

# Measuring Diamond Like Carbon Films by Dispersive Raman Spectroscopy

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## KEY WORDS

Raman  
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Diamond like carbon  
DLC

## INTRODUCTION

Magnetic disk storage media are constantly driven to accommodate more data on smaller physical areas of material. To accomplish this, the area density must increase and the distance between the read/write head and the disk, also referred to as “flying height”, must decrease without catastrophic contact. In decreasing the flying height, it is important to apply a very thin protective coating to the disk, to minimize damage to the disk medium in the event of contact.

One material of choice for this coating is diamond like carbon (DLC), an amorphous carbon layer which combines strength and impact resistance with ease of thin layer application. DLC is an attractive material for such applications because, in the proper form, it has very high wear resistance, low friction and is chemically inert. Because DLC films are typically applied by plasma deposition, it is possible to alter the atomic structure of the film, hence the protective properties, by changing the deposition conditions. In hard disk manufacturing it is extremely important to monitor the structure of the DLC films to ensure maximum protection from the thinnest films possible.

The complete characterization of DLC films is not possible by a single technique, but must involve a full spectrum of analytical measurements. Nuclear magnetic resonance (NMR) and magic angle NMR have been used to determine structural information about DLC films. However, in most cases, thick free standing films must be specially produced and may not represent the structure on the disk. Auger spectroscopy, X-Ray photoelectron spectroscopy, secondary ion mass spectroscopy, neutron scatter and electron energy loss spectroscopy each provide specific structural information but require special sampling considerations such as ultra high vacuum, neutron sources or irregular sample sizes. Infrared spectroscopy has been useful in determining molecular structure, but the bands of interest are very weak.

Raman spectroscopy has proven to offer the best combination of chemical information and ease of sampling. Raman is particularly sensitive to the atomic structure of the DLC coatings, and is non-destructive and non-contact. In addition, Raman analysis can be performed at room temperature and offers high spatial resolution ( $<1 \mu\text{m}$ ). While Raman cannot provide an exhaustive analysis of the film structure, correlations between Raman intensities and band positions can provide insight into the atomic structure of the films as they are deposited on the disk media.

## INVESTIGATION OF FILM PREPARATION

Diamond like carbon films can be formed by ion beam deposition and by hydrocarbon gas plasma deposition. The highest quality polycrystalline and epitaxial films are produced by ion beam or sputter deposition. However, these techniques typically require high temperatures and specialized equipment.

Commercial production of DLC films typically involves plasma deposition of amorphous films because of the milder conditions required for DLC films of sufficient quality. These amorphous films are highly disordered with the atomic structure and film properties being dependent upon deposition conditions. It is necessary to optimize the deposition to provide films of desirable properties, since plasma deposition, under mild conditions can result in carbon films that tend to be low quality, soft cross-linked polymer films with low density. Under more aggressive conditions, the films become more rigid, stronger and more dense; thus they make better protective layers.

One unique characteristic of carbon is the ability to coordinate in two allotropic forms. The first is the  $\text{sp}^3$  or tetrahedral diamond form, where each carbon is bonded to four other carbon atoms throughout the crystalline region. Diamond gives rise to a very strong, sharp triply degenerate phonon Raman band at  $1332 \text{ cm}^{-1}$  as shown in **Figure 1**.

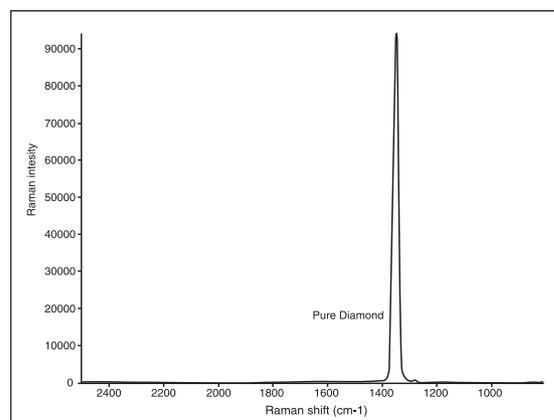
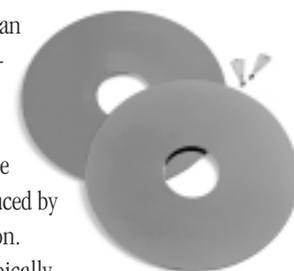


Figure 1: Dispersive Raman spectrum of a diamond film using a 633 nm HeNe laser as the excitation source

A second carbon form is the  $sp^2$  or graphite trigonal form, in which each carbon is bonded to three adjacent carbon atoms in the same plane, at  $120^\circ$ ; giving rise to a graphitic hexagonal structure. Highly ordered, single crystalline  $sp^2$  graphite gives rise to a single sharp doubly degenerate  $E_{2g}$  Raman active band at  $1580\text{ cm}^{-1}$ , typically referred to as the G band. However, the most common source of pure graphite is in naturally occurring crystals. Under normal deposition conditions, this pure phase is uncommon and a more amorphous phase most often seen. As the film becomes more amorphous, the  $1580\text{ cm}^{-1}$  band shifts slightly in position and significantly broadens.

