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ABSTRACT

Amorphous hard carbon films deposited by filtered cathodic arc deposition exhibit very high hardness and elastic modulus, high mass density, low coefficient of friction, and the films are very smooth. All these properties are beneficial to applications of these films for the head/disk interface tribology. The properties of cathodic arc deposited amorphous carbon films are summarized, and they are compared to sputter deposited, hydrogenated (CH₃), and nitrogenated (CNₓ) carbon films which are the present choice for hard disk and slider coatings. New developments in cathodic arc coaters are discussed which are of interest to the disk drive industry. Experiments on the nanotribology, mass density and hardness, corrosion behavior, and tribochemical behavior of cathodic arc films are reported. A number of applications of cathodic arc deposited films to hard disk and slider coatings are described. It is shown that their tribological performance is considerably better compared to CH₃ and CNₓ films.

INTRODUCTION

The continuously increasing storage density of magnetic storage devices is connected to a increasingly smaller spacing between the disk and the slider. The typical fly height for disk drives shipped today with a storage density of about 2 Gb/In² is about 40-50 nm, and for disk drives with a storage density of 10 Gb/In² which is the goal for the very near future the spacing will be about 20-30 nm. It starts to be more and more a question of semantics if this kind of recording is called near contact, pseudo-contact, or contact recording, but in any case the requirements on the tribology of the head/disk interface are harder and harder to achieve. A smaller magnetic spacing can be obtained by using a thinner protective coating on the disks: Materials such as the sputter deposited amorphous carbon overcoat CH₃ which have been used successfully on disks for many years at a thickness of 12-15 nm reach their limit and fail at the smaller thickness required on future disks. A lot of research has been carried out during the last years to improve the existing material (CH₃) and to find new materials which perform adequate at the required smaller film thickness. Amorphous hard films formed by sputter deposition which contain carbon and nitrogen (CNₓ), or contain carbon, nitrogen, and hydrogen (CNₓHᵧ) have been developed and are used for most disks and sliders today. But also these materials reach their limit at about 7-10 nm, and the search for better materials continues. One candidate is cathodic arc deposited amorphous hard carbon, which is among the amorphous, carbon based materials with the highest content of tetrahedral (sp³) bonding which is characteristic for crystalline diamond. Other methods which yield similarly high sp³ content are ion beam deposition [1] and laser ablation [2] for hydrogen-free films, and plasma beam deposition [3] for hydrogenated films. In the present paper we will review the deposition and film formation
process of cathodic arc deposited amorphous hard carbon, describe the study of the mechanical, 
tribological, tribochemical, and corrosion-related properties of these films, and report on a 
number of applications to the head/disk interface tribology.

NEW DEVELOPMENTS IN CATHODIC ARC DEPOSITION

Cathodic arc deposition is based on the production of a plasma by a cathodic arc discharge on 
a graphite cathode in case of amorphous carbon deposition. The cathodic arc discharge is a high-
current (typically 100-200A), low voltage (typically 20V) discharge which forms the plasma in a 
fast sequence of microexplosions on the cathode. The explosive character leads to a fully ionized 
plasma which is beneficial for the deposition since the ion energy which is the most important 
factor for obtaining high sp³ content films can be easily influenced by substrate biasing. It also 
leads to the formation of micron-size particles (solid for graphite cathodes, liquid for metal 
cathodes) which can be detrimental for the film formation since the particles can be embedded in 
the film or cause other film defects such as pinholes. Cathodic arcs and cathodic arc deposition 
are described in great detail in [4].

Over the last decades research was concentrated on the optimization of the deposition 
conditions to form films with the highest sp³ content and the lowest macroparticle content. It 
was found that the ion energy and substrate temperature are the main parameters that determine 
the sp³ content with a maximum value of 85% obtained at ion energies around 100 eV [5-7] and 
substrates at room temperature or lower [8]. While the establishment of these parameters was 
relatively easy, the problem of macroparticle contamination has been severe. Attempts to filter 
the plasma using bent magnetic fields have been successful for applications such as the 
deposition of high quality titanium nitride thin films, but carbon has been a problem because the 
particles are solid and multiply reflected from filter walls. Straight filters [9] and filters with 
bending angles of 20 degrees [10], 45 degrees [11], and 90 degrees [12] were tested, and only a 
system consisting of two connected 90 degrees filters in the shape of an “S” could produce films 
which are acceptable for the application to the disk drive industry [13]. This S-filter has only a 
low efficiency and the larger part of the plasma produced in the source is lost, but due to the high 
plasma production rate of the cathodic arc discharge (the ion current is about 10% of the total arc 
current and therefore in the order of 10 A) and the low film thicknesses required for head/disk 
applications the deposition rate can be in the range of 1 nm/s and sufficient for industrial 
applications.

