Deposition and characterization of ultra thin diamond like carbon films

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Abstract. Amorphous hydrogenated and/or nitrogenated carbon films, a-C:H/a-C:N, in overall thickness up to 2 nm are materials of choice as a mechanical and corrosion protection layer of the magnetic media in modern hard disk drive disks. In order to obtain high density and void-free films the sputtering technology has been replaced by different plasma and ion beam deposition techniques. Hydrocarbon gas precursors, like C$_2$H$_2$ or CH$_4$ with H$_2$ and N$_2$ as reactive gases are commonly used in ion and plasma beam sources. Optimum incident energy of carbon ions, C$,^+$, is up to 100 eV while the typical ion current densities during the film formation are in the mA/cm$^2$ range. Other carbon deposition techniques, like filtered cathodic arc, still suffer from co-deposition of fine nano-sized carbon clusters (nano dust) and their improvements are moving toward arc excitation in the kHz and MHz frequency range. Non-destructive film analysis like µ-Raman optical spectroscopy, spectroscopic ellipsometry, FTIR and optical surface analysis are mainly used in the carbon film characterization. Due to extreme low film thicknesses the surface enhanced Raman spectroscopy (SERS) with pre-deposited layer of Au can reduce the signal collection time and minimize photon-induced damage during the spectra acquisition.

1. Introduction
The main purpose of the carbon overcoat in the hard disk drive is to provide good corrosion and mechanical protection for the underlying magnetic-recording film under unfavorably environmental conditions and occasional contact with the read/write head[1,2]. To improve the disk corrosion protection properties over longer time, a thin flash layer of Cr is usually deposited over the magnetic layer prior the carbon overcoat. In principle, any carbide forming elements like Cr, Ti, Mo, Al or W can be used for such purpose. In industry the Cr is mainly used, and a technique of choice is the magnetron sputtering. In this work we tried to examine the capabilities of the Filtered Cathodic Arc (FCA) source in deposition of the Cr flash layer. With this source one may expect better surface coverage of the magnetic layer and more effectively filled micro-rough sites. An incoming particle flux is almost 100% ionized and possess the higher incident energy[3,4]. By physical and chemical sputtering/etching of the top 0.5 nm of the magnetic layer is also possible to achieve an ultra-smooth and polished surface, especially in combination with the substrate rotation.

In addition to the low thickness and favorable corrosion and wear protection properties of the overcoat there is a need for the low fly-height of the read/write head. This requires a small overall surface roughness of a disk. With easy control of ion energy of the FCA source one can meet most of these requirements, especially in the pre-conditioning of the magnetic layer with respect to the surface roughness and corrosion protection barrier. Up to now the carbon based implementation of the FCA source, e.g. with improved Pulsed Arc Deposition[5] and with better macroparticle filtration with double-band (twisted S-filter)[4,6], still suffers from the carbon
nano-dust particles and a low film deposition rate. Therefore, in this work we are trying to exploit some beneficial FCA source capabilities for metal targets, other than carbon. Protective corrosion properties of such a structure are usually evaluated by e.g.: a) corrosion spot density measurement[7] versus type of a flash layer element, flash layer thickness, eventual presence of macro/nanoparticles from the FCA source and overall surface roughness, b) implementing standard electrochemical tests[8] or some sort of the surface analytical study on the migrated cobalt compounds from the magnetic layer.

In this paper we opted for the analytical surface study of the overall disk structure, before and after the corrosion tests, using elastic collision effects of the highly energetic He+ ion beams with disk depth profiling – Rutherford Backscattering Spectrometry (RBS).

2. Methodology and setup
All films were deposited on a silicon/glass disk in this sequence: a) magnetic layer by DC sputtering in Ar gas (1st magnetron), b) flash layer by FCA source at the base vacuum (10^-5 mbar) and c) carbon overcoat, a-C or a-C:N film, in Ar+ N2 by sputtering of carbon target (2nd magnetron), figure 1.

![Diagram of disk structure and techniques](image)

Figure 1. Disk structure and techniques employed in the film deposition over silicon and a glass disk.

