62	2.1
G Int	6698.9	D Intensity	4123.9	Int.	9290.1	
G Wid	76.10	D Width	175.27	Noise	0.57	
G Area	351024.	D Area	484950.	Slope	4.91	

Figure 1. Raman spectrum of Carbon Film recorded and band-fit on the DiskRAM

Description of Raman Spectra

The Raman spectrum of an amorphous pure, carbon film (as well as films doped with hydrogen and/or nitrogen) is composed of the D and G bands sitting on top of a broad luminescent baseline.
The G band usually occurs between 1480 and 1580 cm^{-1}, while the D band position appears between 1320 and 1440 cm^{-1}. The bands are usually overlapping and the actual positions are to some degree dependent on the laser excitation wavelength.

Using red excitation such as 632.8 nm of the Helium Neon laser results in a smaller separation of the two spectral components and consequently in more ambiguity of the curve fit result. To increase the spectral separation of the D and G bands, it is common to use an excitation wavelength in the green. For this the 532 nm line of a diode-pumped, frequency-doubled, NdYag laser or the 514.5 nm line of an Argon ion gas laser are employed.

The NdYag laser is the more energy efficient of the two lasers and can be run without external cooling fans. This can be a valuable feature, when cleanroom compatibility is of importance.

More recent experiments also focus on the use of the blue Argon ion line at 488 nm, which results in an even better spectral resolution of the two carbon bands. Films containing nitrogen show an additional weak band at 2180 cm^{-1}, corresponding to a nitrile CN triple bond stretching vibration. Over a defined concentration range of the nitrogen in the sputter atmosphere and hence in the deposited carbon film, there is a linear response in the intensity of the band at 2180 cm^{-1}. Mathematical methods for extracting nitrogen concentrations from the Ram an signatures are currently under development.

Nitrogen-doping of the carbon films causes a second, less visible effect on the Raman spectra. While the peak position of the D band remains relatively stable with increasing nitrogen concentration in the film, the G band position decreases significantly, i.e. the two Raman bands increasingly overlap with higher nitrogen concentration. While the G band position principally represents a fairly sensitive measure of the nitrogen concentration, other film processing parameters, mainly the substrate temperature during film deposition, also influences it. Films containing constant amounts of hydrogen or nitrogen show a nearly linear relationship of the G peak position with deposition temperature [2].

A linear regression of the experimental data yields a variation of ca. 0.1 cm^{-1}/ °C. Furthermore, Electron Energy Loss Spectroscopy (EELS) data indicate that films sputtered at higher temperature (higher G peak position) have lower sp3 and higher sp2 carbon content. It has been shown by abrasion and contact start/stop measurements, that higher sputter temperatures yield films with decreasing mechanical performance, which correlates with a higher sp2 carbon (i.e., softer) content.

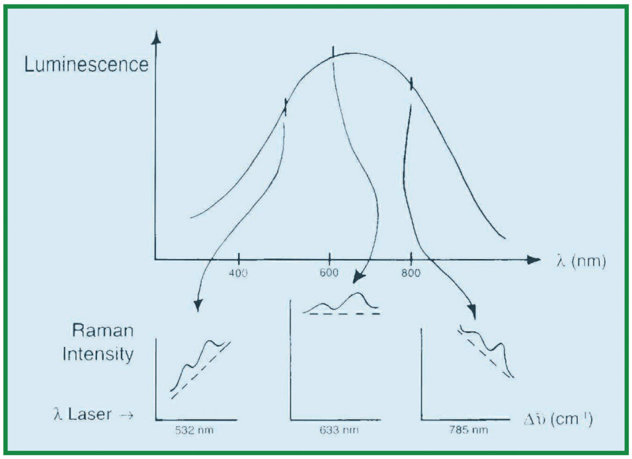


Figure 2. Relationship between Raman spectra and excitation wavelength as determined by fluorescent background

With the curve fitting techniques commonly in use it is almost impossible to decouple the different parameters influencing the Raman peaks positions, such that they can be used to simultaneously monitor nitrogen content of the film and substrate temperature during deposition. In a recent research effort, we applied advanced mathematical methods to analyse the response of the Raman spectra as a function of the variation in processing parameters as a whole.

Initial results of these Chemometrics methods are very conclusive, highlighting the use of such techniques for more sophisticated data analysis (fig.3). The nitrogen content can be determined with an absolute error of ± 0.1% within a range of 7 to 24 %. In addition, an overall better accuracy of quantitative results for other parameters can be obtained by using multivariate data analysis since more spectral information is taken into account.

