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RUTHENIUM AS DIFFUSION BARRIER FOR CARBON OVERCOAT OF MAGNETIC RECORDING MEDIA

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A thesis submitted to the Nanyang Technological University in partial fulfillment of
the requirement for the degree of Doctor of Philosophy

2010

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Summary

Degradation of the magnetic and tribology performances due to diffusion from carbon overcoat is one of the concerns for future magnetic recording media. In this work, a novel film structure with ruthenium (Ru) interlayer in between the magnetic layer and the carbon overcoat has been investigated. Introduction of an ultra-thin Ru diffusion barrier is aimed to prevent carbon diffusion and minimize magnetically dead layer formation. Selection of Ru film deposition process, impact of carbon on magnetic films, carbon diffusion behavior, barrier mechanism of Ru layer, characterization of carbon films deposited with Ru interlayer and their anti-corrosion performance are covered in the project. All carbon films are prepared by hot filament Plasma Enhanced Chemical Vapor Deposition, and other films are deposited by the magnetron sputtering technique.

Ru films deposited at low Ar pressure and high sputtering power showed high density and low roughness. A working pressure lower than 10 mTorr and power density above 5.61 W/cm^2 are desired for Ru film deposition as carbon diffusion barrier. With introduction of Ru as an interlayer of the carbon overcoat, the magnetic properties of CoCrTa and Co-Pt-TiO₂ films are more consistent because of impeded carbide formation and negligible carbon diffusion. Interface integrity is well maintained, and the degree of graphitization is reduced with the Ru barrier.

Secondary Ion Mass Spectroscopy depth profiling studies confirm that carbon readily diffuses into the granular structure of the Co-Pt-TiO₂ film but the diffusion in Ru is limited to sub-surface. This is validated by tests at temperatures up to 200 °C. The diffusion of carbon in Co-Pt-TiO₂ is dominated by grain boundary diffusion but it is

only observed near surface region in Ru. At 200 °C, the diffusion coefficient of carbon in Co-Pt-TiO₂ is 0.3308 nm²/s and only 0.0542 nm²/s in Ru.

The deposition rate of a-C:H films with Ru interlayer is inversely affected by substrate temperature. An apparent activation energy (E_a) of 914.6 Jmol⁻¹ was derived for the process. Higher substrate temperature results in denser structures and increased surface roughness. Graphitization of carbon film occurs at higher temperatures. A process temperature lower than 250 °C is preferred. Deposition rate increases when C₂H₂ flow rate increases from 20 to 40 sccm. Film porosity and surface roughness increase at high flow rates. Hydrogenation process is the key factor affecting the film bonding structure.

Corrosion tests on Ru and Diamond-like Carbon (DLC) coated Al substrates using the potentiostatic polarization technique show that both Ru and DLC provide anti-corrosion protection. Ru itself is not able to offer sufficient corrosion protection to Al substrates. The corrosion rates of samples with a DLC/Ru structure are in the same order as those with a single DLC layer. The increase in pinhole density in thinner DLC films induces faster corrosion rate. DLC combined with 1 nm Ru interlayer is promising to maintain similar level of anti-corrosion property offered by DLC single layer.

Publications

- 1) Jianhui Wang, Sam Zhang, Huili Wang, Ping Xu, Dwight Iha, Steven Sawasaki, Ruthenium Interlayer as Diffusion Barrier Under Carbon Overcoat in Magnetic Recording Media, *Journal of Nanoscience and Nanotechnology*, Vol. 8, 2613-2617 (2008).
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- 3) Jianhui Wang, Sam Zhang, Yibin Li, Jinmin Zhao, Lei Zhu, Fang Yao, Interaction between sputtered β -Ta films and DLC with Ru intermediate layer, *Journal of Nanoscience and Nanotechnology* (2009) In press.
- 4) Jianhui Wang, Sam Zhang, ToF-SIMS Study of Carbon Diffusion in Co-Pt-TiO₂ Composite and Ruthenium Films, *Journal of Nanoscience and Nanotechnology*, Vol. 10, 770-774 (2010).

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Symbols and Abbreviations

Symbols

$2\sqrt{Dt}$	Diffusion length
A	Mass number
C	Diffusant concentration
CR	Corrosion rate
C_s	Surface concentration
C_x	Concentration at a distance x from the reference point
d	density of the material
D	Diffusivity or diffusion coefficient
$D0$	Pre-exponential factor in Arrhenius equations for carbon diffusion
E	Electrode potential
E_a	Apparent activation energy
E_{corr}	Corrosion potential
E^o	Equilibrium potential
erf	Error function
$erfc$	Complementary error function
EW	Equivalent weight
I	Electrical current
$I_0(hkl)$	Standard related intensity of the reflection from (hkl) plane
I_{corr}	Corrosion current
I_D	Intensity of D-peak in amorphous carbon films
I_G	Intensity of G-peak in amorphous carbon films
$I_m(hkl)$	Measured related intensity of the reflection from (hkl) plane
I^o	Exchange current which is reaction dependant constant
k	Boltzmann constant
k	Carbon film deposition rate
Ms	Saturation magnetization
NA	Avogadro's number
R	Gas constant

r_e	Classical electron radius
R_p	Polarization resistance
R_q	Root mean square roughness
R_{rms}	Root mean square roughness
SA	Surface area of the electrode
t	Time
T	Temperature in Kelvin
T_{hkl}	Coefficient of texture
T_m	Melting point of coating material
x	Diffusion distance
Z	Atomic number
z_i	Relative height of point i
z_m	Height of a reference plane
β	Reaction's Beta coefficient
β_a	Anodic Beta coefficient
β_c	Cathodic Beta coefficient
θ_c	Critical angle of total external reflection
λ	X-ray wavelength
μ	Coefficient of friction
ν	Atomic jumping frequency
τ	Time taken to realize the carbon transformation from sp^2 to sp^3

Abbreviations

α -C	Amorphous carbon
α -C:H	Hydrogenated amorphous carbon
α -C:N	Nitrogenated amorphous carbon
ABS	Air bearing surface
AD	Areal density
AFC	Anti-ferromagnetic coupling
AFM	Atomic force microscopy
APF	Atomic packing factor
BCC	Body centered cubic
BE	Binding energy

BPI	Bit per inch
CSS	Contac start stop
CVD	Chemical vapor deposition
CT	Coefficient of texture
DC	Direct current
DIW	De-ionized water
DLC	Diamond like carbon
EDXRF	Energy dispersive X-ray fluorescence
ESCA	Electron spectroscopy for chemical analysis
FCAD	Filtered cathodic arc deposition
FCC	Face centered cubic
FCT	Face centered tetragonal
FCVA	Filtered cathodic vacuum arc
FDLC	Fluorinated DLC
FED	Field emission displays
FWHM	Full width at half maximum
GIXR	Grazing incidence X-ray reflectivity
GMR	Giant magnetoresistive
GPES	General Purpose Electrochemical System
HCP	hexagonal closed packed
HDD	Hard disk drive
HDI	Head disk interface
IBD	Ion beam deposition
IC	Integrated circuit
IR	Infrared ray
KE	Kinetic energy
LSV	Linear Sweep Voltammetry
MD	Middle diameter
MFC	Mass flow controller
MIM	Metal-insulator-Metal capacitor
MR	Magnetoresistive
MrT	Product of remnant magnetization and thickness
PC	Personal computer
PECVD	Plasma enhanced chemical vapor deposition

PFPEs	Perfluoroethers
PLD	Pulsed laser deposition
PVD	Physical vapor deposition
RDM	Rotating disk magnetometer
RF	Radio frequency
RI	Refractive index
RMS	Root mean square
RTA	Rapid thermal annealing
SCE	Saturated calomel electrode
SEM	Scanning electron microscope
SFS	Stiction free slider
SNR	Signal noise ratio
ta-C	Tetrahedral amorphous carbon
TEM	Transmission electron microscope
TOF-SIMS	Time-of-flight secondary ion mass spectroscopy
TPI	Track per inch
ULSI	Ultra large scale integration
WCA	Water contact angle
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRR	X-ray reflectometry

Chapter 1 Introduction

1.1 Overview

A Hard Disk Drive (HDD) consists of single or multiple read-write heads and magnetic disks (recording media). The head-disk interface (HDI) is where all the processes of magnetic recording occur. Any mechanical damage should be prevented during interactions between the heads and the media. On magnetic recording media, a thin layer of overcoat is usually applied to provide protection. The extensive applications of magnetic recording devices necessitate continuously increased storage capacity or areal density (AD), which requires the reduction of spacing between the heads and the media. Hence, the properties of the overcoat become very critical for a stable device performance. Although different materials have been sought for the overcoat application [1], utilization of amorphous carbon films is still dominant. There are a variety of reasons to use amorphous carbon films as the overcoat, and extensive work has been done to investigate their mechanical, tribological, electrical, and chemical properties [2].

The carbon overcoat has been used in recording media for a few decades. It has been recognized, however, that carbon diffusion into magnetic films could cause detrimental effect on the performance of magnetic recording media [3]. Studies of the interface between magnetic and carbon layers are far from complete. The failure mechanism of magnetic and tribological performance due to carbon diffusion is not fully understood. Correlations of film microstructure, composition and changes at elevated temperatures with the magnetic and tribological performance are given limited attention as well. To maintain magnetic layer integrity requires that the carbon deposition process should

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minimize the magnetically dead layer creation. Leng et al [4] showed that a thin dead layer is formed at the interface between the NiFe and Diamond-like Carbon (DLC) overcoat. Furthermore, the thickness of the dead layer increases as the substrate bias voltage increases during the carbon deposition. Therefore, an efficient way to minimize carbon diffusion in magnetic films is needed.

1.2 Objectives of the Project

This study introduces an interlayer between the magnetic layer and carbon overcoat. The interlayer acts as a diffusion barrier, preventing carbon diffusion, and as a capping layer, providing protection to the magnetic layer during the carbon deposition. Ruthenium (Ru), which has been used in magnetic recording media for other purposes, possesses properties suitable for the interlayer to prevent the degradation of magnetic performance and tribology properties. It is a transition metal with very special properties. Ru film can be easily deposited using sputtering processes.