At the moment there are cathodic arc sources available on the market which are equipped 
with 45 degrees and 90 degrees filters, and it can be expected that sources with better filters will 
be available soon.

PROPERTIES OF CATHODIC ARC AMORPHOUS HARD CARBON IN COMPARISON 
TO OTHER AMORPHOUS CARBON FILMS

The properties of amorphous hard carbon films depend strongly on the deposition conditions. 
Generally, one can distinguish between hydrogen-free a-C films, CHₓ, CNₓ, and CHₓNᵧ films. 
Cathodic arc deposition [7,16], laser-arc deposition [17], ion beam deposition [1, 24], and pulsed 
laser deposition [2, 22,23] can produce a-C films which are comparable in their properties and 
have a high sp³ fraction. The sp³ fraction for high-quality films is typically between 75-85%, the 
hardness between 60-90 GPa, the elastic modulus around 500 GPa, the mass density about 2.7-
3.3 g/cm³, and the stress very high with 6-12 GPa. It is remarkable that it was possible to reduce 
the stress of pulsed-laser deposited films to very low values <0.2 GPa by annealing without
reducing the hardness of the films [2]. High compressive stress up to 10 GPa is often considered a problematic property of cathodic arc deposited films. Attempts have been made to decouple high stress and high hardness and were to some extent successful by using a carbon-carbon multilayer approach [14], or by introducing additional elements besides carbon [15]. Sputter deposited hydrogen-free a-C films have a much lower sp$^3$ fraction of typically 15%, a hardness of about 15 GPa, an elastic modulus of about 150 GPa, and a mass density of around 2.0 g/cm$^3$, but also low stress of about 0.5 GPa [18].

Among the methods to deposit CH$_x$ films there is one which results in much more “diamond-like” films than other methods, this is plasma beam deposition [3]. These films show the highest sp$^3$ fraction for hydrogenated films of 75%, a hardness of 60 GPa, and a mass density of 2.9 g/cm$^3$. Hydrogen and nitrogen containing films deposited by other methods such as variations of the sputter technique and plasma enhanced CVD have a lower sp$^3$ fraction around 20-40%, a hardness of 15-35 GPa, an elastic modulus of 100-200 GPa, a mass density of 1.7-2.3 g/cm$^3$, and a stress of 1-3 GPa [16, 18, 19-21, 25, 26].

High sp$^3$ fraction is not necessarily the best optimization parameter for disk drive applications where tribochemical properties play an important role, and the whole system of slider surface, lubricant, and disk overcoat needs to be optimized under realistic wear conditions.

**NANOTRIBOLOGICAL BEHAVIOR OF CATHODIC ARC AMORPHOUS CARBON FILMS**

The nanowear behavior of cathodic arc deposited films has been tested in earlier experiments which showed a superior performance in comparison to other films [27, 28]. For disk coatings it is important that the films keep their excellent properties also at very low film thickness. Nanoindentation measurements showed a reduced hardness for thinner films [7], but it is very difficult to separate film properties and substrate influence for very thin, very hard films on relatively soft substrates. Therefore, nano-scratch tests were performed which probe more the properties of the film in the film plane and less perpendicular to the film as nanoindentation does. It was found before for measurements of the elastic modulus that results vary greatly for identical films if the elastic modulus is measured by a method which probes perpendicular to the film (nanoindentation, E=350-500 GPa) and a method that probes along the film (supersonic method, E=900-100 GPa) [29-32].