Thus, the thickness of a nitrogenated overcoat within a range of 85 to 116 Å can be derived with an absolute error of ± 0.75 Å all over this range.

The improved accuracy of these measurements is of prime importance due to the continuously decreasing size of these structures.

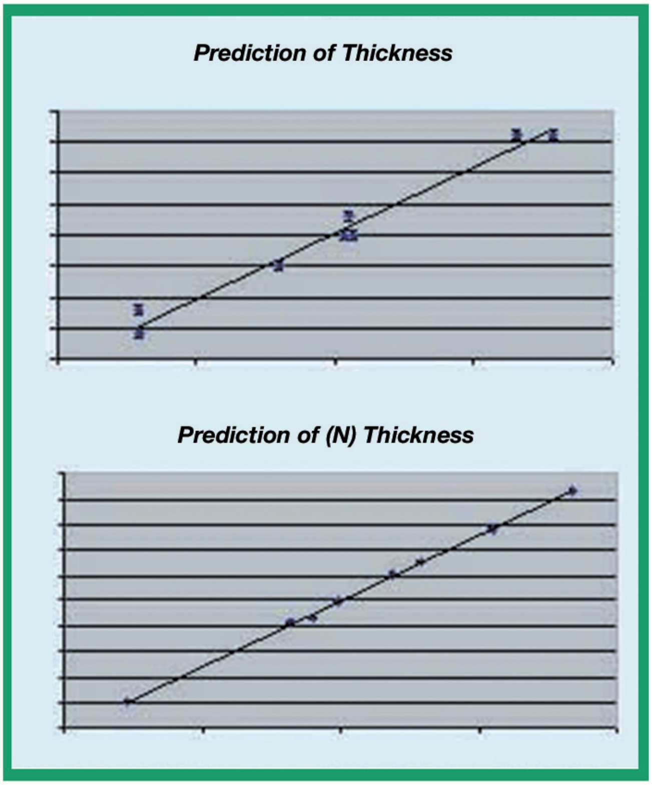


Figure 3. Results of multivariate analysis

Carbon films prepared in a hydrogen- or methane-containing atmosphere show a photoluminescence background in addition to the Raman bands.

The photoluminescence is due to recombination of electron hole pairs within sp2 bonded clusters in an sp3 bonded amorphous matrix. The intensity of the photoluminescence tends to increase with increasing hydrogen content in the film, due primarily to the saturation of non-radiative recombination sites [2]. A spectrum acquired using blue 488 nm excitation shows the luminescence to peak at about 600 nm. Using red excitation at 632.8 nm places the Raman spectrum close to the top of the broad luminescence peak, resulting in essentially a flat background. Refer to Figure 2. For a film of given thickness the intensity of this luminescent background is proportional to the amount of hydrogen in the film. However to avoid the influence of the film thickness on the measure of the hydrogen content, it is advisable to use a laser line in the green or blue, such that the Raman spectrum is on the flank of the luminescence peak.

By exciting with a laser wavelength on the rapidly rising or falling slope of the luminescence peak, the slope of the luminescent background can be used to predict the amount of hydrogenation. The slope, as opposed to the total intensity of the background, is independent of the carbon film thickness.

Bandfitting The Raman Spectrum

For the Raman analysis of the hard carbon film properties one usually limits the spectral region of analysis to the range between 800 and 1950 cm^{-1} (for nitrogenated films up to 2250 cm^{-1}).

The spectra can be fitted with Gaussian or Lorentzian band profiles, or a Gaussian/Lorentzian sum function (usually the Gaussian/Lorentzian sum function works best). To fit the baseline the DiskSpec software permits one to use a polynomial of first, second or third order (to accommodate small deviations of the baseline from linear, it is best to use a polynomial of second order). Once the recipe for the curve fitting is defined in the software, all subsequently collected spectra will be submitted to this curve fitting routine. The parameters derived from the curve fitting, such as peak intensities, widths, positions and background slope, can be automatically stored in a spreadsheet matrix format. Alternatively, the DiskSpec software allows the data stream to be routed to an external terminal for statistical process control (SPC).

Deriving Hydrogen Content

There are mainly two different effects of an increase in hydrogen content on the Raman spectral response. For hydrogen concentrations between 20 and 40 % in the carbon film, the photoluminescence peak around 600 nm increases exponentially. With green or blue excitation, the Raman spectrum is superimposed on the rising flank of this very broad luminescence background. The slope of this background can be used as a very sensitive measure for the hydrogen content in the carbon film.