To address the issue of carbon diffusion in magnetic films, the scope of the project will include the design, deposition and characterization of the film structure with an Ru interlayer, and the understanding of the impact and working mechanism of Ru as a diffusion barrier.

1.3 Scope of the Research

To meet the aforementioned objectives, the work covers:

- Deposition and characterization of Ru films prepared at varied sputtering parameters, i.e. pressure and power density. In addition, a process to deposit Ru barrier with high density and surface smoothness was studied through X-ray

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Diffraction (XRD), X-ray Reflectometry (XRR) and Atomic Force Microscope (AFM) analysis.

- Investigation of the effect of carbon overcoat on magnetic properties of the magnetic films. Magnetic property change due to carbide formation was detected by X-ray Photoelectron Spectroscopy (XPS), and XRD. The change was minimized with introduction of Ru interlayer. Interface integrity was maintained well with Ru interlayer as examined by XRR. Hot filament Chemical Vapor Deposition (CVD) using acetylene as precursor is mainly employed in the project for carbon overcoat.
- Study of carbon diffusion in magnetic and Ru films. Ru interlayer in maintaining magnetic performance of films and its working mechanism as carbon diffusion barrier is demonstrated. Carbon diffusion in magnetic materials is grain boundary diffusion and that in Ru is limited to sub-surface, according to Second Ion Mass Spectroscopy (SIMS), Transmission Electron Microscope (TEM) and XRD results.
- Carbon growth kinetics on Ru template and the anti-corrosion behavior of carbon-Ru hybrid overcoat. Carbon films deposited with varied temperatures and pressures on Ru films were characterized using XRR, AFM, and XPS. Corrosion test using potentiostatic polarization technique showed carbon overcoat with 1 nm Ru interlayer demonstrated comparable corrosion rate to the sample with carbon overcoat only.

1.4 Key Contribution of the Project

A novel overcoat scheme of DLC/Ru dual layer structure was designed for the first time in magnetic recording media application. Ultra-thin Ru interlayers with high film

Chapter 1 Introduction

density were prepared underneath DLC films using magnetron sputtering technique. Analysis using XPS, XRD, and XRR shows detrimental inter-mixing between magnetic and carbon layers, which was reduced with introduction of Ru interlayer. Magnetic films with stable magnetic properties were demonstrated with DLC/Ru overcoat structure. Identical anti-corrosion performance was achieved compared to DLC-only overcoat. Kinetics study of carbon diffusion in Co-Pt-TiO₂ and Ru films using ToF-SIMS technique shows that carbon is much more ready to diffuse in Co-Pt-TiO₂ than Ru. Carbon deep into the Co-Pt-TiO₂ films was detected, while the diffusion of carbon in Ru was only limited at the surface. It was indicated that diffusion coefficient of carbon in Ru is much smaller than that in Co-Pt-TiO₂, which explains why Ru is able to be an effective diffusion barrier.

1.5 Organization of the Dissertation

This dissertation is divided into eight chapters. Chapter 1 gives a brief introduction, project motivations and thesis organization. Chapter 2 provides a detailed literature review on head-disk interface in hard disk drive and carbon films. The experimental methods for this project are described in Chapter 3. Experimental results and discussions are presented in Chapters 4, 5, 6, and 7. In Chapter 4, characterization of Ru films sputtered at varied conditions is discussed, and a process window is proposed to deposit an Ru diffusion barrier. The effect of the carbon overcoat on the magnetic properties of different films is discussed in Chapter 5. Carbon diffusion kinetics in magnetic and Ru films is discussed in Chapter 6. The working mechanism of Ru film as a carbon diffusion barrier is justified. Chapter 6 provides strong theoretical support to the findings in Chapter 5. Characterization of carbon films deposited on Ru template and the anti-corrosion behavior of C, Ru, and C/Ru hybrid overcoat are discussed in

Chapter 1 Introduction

Chapter 7. In Chapter 8, the overall experimental results are summarized and suggestions for future work are given.

Chapter 2 Background and Current Status

2.1 Magnetic Head-Disk Interface Overview

2.1.1 Introduction

Magnetic recording media is a non-volatile storage form which has been widely used in computation, communication, consumer electronics, automotive applications and etc. Its advantages over other devices, such as solid-state memories, are that it is cost effective and provides large storage density which keeps increasing at a very rapid rate. Areal density is one of the fundamental measures of the magnetic recording technology. It is the product of tracks per inch (TPI) and bits per inch (BPI) along a track. By using perpendicular recording, where the magnetization is normal to the film surface, in contrast to the conventional longitudinal recording, where it is parallel to the surface, one terabit per square inch could be achieved [5][6].

The key components of a hard disk drive include recording media (single or multiple rigid disks), a spindle along which disk rotates, a head stack assembly (slider), and an actuator. As shown in Fig. 2-1, a hard disk uses round, flat disks called platters, coated on both sides with Co-based alloy thin films which are designed to store information. Platters are actually mounted by cutting a hole in the center and stacking them onto a spindle. A special device called the spindle motor connected to the spindle rotates the platters at high speed. The data can be written onto the disk with the help of special electromagnetic read/write devices called heads, which are mounted onto sliders. The sliders are mounted onto arms, all of which are mechanically connected into a single assembly and positioned over the surface of the disk by a device called an actuator. A

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logic board controls the activity of the other components and communicates with external devices through an interface port.

Fig. 2-1 Hard disk drive components

The head-disk interface (HDI) is where all the processes of magnetic recording occur. Having a stable and reliable interface is required to ensure proper functioning of a hard disk drive (HDD). Magnetic recording and playback involve relative motion between the magnetic media against the magnetic read-write heads. If the head and the disk are close to each other, it improves recording performance, but the risk of mechanical wear between them is high, which could substantially reduce the HDD lifetime. On the other hand, too large spacing could cause “writing” failure. In addition, the read-back signal is weak, and data errors may happen. Fig. 2-2 is a cross-sectional view of head/disk interface in an HDD [2].

Fig. 2-2 A cross-sectional view of the head-disk interface of an HDD [2]

In recent years, the areal density (AD) of HDD recording media has been growing at a significant rate of 60% to 100% per year since magnetoresistive (MR) heads were introduced. The trend will continue in the coming years as technologies advance further. Magnetic recording mechanism necessitates the reduction of spacing between the heads and the media surface to accommodate the rapid increase in areal recording density of HDD, as well as to keep up with the paces of other developments such as the large signal-noise-ratio (SNR) thin film magnetic media, mechatronics, and signal processing technologies. In Fig. 2-3, AD is plotted against the nominal flying height of the head. It illustrates the important fact that to further increase media areal density, both the head-disk spacing and its tolerance have to be reduced.

Fig. 2-3 Areal density versus clearance for disk drives [7]

The flying height is the distance between the magnetic head and the hard disk during operation. In order to increase the recording density it is necessary to decrease the flying height so that the signal to noise ratio obtained from the read element is within an acceptable range. Ideally, zero spacing is preferred. However, zero spacing or contact recording would lead to higher friction and wear at the head-disk interface, hence degrading the performance of the hard drive.

Fig. 2-4 Progressive shrinkage of head-disk spacing with time

2.1.2 Magnetic Head Slider Review

As discussed earlier, the magnetic spacing affects the stability of read-write process. The size of the magnetic spacing is the flying height of the head plus the thickness of the head and media overcoat. The latest advance has enabled the flying height to reach below 20 nm in HDD of 40 GB/in² and above storage density as indicated in Fig. 2-4. To fly a head safely at such a low height, the surface roughness of the media / head has to be reduced, but this increases the stiction force as well. This sets significant constraints on head and disk parameters, as well as drive design factors such as the internal air filtration, cleanliness within the disk drive environment, and mechanical excitation by spindle bearings or external shock. An ideal head-disk interface would consist of a slider where 99.999% of its weight is supported by the air bearing force

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that is developed beneath the slider as the disk spins. As a result, the normal load on the disk due to the slider is only 0.001% of the total weight of the slider, which will minimize friction and wear at the head-disk interface.

There are various head-disk interface technologies to secure stable flying of the head over the media surface at a low fly height. Air-bearing technology has been employed in HDD in the nanometer range of flying height. For air-bearing technology used in disk drives, a variety of slider designs with improved performances, such as cylindrical crown bearing, Winchester slider, taper flat slider, self-loading slider, and slider of miniaturized design, have been employed to allow decreased head-disk spacing. Elegant texturing schemes have also been applied in a highly controlled manner to prevent head-disk stiction. However, in the case of high stiction force, the conventional Contact Start Stop (CSS) does not work well. Alternative methods include laser zone texturing, padded slider, and ramp load technology. Fujitsu developed a Stiction Free Slider (SFS) having four oval pads on the air bearing surface (ABS) in 1997 [8]. The pads of state-of-art design are made of DLC films and patterned in defined shapes by photolithography and plasma dry etch technologies. According to the report, the SFS has an excellent CSS performance on a surface roughness of 0.3 nm.

2.1.3 Lubricant

To reduce wear and friction between slider and disk, magnetic recording thin film media are lubricated with a molecularly thick layer of liquid lubricant on the top of overcoat. The choice of a lubricant for hard disk media is based on many criteria. The desirable lubricant should ensure minimum lubricant loss, protect the disk surface from chemical damage, be compatible with overcoat materials, and minimize of the impact resulted from head-disk interactions.

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Lubricant loss has to be minimized in order to achieve lasting drive durability. The thickness of lubricant in the latest technology has reached the level of a few atomic layers. Therefore, any loss of lubricant due to evaporation, decomposition, reaction, spin-off, or physical displacement by the slider must be avoided. The lubricants on the disk surface are exposed to atmospheric conditions, and are applied only once during the manufacturing process. Thus, the lubricants need to have a high affinity for the disk surface, a low vapor pressure, and excellent chemical stability.

Chemical protection of the disk surface is accomplished by lubricant which forms an ultra-thin and conformal layer over overcoat. Adsorption of and reaction with environmental contaminants are minimized due to the presence of the lubricant of low surface energy and inert characteristics.