The UHV chamber housed an FCA source and two magnetron sputtering sources with 3” targets. A substrate, either 2.5” glass disk or a Si wafer, was clamped on its holder mounted on the rotational stage and inserted into the load-lock chamber. The first step is sputter deposition of the 30 nm thin CoCrPtB magnetic layer. The substrate plane was parallel to the magnetron surface. After the first layer deposition the substrate holder was further positioned to normally face down the filtered cathodic arc source. During this step the base pressure in the chamber was ~3x10^-6 Torr and the Cr film was deposited in the residual gas environment, without Ar flow. The Cr target temperature increased with deposition time and reached T_max= 620 0C, while the arc voltage was constant at ~ U_arc=24.3 V, throughout the deposition. Deposition pressure after the formed equilibrium condition was ~ 1.5x10^-4 Torr. The third layer, a-C film, was subsequently deposited exposing the substrate to the second magnetron located on the chamber top flange. The deposition conditions were summarized in Table 1.

During sputter deposition Ar flow in the chamber was kept constant at 30 sccm and the necessary deposition pressure was maintained by throttling the exhaust side of the turbomolecular pump. A target-to-substrate distance was ~ 60 mm while for the FCA source with the double bended 45-degree filter, a separation was around 115 cm.
Table 1. Overview of deposition parameters in the UHV chamber.

| Layer      | Deposition pressure (Torr) | Deposition rate (nm/s) | Ar flow sccm | Magnetron power (W) | Arc current (A) | Typical thickness (nm) | Typical deposition times (s) |
|------------|---------------------------|------------------------|--------------|---------------------|----------------|-----------------------|-------------------------------|
| CoCrPtB    | 10x10⁻³                   | 0.26                   | 30           | 80                  | /              | 30                    | 120                           |
| Cr         | 1.5x10⁻⁴                  | 0.045                  | 0            | /                   | 80             | 0.5                   | 12                            |
| a-C        | 7x10⁻³                    | 0.043                  | 30           | 100                 | /              | 2                     | 46                            |

2.1. Business Environment Corrosion Test

This test has been performed on the structure: a) Si substrate/CoCrPtB (30 nm)/Cr(0.5 nm)/a-C (2 nm) and b) Si substrate/CoCrPtB (30 nm)/a-C(2 nm), figure 2.

Corrosion products on the top, Co(OH)₂, CoCl₂

Figure 2. Model of the corrosion affected hard disk structure.

Half of the samples have been exposed to the business environment test (exposure to the 0.5 M HCl vapor for up to 284 hours) to promote corrosion and migration of cobalt to the top of the structure. Samples were analyzed by RBS technique.

2.2. Monte Carlo Simulation

In ultra-thin multilayer films, that can be deposited using energetic ion beams with filtered cathodic arc technology[6,9], is essential to predict interface widths and penetration depths of the ion forming films.

Main assumptions in the Monte Carlo simulations of the ion beam interaction during the film growth were: a) target is homogeneous and b) there are no thermal and vacancy induced diffusions. An ultra-thin, void-free, dense and smooth protective film can be produced by increasing the surface mobility of arriving film forming species. Optimization of the film structural properties, interface widths and a surface roughness can be accomplished by the proper selection of: substrate bias, energy of arriving ions and neutrals as well as their incident angle on the film surface. Ultra-smooth surface can be produced when ion beam polishing takes place along with a carbon film growth. The main process on the surface during ion beam deposition growth is a cascade process in the form of displacement collisions, vacancy production, replacement collision and interstitial atoms production.

3. Results and discussions

3.1. Corrosion study of the migrated Co using RBS technique

A corrosion behavior of the hard disk structure is usually investigated using some electrochemical tests, e.g. polarization resistance method[10,11]. Other extensively applied methods range from the most simplified ones like counting the number of corrosion spots with optical microscope to the more demanding methods that employ surface analysis, like XPS, AES or SIMS to measure the surface concentration of the migrated cobalt atoms. In this paper the corrosion related cobalt surface concentration was measured by RBS technique.

