Nitrogenated carbon layer on magnetic recording disks

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Abstract

Hydrogenated carbon films have been used in the magnetic recording industry as a protective overcoat for memory disks for many years. In recent years, with shortening of the gap between the head and the disk (as in proximity heads), the inclusion of nitrogen in the films to form hydrogenated/nitrogenated films has also aroused tremendous interest. In this study, nitrogenated amorphous carbon films (without hydrogen) (a-C:N) of thickness ranging from 5 to 20 nm were deposited on rigid magnetic disks via the magnetron sputtering of a graphite target. The deposition was conducted in an argon–nitrogen atmosphere under RF (radio frequency) substrate bias power. A scanning probe microscope (SPM) with a contact mode of atomic force microscopy (AFM) mode was used in the roughness determination. A Raman spectroscopic was employed to study the structural evolution of the coatings with varying nitrogen/argon proportion and flow rate, radio frequency substrate bias and target power density. The surface contact angle between the a-C:N coating and deionized water was measured using a Rame–Hart goniometer. Under the deposition conditions, the carbon thickness decreased with gas flow rate, but increases with nitrogen content. An increase in contact angle with bias power and decrease with flow rate were also observed. The roughness ($R_{a}$) of the coatings did not change because the coating was too thin to change the original substrate roughness. Also studied were the Raman peak positions, and the D-band and G-band intensity ratio and their relationship with the processing parameters. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Nitrogenated carbon; Magnetic disc; Sputtering; a-C:N; Carbon overcoat; Lubricant; Raman

1. Introduction

Amorphous hydrogenated carbon films (a-C:H) have been the subject of research for the last two decades and have been used in the magnetic recording industry as a protective overcoat for memory disks for many years [1–3]. In recent years, with shortening of the gap between the head and the disk (as in proximity heads), inclusion of nitrogen in the films to form hydrogenated/nitrogenated films has also aroused tremendous interest [4]. Very recently, the use of nitrogenated amorphous carbon (a-C:N) without hydrogen has been explored [5]. Currently, overcoats are typically on the order of 15–20 nm thick and must possess high durability, low friction coefficient and chemical inertness. The performance of the thin film disks depends largely upon the film microstructures as well as upon their mechanical properties. In this study, nitrogenated amorphous carbon films (without hydrogen) (a-C:N) of thickness ranging from 5 to 20 nm were deposited on rigid magnetic disks via unbalanced magnetron sputtering of graphite target in an argon–nitrogen atmosphere under RF (radio frequency) substrate bias power. The relationship between the microstructures and the deposition conditions has been explored.

2. Experimental procedure

2.1. Deposition

Carbon overcoats of various thicknesses were deposited in a d.c. magnetron sputtering system with premixed argon–nitrogen gas (90% Ar–10% N₂) in an industrial production chamber; the graphite target to
Fig. 1. Typical structure of the thin film medium.

Fig. 2. Film thickness decrease and carbon reflectance increase with deposition gas flow rate.

Fig. 3. Carbon film optical reflectance increase with substrate bias power.

disks distance being 25 mm. For easy control of the gas composition, pure argon and nitrogen were used. The gas composition was controlled by the ratio of the flow rates in a laboratory chamber (Teer Coating UDP 550) measuring 500 mm internal diameter by 500 mm high. Textured and non-textured 95 mm aluminum alloy disks were mounted on the sample holder parallel to 330 by 133 mm rectangular graphite targets (99.9%) mounted on the chamber walls. The distance between the disk surface and the target was set at 100 mm. A pair of facing targets was used for the deposition. Non-textured disks were included to provide a way to assess the coating morphology and roughness change before and after deposition. The substrate used was the typical Al–Mg alloy disk [6]: on top of the Al–Mg alloy is a thick layer (10–25 μm) of NiP followed by a Cr layer and the Co (magnetic) layer. The carbon film is applied onto the Co layer, and finally, outermost, is a lubrication layer. A post-deposition and lubrication disk is illustrated in Fig. 1. During the deposition, the background pressure in the sputtering chamber was below 5 × 10⁻⁵ torr (in the case of the industrial chamber, 5 × 10⁻⁸ torr), and the working pressure was between 3 and 11 mtorr during deposition. For some samples, a standard radio frequency (RF, 13.56 MHz) bias power was also applied to the substrate to study substrate bias effects. The RF-induced bias voltage on substrate was varied from 0 to negative 160 V and the deposition time was varied to give different film thicknesses.

2.2. Physical and mechanical characterization

The coating roughness was determined using a scanning probe microscope (NanoScope III-A) from Digital Instruments Inc. In operation, the contact atomic mode of force microscopy (AFM) mode was used at a set point of 2.5 V, and a scan rate of 0.9988 Hz over a scan area of 1 μm × 1 μm. A Raman spectroscope (Rennishaw RamaScope Model 127) using a He–Ne laser beam of 632.8 nm as the excitation source was employed to study the structural evolution of the coatings with varying nitrogen/argon ratios and flow rates, radio frequency substrate biases and target power densities.