To reduce the impact due to mechanical interaction between the head and the disk, the lubricant is required to have low surface energy in order to minimize adhesive force, and not to form a bridge or meniscus between the head and the disk when they come into contact. In addition, the lubricant should be able to dissipate the energy associated with a head-disk collision in a non-destructive mode. It is normally assumed that this occurs through the introduction of molecular motions into the lubricant molecules, which are eventually dissipated as heat. Therefore, a flexible lubricant molecule with a chemically inert structure is desirable.

Because of their superior properties, such as low vapor pressure, suitable viscosity, high thermal stability and chemical inertness, perfluoroethers (PFPEs) have been extensively used as the lubricants for magnetic recording media in hard disk drives [9].

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Dual-layer lubricants consisting of an unbonded over a bonded film have been employed in the hard disk industry. The design provides the benefit that the unbonded layer is able to heal the disk surface in case of wear while the bonded underlayer offers lubricant persistence. The dual-layer scheme can be achieved either by partially bonding a lubricant film or by applying a bonded lubricant film followed by an unbonded one. The latter method presents flexibility in selecting lubricants of different compositions and structures for desired bonding without compromising lubricant's tribological performance and durability, although it brings extra manufacturing cost and complexity.

2.1.4 Overcoat

The magnetic recording films sputter-deposited on a substrate are not able to withstand friction, wear, and corrosion by themselves due to their weak mechanical properties. Generally, a protective layer of overcoat is applied on the top of the magnetic films to prevent “injury” of the underneath recording layers by dangerous knock.

2.1.4.1 Required Properties of Overcoat

Ideally heads and recording media are designed under steady operating conditions that the contact between the heads and the media is minimum. However, physical contact between the heads and the media during starts and stops is inevitable. The overcoat has to ensure superior hard disk durability for many years of operation including many thousands of drive start/stop cycles. To achieve such a staggering performance, the overcoat must demonstrate enough hardness to prevent the least amount of physical damage between the recording head and the media by avoiding wear and reducing dynamic friction.

Fig. 2-5 Surface roughness vs stiction force (S1, S2, S3, SFS are different sliders) [10]

Reliable operations of a hard disk drive depend on not only the spacing between the recording heads / media, and slider technology, but also the characteristics of the disk. The tiny spacing requires a disk surface to be almost perfectly smooth, flat, and essentially defect-free. As the areal density of HDD increases further, it requires the overcoat surface to be as thin as a few nano-meters (less than 10 stacks of atoms) with well-controlled roughness. That is the roughness of the disk finish must be much smaller than the separation of the head and the disk to avoid head-disk scratch. In addition, the disk must be sufficiently flat to ensure the head is able to track the disk surface to the required tolerances. However, for conventional sliders, when the surface roughness decreases to < 2 nm, the stiction force between the slider and the disk increases considerably. Fu et al [10] has measured stiction force of sliders on varied surface roughness as explained in Fig. 2-5. Stiction force increases as surface roughness decreases. Therefore, control of disk surface roughness definitely is a trade-off between head-disk smash and static stiction. As a corrective way to reduce the

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roughness resulted from overcoat deposition, burnishing is commonly used. Furthermore, glass substrates have been partially replaced Al-based substrates to provide better rigidity and surface flatness. Nevertheless, the inherent roughness of as-prepared overcoat is the key factor to play with.

On the other hand, chemical contaminants at the head-disk interface can degrade HDD's performance. They can be either foreign matters carried by environmental moisture or outgassing of materials used in the drive's construction, such as cables, adhesives, lubricants, circuit boards, etc. Such chemical in vapor can degrade the media performance by penetrating into the materials underneath. Moistures from environment degrade the disk performance. Hence, as a passive coating, the overcoat has to be sufficiently dense to reduce oxidation, humidity absorption, and poisoning of the magnetic under layers. However, overcoats with porous structures have been used to improve lubricant retention. Protrusions or pits on the overcoats are purposely created by deposition through mask. An overcoat with dual layers has been prepared with porous spin-coated SiO_2 over sputter-deposited SiO_2 [1].

The materials of the overcoat also have to be compatible with the magnetic layers below and lubricant layer at the top. Minimum amount of chemical reaction between them is required to sustain a durable recording performance. Outstanding adhesion of the overcoat to the magnetic films is essential too. Stress of the overcoat should not exceed a level which could cause delamination of the film from the substrate.

In summary, an ideal overcoat should be designed to provide:

1. Corrosion protection, which requires complete coverage and high density.
2. Chemical properties, such as lube compatibility, stability and low adsorption.

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3. Surface topography, such as smoothness, complete coverage and absence of particles.
4. Wear resistance, which requires reasonable hardness, low friction and high elasticity.
5. Magnetic layer integrity: the deposition process should minimize the 'dead layer' created by the impinging ion particles.

2.1.4.2 Overcoat Materials

Different thin film materials have been reported. They include plated rhodium and chromium [1], sputter-deposited or spin-coated SiO_2 [11], sputter-deposited SnO_2 , zirconia (ZrO_2) [12], SiN , Zr , SiC , and CVD or sputter-deposited DLC, and others.

Sputter-deposited SiO_2 overcoats can be produced by rf magnetron sputtering using a SiO_2 target. Spin-coated SiO_2 films are prepared by Sol Gel method. Yanagisawa found that spin coated SiO_2 has an amorphous structure. Hardness, friction and wear resistance properties are improved when there is a post thermal treatment on the spin-coated SiO_2 film. This corresponds to a decrease in silane group contents in the film.

SnO_2 overcoats prepared by RF reactive sputtering at around 150 °C and with the oxygen partial pressure of 0.01-0.02 Pa by V.J. Novotny et al. showed good film hardness, minimum stress, low wear rate, and low static friction [13]. However, sputtering conditions with the oxygen as a secondary gas might degrade the media performance by oxidizing the fresh magnetic layers, which makes process and magnetic properties of media more difficult to control.

$\text{ZrO}_2\text{-Y}_2\text{O}_3$ films were deposited from a yttria-stabilized zirconia target by Yamashita et al. These oxide ceramic films provide superior corrosion protection since they are

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insulating and don't provide galvanic action. In addition, increased wear resistance was observed for the ceramic overcoat. The zirconia crystallites were found have cubic structures. However, the traditional transformation toughening mechanism can not directly explain the good wear resistance of the film. Poor adhesion of ceramic films is a well known disadvantage.

Yen, Richard, and their co-workers studied the coverage and tribological properties of amorphous SiN_x film deposited by RF reactive sputtering [14]. Compared with $\alpha\text{-CN}_x$ overcoat which has a coverage limit of ~ 2.0 nm, $\alpha\text{-SiN}_x$ has a low coverage-limit of ~ 1.0 nm. It was suggested the lower coverage-limit of $\alpha\text{-SiN}_x$ may be attributed to its high density of 3.2 g/cm^3 , which corresponds to 93% of bulk density. In comparison, the densities of diamond-like carbon are usually 54% that of diamond. In their study, 1.5 nm $\alpha\text{-SiN}_x$ coated disks have fewer pinhole defects and are more durable in the accelerated flyability test than 4.5 nm $\alpha\text{-CN}_x$ coated disks. The superior performance of $\alpha\text{-SiN}_x$ disk overcoat may be attributed to its dense structure and high hardness ~ 25 GPa.

Li's team developed crystalline [15] CN_x/TiN multilayer nanocomposite coatings using an opposed cathode unbalanced magnetron sputtering system. It was demonstrated that the composite coatings were fully crystalline and dense at small bilayer thicknesses. An amorphous structure was seen when the CN_x layer thickness exceeded 4–5 nm. Nanoindentation hardness of 45–55 GPa could be repeated for coatings produced under low nitrogen partial pressure and high substrate bias (-150 to -250 V). It was found that TiN (111) preferred orientation was strongly correlated to the high hardness.

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Comprehensive studies were conducted by Wei et al. [16] to compare nanotribological properties of thin Cr nitride and oxide films of a wide range of stoichiometry. Their experiments showed that CrO_x had the poorest wear resistance. Although CrN_x showed better smoothness, its hardness was lower than CN_x . Thin Cr underlayer was proposed by Wei et al. as a potential overcoat candidate. TiB_2 and $\text{TiB}_2(\text{N})$ ceramic coatings, which have extremely high hardness and excellent chemical stability, were proposed as potential candidates for high performance protective overcoats by Hong Deng et al. [17]. It was found the film structure and mechanical properties are highly sensitive to deposition conditions, e.g. N_2 flow rate, which make the process difficult to tweak and difficult to implement. Mechanical, tribological, and adhesion properties of silicon carbide (SiC) [18] coatings were characterized by Tsui et al..

Although there are many choices of overcoat materials, amorphous carbon films are still dominant in the media industry. There are a variety of reasons for the use of amorphous carbon films as overcoat, and extensive work has been done to investigate mechanical, tribological, electrical, and chemical properties. Details of carbon overcoats will be reviewed in the following section.

2.2 Carbon

Carbon develops a few crystalline and disordered structures because it is able to exist in three hybridizations, sp^3 , sp^2 and sp^1 (Fig. 2-6) and able to bond with itself [19]. Therefore, carbon has a few allotropes including diamond, graphite, fullerene, and nanotube. Naturally, carbon has two types of crystalline structures. They are diamond and graphite. The crystal structure of diamond is face-centered cubic with an inter-atomic spacing of 0.154 nm. Bonding in a diamond crystal is purely of covalent type which is in the form of sp^3 . Each carbon atom in the diamond is bonded to four other

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carbon atoms with a tetrahedral orientation which explains its poor electrical conductivity, good chemical stability, and extreme hardness. The properties are the results of electron excitation and hybridization of atomic orbitals. The crystal structure of diamond is depicted in Fig. 2-7 [20].

Fig. 2-6 sp^3 , sp^2 and sp hybridized bonding of carbon [19]

Fig. 2-7 The crystal structure of diamond [20]

There are two types of graphite structures, Hexagonal Graphite (2H) and Rhombohedral Graphite (3R). In graphite, carbon atoms are arranged in layers. Atoms are bonded in the form of sp^2 inside each layer. Layer-to-layer bonds are weaker than

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sp^2 , while individual layers are composed of strongly bonded carbon atoms in a network of regular hexagons in a honeycomb pattern. The hexagonal or 2H polytype has layers staggered in an ABAB... sequence, while the rhombohedral or 3R polytype has layers stacked in an ABCABC... sequence. The weak bond of van der Waals force formed between planes accounts for the properties of graphite, such as softness, low friction, and low electrical resistivity. A crystal structure of graphite is illustrated in Fig. 2-8 [20].