Surface area exposed to the beam was up to 1 mm in diameter. The incident He⁺ ion beam was 2 MeV and provided with a 15 keV energy resolution of silicon barrier detector, a depth
resolution of ~ 10 nm for platinum. To improve a depth resolution across a thin scattering depth of Co on the top of hard disk structure, the side geometry has been applied, keeping always the same source-to-detector angle of 20 degree. In the side arrangement more target atoms were involved in the backscattering events and a better depth resolution of the Co and Pt peak has been achieved. The energy difference $\Delta E$ between ions scattered at the surface and ions emerging from the sample at the depth $\Delta Z$ is

$$\Delta E = KE_0 - E_1 = [\varepsilon] N\Delta Z$$ (1)

where $[\varepsilon]$ is the stopping cross-section factor and $N$ is the atomic density of the sample. The kinematic factor $K$ is known for every element. The incident ion with energy $E_0$ suffers first the energy loss on the migrated Co on the top on the surface, and additionally on the return trip to detector, after probing the magnetic layer with platinum content. Therefore, the broadening and energy position of the well resolved Pt peak can be used in evaluating the amount of cobalt on the top of the surface. The leading and trailing edge of Pt peak has been attenuated by passing the beam through the migrated cobalt. The total number of counts in the RBS spectrum is proportional to the beam current $I$, acceptance angle of the Si detector ($\Delta \Omega$), number of scattering centers per cm$^2$ ($N\Delta Z$) and the differential cross section of the scattered species ($d\sigma/d\Omega$)

$$C = I \Delta \Omega N\Delta Z d\sigma/d\Omega$$ (2)

To get initial insight on the RBS spectra, a corrosion measurement on the film CoCrPtB(30 nm)/a-C (2 nm) was first studied, as presented in figure 3.

![RBS Spectrum](image)

Figure 3. RBS spectrum of the simplified hard disk structure before and after 284 hours of exposure in 0.5 M of HCl vapor. The FWHM of the Co peak is 0.125 MeV after the exposure.

Exposure of the hard disk structure to the HCl corrosion vapor can be analyzed and quantified with RBS method by observing the Co signal: a) broadening of the Co peak takes place on the HCl treated sample (an increase of the FWHM of the Co peak from 0.106 MeV to 0.125 MeV), b) decrease in the normalized yield of Co-peak from 37 a.u. (for untreated sample) to 34.2 a.u. for the treated one. Also, on the overall spectrum an oxidization of the top of the surface has been observed.
A low-energy shift in the Pt signal, centered at \( \sim 1.75 \) MeV, for the corrosion treated sample indicates a loss of the He\(^{+}\) ion energy on the migrated Co that started to surface a structure. After experiencing a collision, and a loss of incident energy with migrated Co, the He\(^{+}\) ions start to sense the magnetic layer (Pt) on its original position (dashed line). Therefore, a shift in the leading/trailing edge of the Pt signal may be a good measure of the corrosion susceptibility of such a structure. The RBS corrosion quantification is a spot sensitive in nature. Other examined spots in area of 1mm on the same disk led to different conclusions. Therefore, it is necessary to measure disk corrosion parameters radially, e.g. from outer to inner disk diameter averaging contributions from all spots along the disk circumference. Also, in ultra thin films with thicknesses in the sub-nanometer range the influence of the local surface roughness can have a large impact on the energy position of Cr and Pt peaks and their respective widths. Optical microscopy combined with micro-Raman study proved also to be surface-spot sensitive in nature, implying that only integral evaluation techniques can lead to reliable conclusions.

### 3.2. Monte Carlo Simulation of the Film Growth

With increasing the ion incident angle with respect to the surface normal the number of backscattered ions goes up as well as the lateral and radial range of ions. The surface coverage of a film improves, with less imperfection in the film growth, mainly seen as pinhole defects formed after initial nucleation and coalescent/island film formation phase. To reduce the calculation time, 1000 ions with initial energy of 100 eV were followed in analysis.

In order to make more dense and pinhole-free film there is need for incident ions to impart energy to the target atoms more in the radial direction and improve the surface mobility of “thermalized” film forming species. The surface roughness on the microscope level can thus be also adjusted. In practice, all ion sources suffer from non-uniform flux distribution across its radius and exhibit pressure dependant “beam throw distances”. In the FCA source the beam divergence is additionally influenced by the scanning magnetic field. Plasma electrons are closely guided by the magnetic field lines and ejected ions are tied to the electrons by electrostatic forces. Therefore, the substrate rotation under to the beam slanted incident angle is essential for uniform film coverage and low surface micro-roughness.