Although the luminescent background and hence the spectral baseline is not always linear, the slope can be estimated in first instance by selecting two frequency positions that span the D and G bands (for instance, 800 and 1950 cm^{-1}) and defining a slope derived from the intensities, y1 and y2, at these frequencies. The user has the ability to freely select the way the slope is defined for correlation with hydrogen content. Possible slope definitions are:

y2/yl,
(y2-yl)/(y2+yl), or
(y2-yl)/y2

In any case it is important to work with relative intensities, rather than with absolute values, since absolute values are dependent on instrumental and sample parameters such as the laser power, the optical alignment, the integration time and the carbon film thickness. Using relative intensities cancels these factors out, since all spectral intensity values will be equally influenced by the above parameters. Note that the classical definition of the slope is (y2-yl)/(x2-xl) (where xi is the Raman wavenumber value) is not an effective way to define the slope for this application because any instrumental drift in intensity will effect the spectral intensities (y values), but not the spectral frequencies (x values). It has been found that if the natural logarithm of the slope, calculated from one of the definitions above, is plotted vs. % hydrogen content, the relationship is near linear between 20 and 40 % film hydrogen content. For films with a hydrogen content of less than 20 %, the intensity ratio of the D to G bands (ID/IG) can be empirically correlated to the hydrogen concentration. For those manufacturers who are interested in predicting hydrogen content from 0 to 50%, methods combining slope and ratio are potentially useful.

Calibration Transfer

For manufacturers performing SPC with several DiskRams it is sometimes necessary to correct for small instrument-to-instrument variations, in order to assure that all DiskRams give the same results for the same sample. Instrumental variations are unavoidable and will happen even though all optical components are «identical». It is not possible to acquire exactly identical components! The DiskSpec software allows for the introduction of standardisation coefficients. In order to derive these coefficients, we suggest analysing on all DiskRam tools a series of three or more disks showing, a wide variation in the parameter to be measured. When plotting actual versus measured parameters, every instrument can be standardised to give the same result for the same sample. Most of the time this can be done with a simple correction, such as the inclusion of a factor to correct the slope and a coefficient to correct for the offset.
Refer to Figure 4.

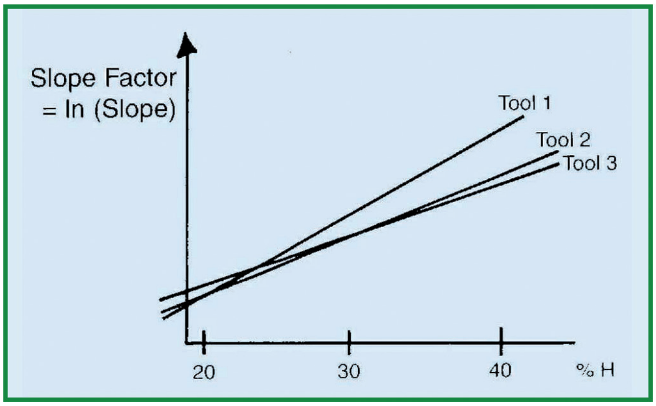


Figure 4. Slope factor vs. % hydrogen recorded on 3 different DiskRAM tools.

Film Thickness

The film thickness can be derived from the intensity of the G band normalised for the integration time. In order to compensate for instrumental effects, the G band intensity should furthermore be ratioed to the intensity of a reference sample. The DiskSpec software allows for a separate entry of spectra collection and curve fit parameters for reference samples different from carbon films.

It is advisable to use an alternative to carbon films as reference since the amorphous carbon tends to adsorb components from the ambient atmosphere, resulting in spectral changes over time. It is suggested to use a silicon wafer cut and polished to the same dimensions as the disk media as a reference that does not change its spectrum in time. The frequency of the reference measurements can be defined in the software by the timeout between references or, alternatively, by the number of actual carbon film measurements between references.

Whenever one of these two conditions is met, the operator is prompted to make a reference measurement. By comparing the actual thickness of a well-characterised carbon film with that measured, a correlation factor can be determined. Subsequently the system is able to measure the film thickness of unknown production samples in Å's.

Conclusion

The DiskRam has been designed to automate the collection of Raman spectra from hard carbon coatings on computer hard disk media and the extraction of parameters that are well correlated with the properties of the films. The extracted information is output in spreadsheet format for SPC at a manufacturing facility.

1. Impact of Raman Spectroscopy on Technologically Important Forms of Elemental Carbon, Jobin Yvon application note # A.N.08
2. Photoluminescence and Raman spectroscopy in hydrogenated carbon films, B. Marchon, J. Gui, K. Grannen, G. Rauch, J. Ager, S. Silva and J. Robertson, to be published in the IEEE Transactions on Magnetics (1997)

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