Fig. 2-8 A crystal structure of graphite [20]

At room temperature and atmospheric pressure, graphite is a stable form of carbon. Diamond is merely metastable. This can be explained by the phase diagram in Fig. 2-9 [21]. However, the phase transformation from diamond into graphite at our living environment is an extremely slow process which normally takes more than a hundred years. Because of the high activation barrier for the transformation from diamond into

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graphite, diamond is also a stable phase of carbon at room temperature and atmospheric pressure.

Due to its unique bonding and crystal structure, diamond shows dramatically different physical properties from graphite. Diamond is the hardest material, a poor electrical conductor, and is transparent. Graphite, however, is soft due to the weak Van der Waals bonding perpendicular to the planes of carbon atoms. It is opaque and a good conductor.

Fig. 2-9 Phase Diagram for Carbon [21]

2.3 Diamond-Like Carbon Films

2.3.1 Introduction

Diamond-like carbon (DLC) is also called amorphous carbon (α -C). It was first discovered by Aisenberg around 1970 as he was searching for an electrically insulating

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layer to use in conjunction with plasma ion-beam-deposited silicon for early demonstration work on thin-film transistors [22]. The name “diamond-like carbon” was created by him for the amorphous, transparent, electrically insulating, and hard carbon films he happened to obtain using ion-beam deposition. As the name suggests, the films showed many properties similar to those of diamond but had no long-range crystalline order. Since then, DLC films have been extensively studied in research and manufactured on industry scale. In fact, DLC is a hybrid configuration of diamond, graphite, and disordered structures. Diamond usually dominates over other DLC structures because a majority of carbon atoms are bonded in sp^3 . The number of carbon coordination states, termed sp^3 and sp^2 , determines DLC film properties such as hardness, optical properties, and electronic properties.

Nowadays, DLC is also used to describe a family of amorphous carbon materials that may contain hydrogen, nitrogen, fluorine, silicon, boron, chromium or other elements and whose properties are similar to, but different from, those of diamond. The chemical bonding within DLC materials is often described as a random covalent network of sp^2 -bonded “graphitic” carbon structures interconnected by sp^3 “diamond-like” linkages, with no long-range crystalline order. Doping by other elements, such as hydrogen, nitrogen, at certain level can enhance some material properties such as wear resistance, adhesion, electrical conductivity, hardness, stress, and oxidation resistance.

Different deposition methods result in dissimilar properties. For a given method, the properties of DLC also vary considerably with deposition conditions. DLC films with extremely high hardness can be achieved. Hardness value of 3000 kg/cm^{-2} has been reported [23] [24]. Discovered by Enke et al [25], the materials generally have a low coefficient of friction (μ) in the range of 0.01 to 0.19 which increases with humidity. A

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sharp increase in μ happens when the relative humidity exceeds 1%. DLC films deposited at high substrate bias potential show high internal stress. Such a high stress could bend substrates and break substrates made of brittle materials. Therefore, DLC film thickness normally has a limit up to 2-3 μm [19] except when it is deposited by special technique like InnerArmor [26].

Generally diamond-like carbon films absorb visible light but are transparent to IR range. It has been used as IR anti-reflection coatings on germanium optics [27] [28] and silicon solar cells [29]. Furthermore, DLC coatings prepared under proper conditions have high electrical resistivity. They are chemically durable and abrasion resistant.

Typical properties of DLC with various forms are compared to other carbon related materials in Table 2-1. [30-32]

Table 2-1 Properties of amorphous carbon compared to other carbon compounds [30-32]

	sp^3 (%)	H (%)	Density (g cm^{-3})	Gap (eV)	Hardness (GPa)
Diamond	100	0	3.515	55	100
Graphite	0	0	2.267	0	
C_{60}	0	0		1.6	
Glassy C	0	0	1.3–1.55	0.01	3
Evaporated C	0	0	1.9	0.4–0.7	3
Sputtered C	5	0	2.2	0.5	
ta-C	80–88	0	3.1	2.5	80
a-C:H hard	40	30–40	1.6–2.2	1.1–1.7	10–20
a-C:H soft	60	40–50	1.2–1.6	1.7–4	<10
ta-C:H	70	30	2.4	2.0–2.5	50
Polyethylene	100	67	0.92	6	0.01

Depending on process capability, DLC can be classified as pure $\alpha\text{-C}$, hydrogenated amorphous carbon ($\alpha\text{-C:H}$), and nitrogenated amorphous carbon ($\alpha\text{-C:N}$). $\alpha\text{-C}$ and $\alpha\text{-C:N}$ films are both called non-hydrogenated. C:H films can be achieved by using hydrocarbon gases as precursors, such as C_2H_2 , CH_4 , C_6H_6 , C_7H_8 and etc in CVD

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process. Reactive sputtering using argon and hydrogen gases is another way to deposit C:H films. In the same manner, C:N films are prepared by reactive sputtering process applying Nitrogen gases. Graphite target is typically used as the sputtering target material. Due to the ubiquitous nature of hydrogen, it is very rare to find films that are truly hydrogen-free, and therefore “non-hydrogenated” in general means that the deposition process does not involve hydrogenated species, and the H content in the film is low, usually below 5%.

2.3.2 Applications of Amorphous Carbon Films

DLC anti-reflection coatings work well in protecting germanium and zinc sulphide IR windows [33] [34]. It is applied to the front surfaces of aluminum mirrors as well. The coatings provide excellent seawater, rain and atmospheric corrosion resistance without deteriorating the optical performance of the devices. Studies on the photothermal properties of DLC coatings were carried out by Ball et al. [35] with the purpose to maximize its efficiency in solar energy conversion by reducing the heat reflection. DLC has also been successfully used in optical fibers coating [19]. A carbon coating inhibited the attack of the silica fiber by moisture so that brittle fracture was reduced. These coatings were also able to restore the properties of ageing fibers, probably as a result of the re-sputtering which removed some of the surface contamination.

Due to its remarkably high hardness and chemical stability, DLC has also been useful for protecting metal parts from scratching and chemical attack. A variety of metal objects ranging from large sheets to nails, twist drills, and machine tool inserts has been coated with DLC. DLC coated tools last longer than uncoated ones. The commercial feasibility of this coating process was not clearly established [19]. DLC films lack of thermal resistance (280 °C-350 °C) due to their poor adhesion to the

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substrates and decomposition (especially for α -C:H) at high temperature. They are not prepared in high thickness because of intrinsic stresses using non-laser coating techniques. Those limitations preclude DLC from cutting and grinding-tool applications. Due to the hydrophobic feature of DLC, it is used as anti-sticking coatings for mold cavity in IC packaging. By applying DLC coatings over CVD diamond coatings on cutting tools, Hanyu et al obtained cutting tools with better anti-sticking properties and successfully increased the tool lifetime [36].

Carbon in various forms has been used for many biomedical applications during the past decades. Due to its bio- and haemo-compatible nature [37] [38], there is a growing interest in the application of DLC in medical implants [39]. Additionally, DLC is an excellent base coating to be alloyed with different elements. The amorphous nature of DLC allows introduction of certain amount of external elements, such as Si, F, N, O, W, V, Co, Mo, Ti and their mixture into the film, while maintaining the amorphous phase of the coating. By this technique, film properties and biological reactions of cells in contact with the surface can be continuously adapted to a desired value. Nowadays, there are two major fields of biological applications for DLC, the application of DLC in blood contacting implants such as heart valves and stents, and the use of DLC to reduce wear in load bearing joints. In addition, it is possible to tune the biological properties of DLC by alloying with different elements. DLC coatings can also be used to reduce the release of metal ions (especially nickel, which is the most common contact allergen) from metallic implants [40].

Special attention has been paid to DLC films as a low k dielectric material for ULSI applications [41] [42]. Fluorinated DLC (FDLC) films with a dielectric constant $k < 2.8$ have been obtained. FDLC films show an intrinsic stress below 200 MPa. FDLC in

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a first level metallization in a Cu damascene structure has been demonstrated, although further integration issues have to be evaluated [43]. Another application of DLC is in field emission displays (FED). Diamond-like carbon films have the potential to serve as electron emitters for FEDs, without needing the 1 μm lithography for the preparation of sharp tips [44]. DLC coatings have also been found to increase the emission current from metallic FED tips [45].

One of the most widespread and important applications of amorphous carbon films is in wear and corrosion protection of magnetic storage media and slider. The primary role of the carbon films is to anti-corrosion, and to separate the Co layer and read / write head from the ambient. When first introduced, simple $\alpha\text{-C}$ was used and the role of carbon films was only to provide protection against corrosion. Later on, reactive sputtered $\alpha\text{-C:H}$ was used for protection against mechanical wear and damage during head crashes. In addition, carbon films provide an interface for lubricants to adhere and move. It is critical that the films isolate metal and lubricant layers since Al (substrate or alloying element) tends to catalyze the decomposition of the lubricants. More recently, $\alpha\text{-C:N}$ has been used. Nitrogen increases the toughness of the films in microscratch tests than $\alpha\text{-C:H}$. Furthermore, $\alpha\text{-C:H}$ reacts with the fluorine emitted from degrading lubricants and causes corrosion of the underlying metals. There is no such concern for $\alpha\text{-C:N}$ since it doesn't give rise to the formation of HF. DLC's applications in media overcoat will be described in more details later.

2.3.3 DLC Preparation Techniques

Various deposition techniques have been developed and employed in industry and laboratories for DLC film. They include DC and RF magnetron sputtering, pulsed laser deposition, ion-assisted evaporation, filtered cathodic arc deposition (FCAD), closed

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field unbalanced magnetron sputtering, PECVD (plasma enhanced chemical vapor deposition), and ion-beam deposition (IBD).