![Energy to Recoils](image)

**Figure 4.** A depth distribution of the energy of the substrate (target) atoms, CoCrPtB magnetic layer, acquired by the varying incident angle of Cr ions at 100 eV energy. The 1000 ions were taken in calculations. The calculated penetration depth of ions was always below 5 Angstrom.

The surface mobility of ad-ions can be substantially increased during the grazing incident angle film deposition. An average energy imparted to recoils (target atoms initially at rest) ranges from 16 eV/ion/Angstrom to 44 eV/ion/Angstrom with an ion incident angle change from 0 degree to 85 degree, respectively, figure 4. In the extremely thin nanometer and sub-nanometer thin films, that are now more common in the hard disk industry, especially when deposited by energetic ion beams, with
energies over 100 eV per incoming ion, the Monte Carlo calculation of the stopping range of ions in material may be a good guidance in selecting the necessary deposition parameters and in evaluation of the interface widths.

3.3. SERS - Micro Raman study of the ultra thin carbon
The 1 nm and 8 nm thin ta-C overcoat films were deposited with filtered cathodic arc technique over the Si/CoCrPtB (20 nm) magnetic layer. To improve the low Raman signal-to-noise ratio for the 1 nm carbon film a flash layer of silver has been sputter deposited on the top of a structure.

![Micro Raman spectrum of the ta-C carbon film close to the detection limit. Lower curve, ta-C film, 1 nm thin. Middle curve- SERS after the surface enhancement with sputter deposited silver film. The preliminary increase of signal-to-noise ratio of at least 30% has been observed.](image)

Carbon film was analyzed in the 1000-2000 cm\(^{-1}\) range. Measurement has been done close to the detection limit of the micro-Raman setup. To improve the signal-to-noise ratio the 10 consecutive collections of the Ar 514 nm laser scattered lights has been acquired. The incident laser light had the output power of ~21 mW. For the reference purpose the micro Raman spectrum of 8 nm thick ta-C film has been presented, acquired under the same conditions, the top curve on figure 5.

Under constant measurement conditions, from run-to-run, and taking care of the same laser light focusing/collecting area, being ~3 micrometer in diameter, the area under the broad carbon band and especially under the deconvoluted G-peak (at around the shift at 1580 cm\(^{-1}\)) is proportional to the carbon film thickness. Deposition of silver nanorods, instead of implemented sputtered silver film may further enhance the excitation of localized surface plasmons. Distribution of metal nanoparticles (Ag, Au, Pt) on top of the carbon film can be a method of choice in the micro Raman carbon film evaluation at extremely thin structures. Surface signal enhancement is especially strong for carbon double bonds, C=C. In the investigated film most of carbon bonds were in the tetrahedral, sp\(^3\) configuration, resulting in the lower signal enhancement. The SERS technique can be used in monitoring the carbon content under the G (graphite) peak and carbon corrosion protection study of the magnetic layer.

4. Summary
The filtered cathodic arc technology can be successfully used not only in the read/write head manufacturing but also on the hard disk surfaces. The low film deposition rate may restrict its implementation to only the extremely thin structures like the flash layer, prior to carbon overcoat. The beam scanning across the magnetic layer at incident angles other than $0^\circ$ with respect to the surface normal may be of advantage for improved surface coverage and reduction of the surface roughness on the microscopic level.

In the corrosion study of the hard disk structure the RBS technique can be successfully implemented. The energy position and broadening of the clearly distinctive Pt peak in the RBS spectra of the magnetic structure containing Pt can be used in the evaluation of the corrosion protective properties of the overcoat material. To improve the depth resolution of the Co and Pt spectrum the incident He$^+$ beam should be oriented at the grazing incident angle, geometry offering more backscattering events with the target material.

Upon assumption of the target elemental composition, its density and thickness from one side, and energy, incident angle and type of the incident ion on another side, a Monte Carlo simulation can give a clue to the expected ranges-penetrations depths of the elements/ions on the boundaries, interface widths and help in selecting the appropriate layer thicknesses for the barrier-flash layer.

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