Scratch tests were performed on a series of cathodic arc carbon films of varying thicknesses to determine any dependence of their mechanical properties on the film thickness. Eight films were fabricated on Si substrates with the following deposition parameters: a pulsed arc current of 300 A for 5 ms with a frequency of 1 Hz, and a pulsed substrate bias of -100 V with a duty cycle of 2µs on/ 6µs off. The scratch tests were done on a Hysitron TriboScope®, which is able to scratch on the film surfaces with controlled forces. The films had thicknesses of 6.6, 10.4, 17.7, 18.2, 23.5, 44, 49, and 66 nm, respectively. The thickness values were measured with an n&k reflectance spectrometer. For films thicker than 17.7 nm, we confirmed the data with a Dektak profilometer measurement in a masked region of the sample. A diamond tip with a radius of about 100 nm was used to scratch a distance of 4 µm. Ramp scratch forces (instead of constant forces) were employed in this study to prevent initial shocks in the loading process. Before scratching each sample, a preliminary scan with 1 µN load across the test area was made to obtain a profile of the surface and to account for the possible tilt of the sample. After each test, the vertical displacement measurement is subtracted by the vertical displacement of the corresponding 1 µN scan to eliminate the errors due to sample tilting.
Figures 1-3 show the scratch depth vs. horizontal displacement (scratch curves) for the samples with film thickness 6.6, 23.5, and 66 nm, respectively.

![Figure 1](image1.png)

**Figure 1:** Scratch depth vs. horizontal displacement (scratch curves) for sample with a film thickness of 6.6 nm. The legend indicated the scratch force in μN.

When scratching with low loads, the scratch depth changes linearly with the horizontal displacement. This is due to the linear loading forces and the uniformity of film properties. With scratch forces of 400 μN or more, the sample with the 6.6 nm thick film shows two regimes on the scratch curves. The regime with the smaller slope reflects the scratch resistance of the film itself, and the regime with the larger slope is largely due to the silicon substrate. It can be seen that the cathodic arc films are more scratch resistant than the silicon substrate. Similar trends are observed for the samples with 23.5 and 66 nm thick films, also.
Figure 3: Scratch depth vs. horizontal displacement (scratch curves) for sample with a film thickness of 66 nm. The legend indicated the scratch force in \( \mu \text{N} \).

The intersection of the two slopes could be related, but not limited, to the breakage of the film. For samples with film thicknesses of 6.6, 23.5, and 66 nm this point is at about 25 nm, 25 nm, and 55 nm, respectively. Thus, only the point for the sample with a film thickness of 23.5 nm agrees well with its thickness. For thinner films, the turning point is deeper than the film thickness. For thicker films, the turning point is shallower than the film thickness.

The scratch curves for each sample under a scratch force of 50 \( \mu \text{N} \) are plotted together in order to compare the scratch resistances of the eight films (figure 4). No significant difference can be noted from these curves. Figure 5 shows the scratch curves for each sample with a scratch force of 100 \( \mu \text{N} \).

Figure 4: Scratch curves for all 8 samples under a scratch force of 50 \( \mu \text{N} \).
The curves for the 6.6 nm and 10 nm thick films have slightly larger scratch depths at the end of the test due to the substrate effect on the thinner films. Excluding that, no appreciable difference was noted in these curves either. For larger scratch forces, thicker films show relatively small scratch depths, because the substrate is not influencing the measurements. We find that thin cathodic arc carbon films (6.6 nm) show the same scratch resistance as thick ones (66 nm). No thickness dependence of the mechanical properties of these films is observed as measured by the scratch tests.

MASS DENSITY AND HARDNESS OF CATHODIC ARC AMORPHOUS CARBON FILMS

We investigated two material properties, film hardness and density, of cathodic-arc deposited amorphous carbon films as a function of substrate-bias during deposition. It is described in the literature that the ion energy during deposition affects the ratio of sp²/sp³ bonding in carbon films, which in turn correlates to material properties such as hardness and elastic modulus [6, 7, 33]. Earlier work has been done to study the hardness and density of similar films, but the density measurements were taken often indirectly from Electron Energy Loss Spectroscopy (EELS) spectra [7].

Three films were deposited on low-resistivity Si wafers at substrate biases of -100, -500, and -1000V. An S-shaped filter for macroparticle reduction was applied, and the following deposition parameters were used: a pulsed arc current of 300A, 5 ms arc duration at a frequency of 1 Hz, and a pulsed substrate bias with a duty cycle of 2µs on/ 6µs off. The film thicknesses of the -100, -500, and -1000V bias samples were 71.5, 122.5, and 98.5 nm determined using a Dektak profilometer.