2.3.3.1 Ion Beam Deposition (IBD)

Over the last several years, ion beam deposition using gas precursors as source materials has become an established process in data storage industry for carbon overcoat deposition. The first DLC films were prepared using ion beam deposition (IBD) by Aisenberg and Chabot [46]. In a conventional IBD system, carbon ions are generated by plasma sputtering of a graphite cathode in an ion source. More recently, a hydrocarbon gas is ionized and forms a plasma. The positive carbon or hydrocarbon ion beam is then formed and extracted through a grid from the plasma source by a bias voltage. The ions are accelerated by and deposited on a negatively biased substrate. The ion-beam coating energy provides a thin film with improved surface coverage. Moreover, the ion energy also densifies the thin film coating and produces a smooth surface. This ultra-smooth film deposited by ion-beam techniques will allow for a very thin layer (<5 nm) of DLC for the next generation of magnetic head and disk overcoats. A schematic of an IBD tool is shown in Fig. 2-10.

Fig. 2-10 A simplified IBD system

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2.3.3.2 Sputtering

Sputtering is the most common method to deposit DLC films in industry. In sputtering an argon plasma is generated in a vacuum system by connecting a DC or RF voltage source to a graphite target surrounded by an argon atmosphere. Plasma ions or an ion beam is used to bombard the target. Among the various sputtering systems, DC magnetron sputtering using graphite targets is most widely used in the HDD industry. Magnetron sputtering was developed to enhance deposition rates and ionization efficiencies in the plasma. The magnetron system consists of an array of magnets which are arranged in such a way that one pole is positioned on the central axis of the target and the second pole is around the outer edge of the target. Target is the cathode and water-cooled. Hydrogenated or nitrogenated carbon coatings can be obtained by seeding the argon gas with a certain amount of hydrogen or nitrogen. A comparison of different magnetron modes is shown schematically in Fig. 2-11 [47].

Fig. 2-11 Schematic representation of the plasma confinement observed in conventional and unbalanced magnetron sputtering [47]

Sputtering is preferred in industry for DLC carbon films due to its flexibility in control and its ease to scale up [48-50]. Deposition conditions can be controlled by adjusting

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power, gas flow, substrate temperature and bias. A weakness of sputtering is that the ratio of energetic ions to neutrals in the plasma is relatively low. So the hardness of DLC films is not high enough. Furthermore, for ultra-thin film preparation, the coverage and density of DLC is relatively poor compared to other processes. Sputtered DLC film is generally used as the top layer for dual carbon overcoat scheme in the recording media application. Its porous structure provides better bonding for lubricants.

2.3.3.3 Pulsed Laser Deposition (PLD)

Pulsed Laser Deposition is similar to sputtering in physical mechanism. Instead of ion bombardment, a series of high intensity laser pulses is used to irradiate the carbon target. The carbon target is heated to extremely high temperatures due to the high power density. A mixture of ions, neutrals, and macro-particles spreads out toward the substrate and forms DLC films. The mean ion energy is proportional to the laser fluence concentrated on the target spot [51]. The incoming energetic ion bombardment during the film growth is believed to contribute to the high sp^3/sp^2 ratio of the carbon film. PLD is preferred for laboratory scale applications.

The uniqueness of PLD is that the ion productions in a PLD are not sensitive to the gas pressure (Fig. 2-12) [52]. This facilitates a wide range of operating pressures (10^{-10} Torr to 100 Torr) during film growth. By controlling the deposition pressure and temperature a variety of nanostructures and nanoparticles can be produced. PLD has received less attention in DLC production, owing to difficulties in scaling up the process and the high initial cost of high power lasers and related equipments, and has not been as successful as other DLC deposition techniques, in particular, ion-beam and magnetron sputtering.

Fig. 2-12 A schematic picture of a PLD system [52]

2.3.3.4 Filtered Cathodic Vacuum Arc (FCVA) Deposition

The invention of vacuum arc deposition can be traced at least as far back as 1877 [53]. Scientific interest in the technology in the last decade has been focused on its application in electronics and optics.

The filtered arc technology has been applied in carbon film deposition 10-20 years ago [54]. In FCVA, a plasma beam with macroparticles and neutral atoms is emitted from the cathodic arc spot by a cathodic vacuum arc process. Unwanted macroparticles and neutrals are then be filtered out by a cross-magnetic and electric field. Only those species within a well-defined energy range are allowed to reach the substrate. Films with good adhesion and favorable structures can therefore be realized. Unlike ion beam deposition, the beam in FCVA is a neutral beam so that it can deposit onto insulating substrates. Another advantage is that it is able to deposit films onto unheated substrates due to the high beam energy, which makes coating on temperature sensitive substrates e.g. plastics possible. The disadvantages are that the filtering is not sufficient for some applications, and that the cathode spot is unstable. Compared to other methods, setup of a FCVA system is more complicated and expensive. Fig. 2-13 is a schematic

diagram of a FCVA apparatus [8].

Fig. 2-13 An example of FCA system [8]

2.3.3.5 Plasma enhanced chemical vapor deposition (PECVD)

Plasma Enhanced Chemical Vapor Deposition (PECVD) uses electron activation to enable deposition to occur at a low temperature and at a reasonable rate. Power supply at a sufficiently high voltage to a precursor (liquid or gaseous) at reduced pressures (<1.3 kPa) results in breakdown of the precursor and generates a glow discharge plasma consisting of electrons, ions and electronically excited species. The vapor reactants are ionized and dissociated by electron impact, and hence generating chemically active ions and radicals that undergo heterogeneous chemical reactions at or near the substrate surface and form thin films.

PECVD, together with sputtering, has been the most popular deposition method for DLC films in hard disk media application. Plasma enhanced CVD techniques

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employing RF or DC glow discharges in hydrocarbon gases, such as methane, butane, acetylene, and etc., produce smooth amorphous carbon and hydrocarbon films of mixed sp^2 and sp^3 bonds. The gases fed into the vacuum chamber are activated by electrical field. When the substrate is heated, chemical reactions take place on the substrate surface and carbon films are formed. Carbon films grown by PECVD exhibit average hardness of 9-20 GPa. Conventional CVD processes will generally require deposition temperatures of at least 600 °C to achieve similar hardness. However, low temperature deposition is possible in PECVD. PECVD gives good deposition rates and very uniform coatings, and is suited to very large-scale production. Low-temperature deposition using PECVD allows many more choices of substrates than those of high-temperature processes. In general, PECVD has difficulty in depositing high purity films. This is mostly due to the incomplete desorption of by-product and un-reacted precursors at low temperatures, especially hydrogen. The presence of impurities affects the stoichiometry of the films and hence the physical, chemical, mechanical and electrical properties of the films. For data storage applications, heat generation during deposition and plasma damage are also of concerns. Fig. 2-14 is a schematic setup of a carbon film deposition apparatus using a hot filament PECVD process.

Fig. 2-14 Schematic diagram of a hot filament PECVD apparatus

The gases used in PECVD have a significant impact on the film properties. In the early years, benzene was chosen as a precursor because it had a high deposition rate. For tribological applications, using a precursor which leads to small H/C ratio in the carbon film is desirable to maximize film hardness. Acetylene meets the requirement and is widely employed in industry. Acetylene is in fact an attractive precursor for low pressure deposition of DLC films because it has a simple dissociation pattern due to its $\text{C}\equiv\text{C}$ bonding structure. In the deposition process, mainly C_2H_n^+ ions are released [55]. There is also less amount of polymerization than that of processes using methane. The disadvantage of acetylene is that it is not readily available in high purity form [56]. Substantial amount of nitrogen contained in acetylene causes unwanted doping effect. Methane is another choice of precursor for DLC deposition in electronic application because it is available in high purity. However, the growth rate is lower and like benzene, the hydrogen content is too high.

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2.3.4 DLC as Magnetic Recording Media Overcoat

As mentioned earlier, ultra thin carbon overcoat is applied on the magnetic storage media to protect the magnetic films against corrosion caused by environmental exposure and mechanical wear due to head dragging over the disk surface. Currently, a thin nanolayer (3-5 nm thick) of amorphous carbon is applied on the media surfaces for improving the tribology of the head-disk interface. DLC is chosen because of its chemical inertness to environmental exposure, ease of tailoring mechanical and electrical properties, availability of mature deposition processes, excellent compatibility with lubricant layer, and low manufacturing cost.

There are various types of DLC films according to their bonding types, mechanical and structural properties, and doping. With or without doping, DLC can be categorized as α -C which is undoped, α -C:H and α -C:N which are doped with hydrogen and nitrogen respectively. In the earlier 30 years, DLC was mainly prepared by sputtering using a pure graphite target. Doping can be achieved by introducing H_2 or N_2 gas into the vacuum during process. To meet the future high areal density requirements, DLC overcoat thickness is expected to be about 1 nm which is only a few atomic layers. Sputtered α -C, doped or undoped, is definitely not able to provide corrosion protection at such thickness level since sputtering fails to make continuous ultra-thin films. Tetrahedral amorphous carbon (ta-C) which has a high fraction of sp^3 bonds (80-90%) has been a preferred form of carbon overcoat because it offers atomic smoothness besides its outstanding physical and chemical properties.

α -C:H films for magnetic storage applications can be prepared by reactive sputtering or PECVD. Hydrogen plays a key role in the properties of α -C:H films. Bonding states of carbon and their vibrational modes also have significant contributions. Structures and

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properties of α -C:H films highly depends on substrate bias voltage during deposition, since ion bombardment plays a critical role affecting the H content, film density [57], and deposition rate by subplantation mechanism. α -C:H film with the highest H content (40-60 at.%) can have up to 70% of sp^3 bonds. However, most of its sp^3 bonds are hydrogen terminated and the film has low density and hardness [58]. It is called polymer-like α -C:H. These films are usually deposited by PECVD at low bias voltage [59]. α -C:H with low H content (less than 20 at.%) is called graphite-like α -C:H. It has high sp^2 content and is generally prepared by PECVD at high bias voltage [60] or sputtering [61].

It has been commonly accepted that a high H content decreases film hardness due to C-H bond termination and polymerization [62] [63]. However, Wu [64] found that even though the hardness and elastic modulus decrease with the increasing hydrogen content, the durability significantly improves in the highly hydrogenated carbon films. Due to the dangling bonds formed at the hydrogen terminated carbon surface, the α -C:H films may be more compatible with the tribo contact surface or provide better mobility for the lubricant, thus enhancing the durability of the films in the tribological tests.