The surface contact angle between the a-C:N coating and the deionized water was measured using a Rame-Hart goinometer. To characterize the bonding between the lubricant and the coating surface, the disks were taken from the sputtering chamber, buffed, and lubricated via a dip coating process in a Fomblin Z-dol solution at the same withdrawal rate. Then, the disks were immersed in fresh PF5060 delube solution three times for 10 s each to dissolve the physically bonded lubricant. After delubrication, the remaining lubricant thickness was measured by the Fourier transform infrared (FTIR) method. The average thickness of the remaining lubricant layer is termed the residual lubricant thickness. Since the delubrication process removes the physically bonded layers but retains the chemically bonded layers, the residual lubricant thickness is therefore a measure of the chemical bonding of the lubricant onto the coating surface. An abrasion test was conducted on samples with different flow rates and deposition power densities using a Selket Profile-Abrader System 1000 under the standard load. The abrasion was
measured as the change in percentage of fiber optic sensor output in terms of voltage after 60 s:

\[
\text{Wear rate} = \frac{V_f - V_0}{V_0} \times 100\% 
\]

where \(V_0\) is the initial voltage and \(V_f\) the voltage after 60 s. A Keithley ohmmeter was configured to perform the resistance measurements on the textured surface of the coating at a voltage of 0.35 V.

3. Results and discussion

3.1. Physical properties

3.1.1. Film thickness

The gas flow rate has a significant influence on the film thickness. The deposition rate was found to decrease with increasing flow rate, as plotted in Fig. 2 as solid circles. This was confirmed by the carbon film optical reflectance which decreases with increasing thickness (open circles) shown also in Fig. 2. The measurements were done on a CIE-1931 Chroma Meter.

The negative dependence of the deposition rate on the gas flow rate, and hence on the chamber pressure, can be attributed to reduced gas species collision with the substrates according to kinetic theory.

Fig. 3 shows the dependence of the reflectance on substrate bias at various \(\text{Ar:N}_2\) mixture ratios. Increasing bias generates more bombardment on the substrate and the film up to a point where further increase results in loss of the film already deposited due to back-sputtering. This is best seen in Fig. 4.

Also seen in Fig. 3 is the effect of the nitrogen content; higher concentration of nitrogen gives lower reflectance, or a thicker coating, since \(a-C:N\) has a faster deposition rate than \(a-C\) or \(a-C:H\). Chen et al. [7] suggested that a likely explanation is that the atomic mass of nitrogen is closer to that of carbon than argon, thereby resulting in better momentum transfer during sputtering and hence a higher sputter rate and therefore a higher deposition rate.

3.1.2. Surface roughness and contact angle

The surface roughness of the film is another important physical property, especially on magnetic recording disks. However, since the coating is very thin (up to 20 nm), the roughness does not seem to change much with the deposition parameters. Fig. 5 illustrates the roughness change with bias power.

The water contact angle, on the other hand, is more sensitive to deposition parameters. Fig. 6 plots the contact angle as a function of the substrate bias power for non-textured and textured disks at different nitrogen concentrations. A slight increase of contact angle was observed with bias power but little effect was seen measured as the change in percentage of fiber optic sensor output in terms of voltage after 60 s:

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The surface energy of the coating is related to the surface contact angle through Young’s equation:

\[ \gamma_f = \gamma_w \cos \theta + \gamma_{w-f} \]

where \( \gamma \) is the surface energy, \( f \) is for film and \( w \) for water. From Fig. 6 it is seen that the surface energy of the a-C:N film decreased with bias power. The increase in gas flow rate, however, brought about a decrease in the contact angle, as shown in Fig. 7.

### 3.2. Raman spectroscopic and wear characteristics

The Raman spectra of the samples were fitted into two Gaussian peaks; one centered around 1350 cm\(^{-1}\) (the D-band) and the other around 1560 cm\(^{-1}\) (the G-band). Plotting the G-band peak position (right-hand ordinate) and the band intensity ratio \( I_d/I_g \) (left-hand ordinate) against substrate bias gives Fig. 8. According to theoretical work by Beeman et al. [8], a shift of the Raman G-peak to a lower frequency indicates a greater sp\(^3\):sp\(^2\) bonding ratio: this is seen in Fig. 8. Decreasing \( I_d/I_g \) indicates reduction in the total number and/or size of graphitic micro-domains, or increase in the number of four-fold coordinated carbon atoms (sp\(^3\):sp\(^2\)), as demonstrated by Lee and co-workers [2], Marchon and co-workers [1] and Ager III [9] in hydrogenated amorphous carbon films with increasing hydrogen content. The influence of the bias power is believed to originate from the increased degree of bombardment as the bias power is increased.

However, with increasing target power density (through reduction of the number of targets from three pairs to two pairs and then to one pair), an increase in \( I_d/I_g \) (open circles) and G-Peak wave number (solid triangles) were observed (Fig. 9). This means that increased target power density hindered sp\(^3\) formation or promoted sp\(^2\) bonding, as also indicated by the increased wear rate (the solid points Fig. 9).
4. Conclusions

Magnetron sputtering of graphite target in the presence of nitrogen was employed to deposit a-C:N film on Al–Mg rigid magnetic disks. The effects of the processing parameters on the growth, the contact angle and the Raman spectra of the carbon overcoat were studied. The following gives the main points again:

1. Increasing flow rate (chamber pressure) or bias power suppresses the film growth.
2. The surface energy of the film increases with flow rate and decreases with bias.
3. Increasing substrate bias decreases the G-band peak position and the band intensity ratio \( I_d/I_g \), indicating favored carbon four-fold coordination.
4. In the range of thickness coated, no obvious correlation is found between the coating roughness and the deposition parameters (flow rate, substrate bias, etc.).

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