Film hardness was measured with a commercially-available Hysitron TriboScope® system. We defined hardness as the maximum indentation force divided by the contact area during indentation. All measurements were done with a tip of radius 60 nm and limited to indentations with residual depths less than 20% of the total film thickness.

Film density measurements were taken with a high-precision scale with 10⁻⁷ gram accuracy. The weights of each wafer were taken before and after each deposition. The film thickness was
determined using a Dektak profilometer. Density values were then calculated directly from the weight difference and film volume as determined by the thickness measurement.

Figure 6 is a plot of the film hardness and mass density versus substrate bias during deposition.

Figure 6: Film hardness and mass density versus pulsed substrate bias of cathodic arc deposited films.

From Fig. 6 it can be seen that the highest hardness (68 GPa) and density (3 g/cm³) values belonged to the sample deposited at -100V bias, which corresponded to an ion energy of about 120 eV. With increased substrate bias, these values decreased due to increased graphitization of the film.

In summary, the most diamond-like (in hardness and density) cathodic-arc amorphous carbon films were produced at a pulsed substrate bias of -100V. The film hardness from these studies was consistent with earlier published work on similar films, and our direct measurements of film density confirmed the estimated mass density based on EELS measurements.

CORROSION STUDIES

The corrosion-resistance of cathodic-arc amorphous carbon films was studied in a series of samples with film thicknesses ranging from 2 nm to 40 nm. These films were deposited on low-resistivity Si wafers that were previously coated with a layer of 100 nm permalloy (80% Ni / 20% Fe). We applied an S-shaped filter for macroparticle removal and used the following deposition parameters: a pulsed arc current of 300A, 5 ms arc durations at a frequency of 1 Hz, and a pulsed substrate bias of -100V with a duty cycle of 2μs on/ 6μs off. Thickness measurements of the films were conducted with an n&k Analyzer 1100 reflectance spectrometer.

The corrosion comparison was based on a simple, yet effective decoration technique -- a NaCl dip test. Samples were immersed for 24 hours in a pre-mixed solution consisting of 0.5 mol NaCl, 0.5 mol (NH₄)H₂PO₄, 1 gram Liquinox, and 1000 grams of H₂O. Upon removal, the specimen were rinsed in deionized water and dried with a N₂ air gun. Inspection of the surface was done under an optical microscope, where an image analysis system counted the defect density (number of defects per unit area) and defect size (percent area occupied by defects).
Figure 7 is a plot of the pinhole count (number of defects per 0.8 x 1 mm² area) per sample versus film thickness.

![Graph showing pinhole count versus film thickness](image)

**Figure 7:** Pinhole count versus film thickness of cathodic arc deposited films in comparison to 7 nm thick sputter deposited film.

Higher pinhole counts infer poorer corrosion-resistance of the film. No significant difference in corrosion performance was noted for film thicknesses between 4 and 40 nm, which indicated a continuous film on the sample surface even at 4 nm. However, below 4 nm, the pinhole count rose an order of magnitude, which coincided with the values for an uncoated sample, indicating a breakdown of the film continuity/coverage. As a relative comparison, a 7 nm, RF-sputtered, hydrogenated amorphous carbon film (CHₓ) was also subjected to the test. This film thickness was chosen because it corresponds to the current overcoat thickness used in today’s advanced media products. Its pinhole count was 100.

Based on these results, we demonstrated that cathodic-arc amorphous carbon films provide complete coverage of the substrate surface with film thicknesses as thin as 4 nm, and acceptable levels of corrosion-resistance in this regime. The corrosion performance of a 4 nm cathodic-arc carbon film is comparable to that of a 7 nm sputtered CHₓ film.

TRIBOCHEMICAL STUDIES

For the application of the cathodic-arc deposition technique in the area of disk drive technology tribochemical properties of the films are of great importance. In these studies, we examine the tribo-chemistry of cathodic arc deposited films during drag tests in an ultra-high vacuum (UHV) tribochamber.

The UHV tribochamber consists of a disk spindle, a slider actuator, a substrate heater, and a high-resolution quadrupole mass spectrometer (QMS) in a vacuum chamber with a base pressure < 10⁻⁶ Pa. The QMS provides in-situ detection of gaseous products generated at the head/disk interface during drag tests. The QMS monitors 15 different atomic mass units (AMUs) simultaneously along with friction data. Further details about the system may be found...
Drag tests were conducted at a drag speed of 0.2 m/s, a load of 30 mN, and drag time of 600 seconds.