Tetrahedral amorphous carbon (ta-C) is a peculiar form of amorphous carbon. Much research has been performed on ta-C film, and the term tetrahedral amorphous carbon (ta-C) has been used to describe it owing to the large percentage of sp^3 bonding (up to 90%). Lots of experimental studies have shown that the structure of ta-C consists predominantly of a disordered tetrahedral network with a small volume of sp^2 bonding and no discernible sp^1 bonds [65] [66]. An interesting property of ta-C is its superior surface smoothness. The low value of roughness ensures high quality of coverage in media storage applications.

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ta-C is usually deposited by FCVA or PLD. The ion energy has a great impact on the film density, intrinsic stress, hardness by changing its sp^3 bond fraction. ta-C films have an intrinsic compressive stress due to the ion bombardment during deposition. Stresses of 10 GPa or even higher values have been reported [67]. McKenzie [68] and Fallon [69] showed a significant correlation between the stress and the sp^3 fraction. ta-C is only formed when the deposition temperature is below a critical value of around 150-200 °C [70]. There is a sharp drop in sp^3 bonds and film density and sharp increase in surface roughness when temperature is above the critical point [71]. Although ta-C is metastable and formed below 200 °C, it is stable if annealed at 1000-1100 °C in vacuum, and it starts to oxidize at about 500 °C in atmospheric environment. It has been observed by Siegal [72] that annealing of ta-C films up to 600 °C creates nano-phase inclusions in the structure, giving about 15% increase in film hardness. The growth of the inclusions is explained as a stress-reduction mechanism.

It has been reported that ta-C shows uniform coverage, great corrosion protection, ultra-smooth surfaces and reasonable mechanical properties down to ~1 nm thickness [2,73-76]. However, if the issue of macroparticle filtering during ta-C deposition by FCVA is not solved, it will limit ta-C film in head applications only while it might not be appropriate for the disk.

Nitrogenated amorphous carbon (α -C:N) has drawn a lot of interest from researchers since Liu and Cohen [77] predicted the existence of carbon nitride of a special structure and properties similar to diamond. α -C:N is prepared by reactive sputtering in an Ar/N₂ atmosphere. Due to the doping of nitrogen, α -C:N shows better friction and scratch test performance than α -C:H, which can be explained by the increase of its elastic recovery and toughness. Another advantage of α -C:N as overcoat is its

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compatibility with lubricant layer and resistance to HF formation due to lubricant degradation [78].

α -C:N films have been prepared by a variety of deposition methods [79-84]. The film structure of α -C:N is either amorphous or in rare cases embedded with nanocrystallites. It is always carbon-rich with a maximum nitrogen content up to 45 at.% [85]. Nitrogenated carbon films are essentially described as a sp^2 hybridized C network where N atoms forms either in aromatic rings or connects these sp^2 microdomains depending on the deposition settings. Higher nitrogen content favors sp^2 clustering and incorporation of other forms of N-bonding as terminal groups ($-NH_2$ or $-C\equiv N$) in the periphery of the sp^2 domains. Different friction coefficients of nitrogenated carbon films have been reported [86-88]. However, it is well established that the mechanical properties is correlated with the N content and C bonding types. $-NH_2$ or $-C\equiv N$ terminal groups in the high N content structures interrupt network connectivity and thereby reduce the film hardness. As the N content decreases, film hardness and wear resistance are increased due to the reduction of terminal nitrogen groups. Any process promoting the formation of carbon sp^3 bonding hardens the film, and development of graphite-like domains interconnection improves wear resistance.

In hard disk applications, carbon overcoat is usually deposited in such a way that the α -C:H layer is covered by a thinner film of α -C:N to achieve the best performance due to contributions from their complementary properties.

2.3.5 Challenges and Motivations

Although the application of carbon films as overcoats for magnetic recording media has been a well developed practice, there are still several unanswered questions

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regarding the effect of structure and bonding on the tribological properties of DLC and CN_x overcoats, especially in the region just below the overcoat surface and near the overcoat / magnetic layer interface.

It has been reported that carbon could diffuse into the magnetic layer due to its small atomic size. Jack found that diffusion of carbon atoms from the carbon overcoat into the magnetic layer imposes a positive effect on the performance of cobalt chromium tantalum (CoCrTa) alloy recording media [89]. Carbon diffusion reduces saturation magnetization (M_s), and may enhance the decoupling of magnetic grains to give low media noise. The effect of overcoat diffusion is stronger for low thickness magnetic films and thus, will play an important role in low MrT media. On the other hand, Thiele et al. studied the reaction between Co-based alloys and carbon overcoat at their interfaces [90]. They observed a drop in magnetic coercivity up to 200 Oe for carbon (3.5 nm) coated media. The creation of magnetically “dead” layer is consistent with results by Han [3]. Even though carbon diffusion helps improve media’s signal-to-noise ratio, a detrimental effect of carbon diffusion into the magnetic layer on the overcoat tribological properties has already been observed [91].

Magnetically dead layer formation has been found at the interfaces between magnetic films and substrates by Hayashi et al. [92]. It is known that in the Fe films grown epitaxially on a substrate with a great lattice mismatch, a strain at the interface causes elastic deformation of the films, i.e. the Poisson effect, and leads to a tetragonal structure. The strain at the interface is released during the film growth by the change of the lattice constant or by the dislocation at the interface, which modifies the structural and magnetic phases of the iron (Fe) films. It has been theoretically shown that FCC and FCT Fe reveal diverse magnetic phases depending on the lattice constant [93] [94].

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Kallmayer et al. [95] observed the magnetization of cobalt iron silicon (Co_2FeSi) alloy film decreases considerably for thickness less than 10 nm. The thickness dependence of the magnetic moment can be explained by the number of dead layers representing a deficiency of magnetization at the interfaces. Quantitatively, a dead layer has a thickness of 0.8 nm at room temperature. 0.1 nm of the dead layer is due to temperature induced size effect. 0.15 nm at the top and 0.55 nm at the bottom interfaces are because of surface effect.

Nowadays, tantalum, copper, boron, platinum, chromium, and other elements have been widely used to alloy with cobalt in the magnetic recording media. Tantalum has been broadly used in hard disk industry as a buffer layer [96], seed layer [97], and alloying element to improve film crystallographic structure and magnetic properties [98] [99]. Addition of copper (Cu) as low as 4% into the iron platinum (FePt) alloy shows great impact on the ordering kinetics and coercivity of magnetic films [100] [101]. Media alloyed with Cu demonstrate lower noise resulted from better segregation between grains [102]. However, tantalum is metallurgically miscible with carbon. Copper is a well-known fast diffuser even at low to medium temperature range. Diffusion of Cu into the overcoat might cause degradation of carbon layer.

Based on the above-mentioned facts, it calls for an in-depth investigation on the inter-diffusion behavior and chemical reaction between atoms from magnetic films and overcoat. In addition, there is a need to develop a thin atomic level to reduce the side effect caused by the interaction. The scheme should be able to minimize the impact from the diffusion, dead layer formation, as well as corrosion and wear.

Ruthenium (Ru) is a transition metal of very special properties, and extremely inactive with very high density (12.30 g/cm^3). It is non-reactive with acids or aqua regia at

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room temperature. Ru has been successfully used in various engineering applications. It is harder than Pt and Pd, and is alloyed with these metals to make electrical contacts for severe wear resistance [103]. Corrosion resistance of CoCr alloys is improved by addition of a small amount of Ru [104]. Ru is also used as a dopant of SnO₂ for gas sensor applications [105]. As a catalyst, it encourages decomposition and removal of H₂S from oil. In recent years, Ru has been increasingly used in research as a diffusion barrier for Cu in IC fabrication [106]. Its application in AFC (Anti-Ferromagnetic Coupling) media as coupling spacer is due to its highly dense structure and inert behavior at the interface with magnetic alloys [107]. In this project, Ru has been selected as the barrier material because it has those unique properties aforementioned. In addition, it is readily available since it has been used in hard disk manufacturing for other purposes. Ru films can be deposited using conventional magnetron sputtering process which has a long history.

2.4 Fundamentals of Diffusion in Solids

2.4.1 Diffusion Mechanism

Diffusion is a net transport of ions, atoms, molecules from a region of higher concentration to one of lower concentration by random (thermal) particle motion. In general, there are three types of diffusion, i.e., vacancy, interstitial, and substitutional, which are illustrated in Fig. 2-15.

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Fig. 2-15 Three different types of diffusion: a) vacancy diffusion; b) interstitial diffusion; and c) substitutional diffusion

The vacancy diffusion involves an atom leaving a regular lattice position to fill up a vacancy in the lattice. Vacancy is a defect in the lattice. If an adjacent atom or impurity atom migrates to this empty site, this is known as vacancy diffusion. Interstitial diffusion occurs when small atoms, known as solute atoms, move from one interstitial position to another in the host solvent crystal structure. This mechanism is relevant for

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diffusion of small foreign atoms such as H, C, N, and O in metals and other materials. Small atoms fit in interstitial sites and in jumping, which do not greatly displace the solvent atoms from their normal lattice sites. In the case of substitutional diffusion, the solutes substitute for the host atoms by displacing them from their lattice sites. This is a process involved high activation energy and features low diffusion coefficient [108]. Boron and phosphorous doping in bulk silicon is a representative example of substitutional diffusion.

2.4.2 Diffusion Equations

The mathematical description of the diffusion processes is based on Fick's laws. Fick's laws of diffusion were derived by Adolf Fick based on his work on a salt-water system [109]. Later on, the theories were extended to diffusion phenomena in solid materials. Two equations, i.e., Fick's first law and second law, set the fundamental bases for diffusion.

2.4.2.1 Steady State Diffusion

In the steady state, there is no change of concentration, and the diffusion flux does not vary with time. The steady-state diffusion is characterized by:

$$\frac{\partial C}{\partial t} = 0 \quad (2-1)$$

It leads to a stationary concentration distribution for linear flow, a simplified case. A constant concentration gradient and a linear distribution of concentration are established under linear flow steady-state conditions, if the diffusivity is a constant. As

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a result of Eq. (2-1) and the continuity equation, or mass conservation, Eq. (2-2) can be established.