Distortions in the crystalline structure of amorphous graphite are associated with the addition of small domains of  $sp^3$  carbon. This disorder produces a second Raman active band ( $A_{1g}$  mode) at  $1360\text{ cm}^{-1}$ , typically referred to as the D band. A spectrum of an amorphous film is shown in **Figure 2**, which clearly exhibits both a G and a D Raman band.

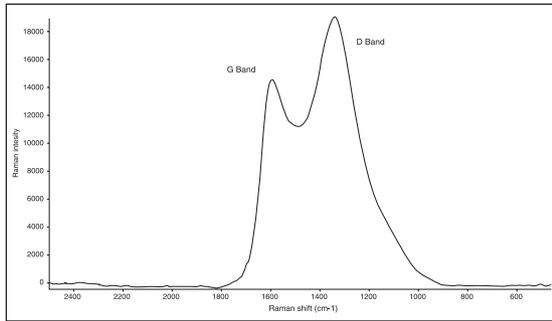


Figure 2: Dispersive Raman spectrum of a DLC film using a 633 nm HeNe laser as the excitation source

Deposition conditions have a very strong effect on the atomic structure and hence the physical characteristics of the DLC films. In the following study, plasma conditions were varied for the deposition of a number of films and the Raman spectra were measured. As noted before, Raman alone cannot fully characterize the films, however, many correlation studies have indicated relationships between Raman spectra and DLC film properties.

It has been found that the relative intensities of the D and G bands and the position of the G band can indicate  $sp^3$  content, which is also correlated with film hardness. These Raman measurements are therefore useful in optimizing deposition conditions to maximize the  $sp^3$  content, thus providing the hardest films possible.

A series of films were grown under different plasma conditions, in which both the plasma current and the gas partial pressure were varied. By altering the current or the partial pressure, harder films containing more  $sp^3$  carbon can be produced. A table of deposition conditions for this set of experiments is provided in Table 1, (due to the proprietary nature of this work, exact deposition conditions could not be divulged).

In **Table 1**, the values for the “low” and “high” designations are the same within each field, meaning that samples A and B were deposited with the same plasma current but with different partial pressures. Samples C and D were also deposited with the same applied current, but the gas partial pressures was varied to the same values used for A and B, respectively.

SAMPLE DESIGNATION	PLASMA CURRENT	PLASMA GAS PARTIAL PRESSURE
A	Low	Low
B	Low	High
C	Low	Medium
D	High	Medium
E	High	Low

Table 1: Plasma conditions for deposition of DLC films. The terms “High and Low” are relative quantities and do not imply values outside of those commonly used for such processes

Raman spectra were collected using a 633 nm HeNe laser as the excitation source. It has been observed that visible lasers routinely used for dispersive Raman spectroscopy have energies corresponding to the  $\pi \rightarrow \pi^*$  transition of the  $sp^2$  electronic configuration. This often causes resonant enhancement of this mode.

The enhancement increases the intensity of the Raman scatter, but can also affect the absolute values of the individual peak intensities differently, depending on probable differences in resonant enhancement. It is, therefore, useful to compare the ratio of Raman bands instead of monitoring the absolute intensities.

**Figure 3** shows Raman spectra of the five samples under various deposition conditions. These spectra clearly show the presence of both the D and G bands, and it is apparent that there is a difference in the relative amounts of the bands as well as an overall difference in spectral intensity. The greater overall intensity is likely attributed to differences in the thickness of the film grown.