Supersmooth-textured 65 mm disks were coated with a 5 nm cathodic-arc amorphous carbon overcoat and lubricated with 0.85 nm of perfluoropolyether ZDOL lubricant. These samples were subjected to drag tests with uncoated Al₂O₃-TiC negative-pressure sliders in the UHV tribochamber. A commercial 65 mm disk with a 7 nm RF-sputtered CHₓ film and 1.25 nm of ZDOL lubricant was subjected to similar tests as a comparison.

Figure 8 is a plot of the friction data versus drag time for both samples.

Comparable friction performance (μ = 3) was noted between the cathodic arc coated disks and CHₓ coated disks before failure. Based on a visual inspection of the drag track and corresponding drops in the friction data, both overcoats had catastrophic failures after 40 seconds of dragging.

Figures 9 and 10 are plots of selected AMUs versus drag time for the cathodic arc deposited films and sputter deposited CHₓ samples, respectively.

For the cathodic arc coated sample we noted a two-fold reduction in the generation of mass fragments associated with the catalytic decomposition of ZDOL (CF₃, C₂F₅) due to the Al₂O₃-TiC slider material [35]. No significant difference was observed in the mass fragments used to monitor the friction/thermal decomposition (CFO, CF₂O) between the two samples. These results indicated that the chemistry between the cathodic arc deposited films and the lubricant molecule may prevent the catalytic decomposition of ZDOL that occurs in the presence of Al₂O₃-TiC material. Further studies of the surface chemistry of cathodic arc films versus sputter deposited CHₓ films are in progress to explain this phenomenon.

APPLICATION OF CATHODIC ARC AMORPHOUS CARBON FILMS TO SLIDER AND DISK SURFACES

The applications of cathodic arc deposited films to sliders and disks are still relatively scarce. A few studies have been performed and are published elsewhere in detail [33, 36, 37]. Here, we summarize briefly the main results.
Cathodic arc surface modification using pulsed bias can be performed in two ways - as a thin film deposition and as a low-energy ion implantation/deposition process. First tests showed that both methods can lead to drastic improvements of the slider performance.

In case of a thin film deposition typically a high bias of 1-2 kV is applied for the first 10% of the deposition process to ensure good film adhesion, and a bias of -100V is applied for the rest of the deposition for maximum film hardness. While uncoated sliders failed in a Contact Start Stop testing after 7500 cycles, the sliders coated with 2 nm cathodic arc carbon did not fail even after 100,000 when the test was interrupted [36,37]. In case of a low energy (2-4 keV) ion implantation/deposition process sliders were modified with C, Ag, and Ti ions at a low dose of 2x10^{16} cm^{-2} [33]. This fast and easy surface treatment led to a reduction of the coefficient of friction by a factor of about 5-6 in a continuous sliding test in comparison to untreated sliders.

The coating of disks with 10 nm cathodic arc carbon led to the reduction of the worn volume on the face of the slider by almost a factor of 20 in a continuous sliding test in contact [36, 37]. Even though more systematic studies are necessary to fully explore the capabilities of cathodic arc amorphous carbon films for disk and slider coatings, first results are very promising.

**CONCLUSIONS**

Cathodic arc deposited amorphous hard carbon films have properties which are desirable for the application as disk and slider hard overcoats. The hardness and mass density are very high for films formed at optimum deposition conditions. Nano-scratch tests show that the films remain their high scratch resistance also at very low film thickness of 6.6 nm. Corrosion measurements demonstrate that continuous films with corrosion rates comparable to 7 nm sputter deposited films can be obtained at a film thickness of 4 nm. Cathodic arc deposited films reduce the catalytic erosion products formed during wear in comparison to sputter deposited films. A number of experiments applying cathodic arc deposited films to slider and disk surfaces show a
considerably improved performance. More systematic studies are required for the optimization of the films for disk drive applications.

The problem of macroparticle contamination of the films which has been a problem for the last two decades has been overcome by sophisticated filtering techniques. These filtering techniques have a reduced deposition rates as a consequence, but the rate is still reasonably high for hard disk and slider coating. New developments in cathodic arc deposition equipment manufacturing will make filtered arc sources available in the very near future which will facilitate a wide-range systematic testing of these films for the disk drive industry.

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