Fig. 2-16 Illustration of Fick's first law [108]

$$D \frac{\partial^2 C}{\partial x^2} = 0 \text{ and } C(x) = a + Ax \quad (2-2)$$

In Eq. (2-2) a and A are constants. D is diffusivity. Assuming the flux of diffusants is in one direction as illustrated in Fig. 2-16, Fick's first law, which is normally applied for steady state diffusion, can be written as:

$$J_x = -D \frac{\partial C}{\partial x} \quad (2-3)$$

where J_x is the diffusion flux along the x direction.

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2.4.2.2 Non-steady State Diffusion

Most instances are non-steady state when the diffusion flux and concentration gradient vary with time. Therefore, Fick's first law is no longer valid, and an equation known as Fick's second law is used. Fick's second law states that the rate of change of concentration within the diffusional field is proportional to the gradient of the flux (as in Eq. 2-2) at that point in the field, as given by:

$$\frac{\partial C_x}{\partial t} = -\frac{\partial}{\partial X} \left[-D \frac{\partial C_x}{\partial X} \right] = D \frac{\partial^2 C_x}{\partial X^2} \quad (2-4)$$

where C_x is the concentration at a distance x from the reference point, and t is time.

In practice, the diffusant concentration is often kept constant at the surface of the sample. The linearity of the diffusion equation permits use of the "principle of superposition" to produce new solutions for diffusion with different geometric arrangement. In the Constant Surface Concentration Model, it is assumed that the amount of diffusant atoms at the surface of the samples will be constant throughout the process. The presumed property leads to the construction of a solution to the diffusion equation for constant surface concentration C_s and for various values of the diffusion length $2\sqrt{Dt}$:

$$C = C_s \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2-5)$$

where C is diffusant concentration at distance x , C_s is the surface concentration, D is the diffusion coefficient or diffusivity, t is the diffusion time, and erfc is the complementary error function. The complimentary error function erfc is defined

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by $1 - \operatorname{erf}(2\sqrt{Dt})$ where $2\sqrt{Dt}$ is known as diffusion length. The Eq. 2-5 will be used below to understand the diffusion kinetics of carbon in magnetic and Ru films.

2.4.3 Grain Boundary Diffusion

Grain boundary is the transition region between two adjacent perfect crystals (grains), which are in contact with each other but differ in crystallographic orientation [110]. Because the diffusivity is high in the region, grain boundary is one of high-diffusivity paths or diffusion short circuits among others like free surface and dislocation. Grain boundaries are characterized by atomic disorder and incomplete bonding, which can lead to low migration barriers and high concentrations of diffusion-mediating defects. Hence, atomic mobility along grain boundaries is usually higher than within grains [111]. Because of the high density of grain boundaries in polycrystalline thin films, grain-boundary diffusion is often the dominating transport process of interest.

In the structures studied in this project, all metal films can be treated as of polycrystalline composition. The diffusion behavior of carbon, which is known as a fast diffuser, will be therefore analyzed based on the theoretical diffusion model developed by J.C. Fisher [112]. He proposed a quantitative profile describing lattice-diffusion coupled with grain-boundary diffusion. Based on Harrison's classification of the diffusion kinetics for grain boundary diffusion, there are three regimes called type A, B, and C [113]. This classification is the first and still the most widely used one for polycrystalline structure. The kinetics which is observed after diffusion anneals at high temperatures, or/and with long annealing times, or/and in materials with small grain size is type A. Type B kinetics regime is defined when the samples are annealed at lower temperatures, and with relatively short annealing time. Type C kinetics

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corresponds to conditions when lattice diffusion is practically ‘frozen in’, in which diffusion takes place along grain boundaries only, essentially without any leakage into adjacent grains. Fig. 2-17 illustrates Harrison’s classification of the diffusion kinetics in a polycrystal.

Fig. 2-17 Type A, B, and C diffusion kinetics according to Harrison's classification

[113]

2.5 Summary

Head-disk interface in a hard disk drive plays a critical role in its performance. Diamond-like carbon films were introduced to provide protection to media against corrosion, and mechanical damage. It has been recognized that the intermixing between magnetic films and carbon overcoats degrades both magnetic and tribological performances. A thin interlayer of Ru film is proposed to address the issue. Study of Ru as the carbon overcoat diffusion barrier in magnetic recording media is the topic of the project.

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3.1 Overview of the Project

From Chapter 2, the issue of carbon diffusion into magnetic layer in recording media, which causes dead layer formation, and leaves carbon voids in the overcoat, has been raised. To address the issue, introduction of a Ru barrier is proposed as a solution.

Fig. 3-1 An overview of the project

In the project, Ru diffusion barrier will be prepared using DC magnetron sputtering. Its structure and properties as a barrier will be characterized by changing process parameters, e.g., working pressure, power density and etc. Impact of a carbon deposition on magnetic performance of Co-based alloys, interaction between carbon

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and magnetic films, as well as tribological effect on carbon with a Ru interlayer will be investigated according the flow chart in Fig. 3-1.

3.2 Film Deposition and Post Treatment Instruments

3.2.1 Magnetron Sputtering

All samples with various film stacks in the research are deposited using an Intevac MDP-250B cluster film deposition system. The MDP-250B has twelve process chambers that are separately vacuum pumped and vacuum isolated. It has a number of processing options, including multiple options for the sputtering of magnetic films, sputtered or CVD carbon overcoats, heating chambers and cooling chambers. Moreover, the twelve process chambers in MDP-250B system can be simply reconfigured to accommodate process changes and product design. Fig. 3-2 and Fig. 3-3 show the aspect of the machine and chamber layout sequence in the system.

Fig. 3-2 Side view of an Intevac MDP-250B machine

Fig. 3-3 Chamber layout of the MDP-250B sputtering system

The MDP-250B is a production disk coating system designed to automatically sputter thin films of magnetic materials and supplementary materials onto substrates. In each deposition chamber, two circular magnetron sputtering sources, which match disk geometry, simultaneously coat both sides of a disk with films of uniform thickness. A DC bias unit can be turned on at any deposition chamber for aluminum substrates.

3.2.2 Hot Filament PECVD

All hydrogenated carbon films in the study were prepared in a hot filament PECVD chamber right after the deposition of magnetic or Ru films without breaking the vacuum. Substrate temperature can be tuned by adjusting the power to a heater filament, and monitored by an Infrared Ray (IR) sensor. Fig. 3-4 illustrates the setup of the hot filament PECVD system. As discussed earlier in the chapter 2, PECVD process provides more uniform film structure than sputtering, and is cheaper than FCVA.

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Fig. 3-4 Assembly of a carbon deposition chamber

The working mechanism of the carbon process is demonstrated as in Fig. 3-5. Neutral molecules of the C_2H_2 gas were introduced into the chamber from an inlet (1) behind the anode (3). Electrons are emitted from the hot filament (2) with sufficient energy to ionize the neutral gas molecules. Each ionization produces an electron-ion pair. Plasma formed at a potential slightly above the anode voltage. Positively charged ions that left the source eventually strike either the shields or the substrate (4) as a result of the repellent force from the anode or attractive force from substrate bias, forming the carbon film. As an ion strikes the substrate, its energy is approximately equal to the difference between the anode voltage and the bias voltage. Therefore, the anode and bias voltage difference determines the kinetic energy at which hydrocarbon ions impinge the substrates and thus the resulting carbon film properties.

Fig. 3-5 Carbon film deposition by hot filament PECVD

1. Source gas inlet; 2. Electron filament; 3. Anode; 4. Substrate

3.2.3 Rapid Thermal Annealing (RTA)

To study the annealing impact on the film properties, a JetFirst furnace manufactured by Jipelec was utilized for thermal treatment of the substrates in different gas (N_2 or Ar) environment. A mass flow controller (MFC) is attached to the system to control gas input. Chamber is able to be pumped down and Ar purged prior to annealing operation. The furnace has excellent repeatability and uniformity for a wide range of temperatures. The lamp array, upper flange and quartz window are mounted in a rotating top lid to allow full access to the chamber for easy loading and unloading of the wafers. Silicon carbide coated graphite susceptors are available for processing of small samples. The operating ambient temperature range can be tuned up to $1300\text{ }^{\circ}\text{C}$ with a ramp rate ranging from $1\text{ }^{\circ}\text{C/s}$ to $300\text{ }^{\circ}\text{C/s}$. Pyrometer control range is from $150\text{ }^{\circ}\text{C}$ to $1300\text{ }^{\circ}\text{C}$. In this project the temperature was varied from $50\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$.

3.3 Sample Preparation Procedure

3.3.1 Pure Ru Films

Ru films were deposited on glass substrates by dc magnetron sputtering to understand the effect of process on film quality, and to find out the optimal conditions as presented in chapter 4. The sputtering target (Ru) used is 99.98% pure. The base pressure of the chamber was about 5×10^{-7} Torr. The target-to-substrate distance was 40 ± 5 mm. During sputtering, turbo pumping rate is controlled by a throttle valve through its opening angle. Chamber pressure was measured by a capacitance gauge (MKS Baratron) and the argon gas flow was regulated by an N₂ calibrated MFC. Sputtering was carried out at a power density of 9.34 Wcm^{-2} with high purity Ar gas (99.999%) under varied working pressure ranging from 5 to 100 mTorr. Working pressure was fixed at 5 mTorr for a scan of sputtering power density which was changed from 2.34 to 9.34 W/cm^2 . Sputtering time was the same to compare the film thickness for different power densities. There is no external substrate heating. All key deposition parameters are listed in Table 3-4.