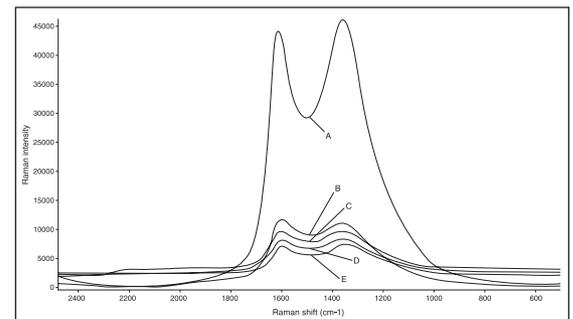


Figure 3: Dispersive Raman spectra of DLC films deposited under the conditions outlined in Table 1

Under the conditions of this data collection, the Almega™ spectrometer is likely sampling close to the full thickness of the film. The typical maximum sampling depth into graphite films by dispersive Raman microscopy is approximately 50 microns and the films in this study were estimated to be 30-50 microns in thickness.

It is possible to correlate the intensity ratio of the D and G bands to the  $sp^3$  content and the film hardness. The intensity ratio of the D and G bands was calculated by curve fitting the corresponding two bands to a pair of Gaussian peaks. A typical fit is shown in **Figure 4** and the ratio of the area under the fit curves provides the data for the experimentally determined ratios.

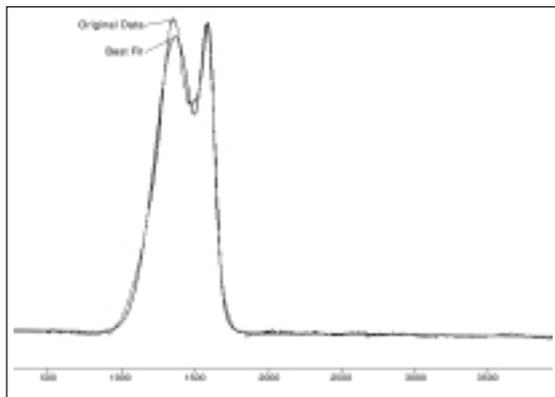


Figure 4: Gaussian fit of data from the Raman spectrum of Sample C. It shows the trace of the original data and the trace which is the best fit. The area under the individually fit curves was used to determine  $I_D/I_G$

**Table 2** shows the experimentally determined ratio of  $I_D/I_G$  for the spectra presented in Figure 3. The ratio of  $I_D/I_G$  is affected by varying both the current and the pressure, however the degree to which these affect the ratio, hence the film quality, appears to differ. By rearranging the values of Table 1 and Table 2, it is possible to detect some definite trends in the limited data set analyzed. These are shown in **Table 3**.

SAMPLE DESIGNATION	$I_D/I_G$
A	3.06
B	3.82
C	3.59
D	4.15
E	3.26

Table 2:  $I_D/I_G$  values for the five films deposited under the conditions outlined in Table 1 and corresponding to the spectra in Figure 3

SAMPLE DESIGNATION	PLASMA CURRENT	PLASMA GAS PARTIAL PRESSURE	$I_D/I_G$
E	High	Low	3.26
D	High	Medium	4.15
A	Low	Low	3.06
C	Low	Medium	3.59
B	Low	High	3.82

Table 3: Rearrangement of values from Tables 1 and 2 to illustrate possible experimental trends

By first examining the films resulting from holding the plasma current constant at a “Low” value and varying the partial pressure in samples A, B, and C, it is evident that at higher partial pressures, the  $I_D/I_G$  increases. The difference in the ratio value from High Pressure to Low is 0.76. Comparing the two samples, D and E, where the current is constant at a “High” value, the same trend is seen, although the  $I_D/I_G$  ratio values are overall much larger. This data indicates that  $I_D/I_G$  increases on increasing both the pressure and the current. Furthermore, comparing samples A and E, where the pressure is constant at a “Low” value, it is obvious that increased current does cause a rise in the  $I_D/I_G$ , however, the difference in the ratio values between the High current and Low current is only 0.20.

The experimental results indicate that the plasma current has a smaller effect on the atomic nature of the film. The data suggests that higher plasma currents yield harder films, a result that is consistent with the literature claims that more aggressive plasma conditions favor the disordered formation of harder DLC films.

## CONCLUSIONS

Raman spectroscopy is a powerful technique for monitoring the physical properties of diamond like carbon films. Though Raman does not give complete film characterization, correlations between peak positions and band intensity ratios can be used to predict the physical properties of the deposited film.

The combination of ease of sampling, no sample preparation and abundant chemical information make it possible to make non-destructive measurements directly on the desired substrate without the need for extreme temperature or vacuum.

In this study, Raman spectroscopy exhibited the ability to monitor DLC films that resulted from varying the plasma conditions. It is known that deposition conditions have a strong influence on the atomic structure of the resulting films. This work suggested that harder, more inert films result from higher plasma current and higher partial gas pressures.



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