Table 3-1 Deposition conditions for Ru films sputtered on glass substrates

Substrate	Glass
Substrate temperature	Room temperature
Target-to-substrate distance, mm	40±5
Ru target purity, %	99.98
Gas	5N Argon gas
Chamber base pressure, mTorr	5×10 ⁻⁷
Sputter pressure, mTorr	5-100
Target power density, W/cm ²	2.34 - 9.34
Film thickness, nm	25+/-1.5

3.3.2 C/CoCrTa (MAG01) and C/Ru/CoCrTa (MAG02)

NiP-plated aluminum disks were textured with 0.2±0.05 nm of roughness as substrates. Magnetic films were prepared with 99.999% pure Ar as the working gas for sputtering. Prior to any deposition, the substrate was pre-heated to 285 °C. A 7.5 nm thick Cr-based alloy underlayer was first deposited; then followed by a CoCrTa magnetic layer of 17.5 nm. The base pressure for the Cr and magnetic layer deposition was controlled at 7 mTorr. Some of them were directly coated with a 12 nm of carbon film while others were coated with an ultra-thin Ru film (about 0.8 nm) before the carbon deposition of the same thickness. All depositions were done without breaking the vacuum. Hydrogenated carbon was CVD deposited at a substrate bias voltage varied from 0 to 160 V. The carbon film thickness was controlled at 12 nm for all samples by fixing the gas flow, the anode voltage, the filament current, and the substrate pre-deposition temperature. The different film layers are illustrated in Fig. 3-6.

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Table 3-2 gives the deposition parameters for C/CoCrTa (MAG01) and C/Ru/CoCrTa (MAG02) samples studied.

C/CoCrTa and C/Ru/CoCrTa films underwent a thermal annealing at 200 °C for 30 minutes in a N₂ atmosphere. Chamber pressure was controlled at 1 atm by fixing N₂ gas flow at 2000 sccm. Before temperature ramping, the annealing chamber was purged with N₂ for 8 cycles to minimize the side effect from the residual air.

Fig. 3-6 Film structure for sample C/CoCrTa and C/Ru/CoCrTa

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Table 3-2 Deposition conditions for C/CoCrTa (MAG01) and C/Ru/CoCrTa (MAG02) films

Process parameters	MAG01	MAG02
1) CoCrTa deposition		
a. Ar gas flow, sccm	25	25
b. Working pressure, mTorr	7	7
c. Sputtering power density, W/cm ²	4.03	4.03
d. Thickness, nm	17.5	17.5
2) Ru deposition		
a. Ar gas flow, sccm		36
b. Working pressure, mTorr	NA	10
c. Sputtering power density, W/cm ²		1.61
d. Thickness, nm		~1.0
3) DLC (α-C:H) deposition		
a. C ₂ H ₂ / Ar gas flow, sccm	30 / 5	30 / 5
b. Anode voltage, V	60	60
c. Filament emission current, A	0.6	0.6
d. Substrate bias, V	0-160	0-160
e. Thickness, nm	12	12

3.3.3 C/Ta (TA01) and C/Ru/Ta (TA02)

Tantalum (Ta) films were sputter deposited on glass substrates at room temperature in an Intevac MDP-250B facing target sputtering system with 99.999% Ar as the working gas. Prior to deposition, the glass substrates were cleaned with 5% Oakite TCL300

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solution. The deposition pressure was fixed at 3 mTorr. Argon gas flow was controlled at 7 sccm by a mass flow meter and the Ta target power density at 12 W/cm². DLC was deposited on the tantalum films in another chamber without breaking the vacuum in a Plasma Enhanced Chemical Vapor Deposition (PECVD) process using acetylene (C₂H₂) mixed with argon. The C₂H₂ inlet and C₂H₂/Ar gas ratio were kept constant during deposition. Carbon thickness was controlled at 20 nm for all samples by fixing the C₂H₂ gas flow, the anode voltage, and the hot electron filament current. There was no extra substrate heating for carbon deposition except for the plasma heating effect from the sputtering that caused substrate temperature rise to 70-80 °C. The detailed deposition parameters are listed in Table 3-3. 1.0 nm of Ru layer was deposited on the top of the Ta layer before the DLC layer was deposited, to create C/Ru/Ta (TA02) architecture. In comparison, C/Ta (TA01) architecture (i.e., without Ru in between) is also deposited with the same deposition parameters. Film structures are shown in Fig. 3-7.

Fig. 3-7 Film structures for sample C/Ta and C/Ru/Ta

Post-sputter annealing of C/Ta and C/Ru/Ta samples was carried out in a JetFirst furnace (Jipelec) at 300, 400, and 500 °C for 20 seconds under 1 atm N₂ ambience.

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Table 3-3 Deposition parameters for C/Ta and C/Ru/Ta films

Process parameters	TA01	TA02
1) Ta deposition		
a. Ar gas flow, sccm	7	7
b. Working pressure, mTorr	3	3
c. Sputtering power density, W/cm ²	12.08	12.08
d. Thickness, nm	~65	~65
2) Ru deposition		
a. Ar gas flow, sccm		30
b. Working pressure, mTorr	NA	60
c. Sputtering power density, W/cm ²		2.42
d. Thickness, nm		~1.0
3) DLC (α -C:H) deposition		
a. C ₂ H ₂ / Ar gas flow, sccm	30 / 5	30 / 5
b. Anode voltage, V	60	60
c. Filament emission current, A	0.6	0.6
d. Substrate bias, V	100	100
e. Thickness, nm	~20	~20

3.3.4 Co-Pt-TiO₂ and Ru Films with C Overcoat

Samples were deposited on glass substrates at room temperature by dc magnetron sputtering for diffusion study. Sputtering working pressures for Co-Pt-TiO₂ composite films were chosen to be at 50, 80, 120 mTorr through throttle valve. The Co-Pt-TiO₂ film thickness was about 20 nm. A Ru film of 10 nm was used as a seed layer for all

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samples to obtain a good crystal orientation of the Co-Pt-TiO₂ layer. To understand the impact of the Ru barrier on magnetic property, a hybrid overcoat with Ru and carbon dual layer structure was deposited on the top of Co-Pt-TiO₂ film. Samples (MAG03) with variable Ru and carbon thickness were prepared, while the total thickness of carbon and Ru film was kept at 4nm. Carbon films were prepared in a hot filament CVD system using acetylene (C₂H₂) as the precursor. Gaseous C₂H₂ is ionized by hot electrons emitted from a filament, and the carbon containing ionic species are repelled to the substrate by the anode voltage. For diffusion kinetics study, two types of samples were prepared. One (MAG04) was 20 nm Co-Pt-TiO₂ films which were prepared at 80 mTorr and coated with carbon, and the other (RU01) was 20 nm pure Ru films coated with carbon. The carbon film thickness was controlled at 10 nm for all samples by fixing the anode voltage (60 V), and the filament current (0.8 A). Sample B and C were split into 5 groups, and four of them underwent argon annealing at an elevated temperatures of 50, 100, 150, 200 °C for 30 s respectively. The working pressure of the furnace was 1 atm. The film structures for the sample MAG3, MAG4, RU1 were represented in Fig. 3-8. All key deposition parameters are listed in Table 3-4.

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Fig. 3-8 Film structures for the diffusion study

Table 3-4 Deposition conditions for the samples in Fig. 3-8

Layer	Parameter	Sample MAG03	Sample MAG04	Sample RU01
Carbon	C ₂ H ₂ flow, sccm	30	30	30
	Anode voltage, V	60	60	60
	Filament current, A	0.8	0.8	0.8
Co-Pt-TiO ₂	Ar pressure, mTorr	50, 80, 120	80	NA
	Sputtering power density, W/cm ²	8.05	8.05	8.05
Ru	Ar pressure, mTorr	5	5	5
	Sputtering power density, W/cm ²	9.34	9.34	9.34

3.3.5 Hydrogenated Carbon Grown with Ru interlayer

The Ru films were deposited on NiP coated aluminum substrates by dc magnetron sputtering using MDP-250B. The sputtering target used is 99.98% pure. The base pressure of the chamber was about 5×10^{-7} Torr. The target-to-substrate distance was 40 ± 5 mm. The chamber pressure was measured by a capacitance gauge (MKS Baratron) and the argon gas flow was regulated by an N₂ calibrated MFC. Sputtering was carried out at a power density of 0.8 Wcm^{-2} with high purity Ar gas (99.999%). Sputtering working pressure is regulated to 3 mTorr with fixed Ar gas flow of 10 sccm. All key deposition parameters are listed in Table 3-4. Carbon films were prepared in a hot filament CVD system using acetylene (C₂H₂) as the precursor after Ru deposition without breaking the vacuum. Gaseous C₂H₂ is ionized by hot electrons emitted from a filament, and the carbon containing ionic species are repelled to the substrate which is negatively biased. The carbon film thickness was controlled at 12 nm for all samples through deposition time adjustment and the fixed anode voltage (60 V), filament current (0.8 A), and substrate bias (-120 V). The substrates were pre-heated to desired temperature in vacuum through thermal radiation from a lamp heater, and the temperature was monitored by an IR sensor.

3.3.6 C, Ru, and C/Ru Overcoat for Anti-corrosion

In order to evaluate the anti-corrosion behavior of carbon, Ru, and carbon with Ru interlayers, three types of overcoat were prepared. Firstly samples (COR01) have only carbon. Second type of samples (COR02) has only Ru. It is to test the extreme case of anti-corrosion performance of Ru without carbon. Samples with carbon and Ru dual-layer structure (COR03, COR04, and COR05) were also prepared. Bare NiP plated Al substrate without any overcoat serves as the baseline for the three types of samples.

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Total thickness of overcoat was fixed at 3.5 nm to align with the current industry practice. Table 3-5 gives some important deposition parameters. Film structures for the three types of overcoat are shown in Fig. 3-9.

Fig. 3-9 film structures for three types of overcoat

Table 3-5 Key deposition parameters for overcoat samples

Layer	Parameter	Sample COR1	Sample COR2	Sample COR3/4/5
Carbon	C ₂ H ₂ flow, sccm	30	NA	30
	Anode voltage, V	60	NA	60
	Filament current, A	0.8	NA	0.8
	Bias, V	120	NA	120
	Thickness, nm		0	3, 2.5, 1.5
Ru	Ar pressure, mTorr	NA	5	5
	Sputtering power density, W/cm ²	NA	9.34	9.34
	Thickness, nm	0	3.5	0.5, 1, 2

3.4 Microstructure Characterization

3.4.1 Raman Spectroscopy

Raman spectroscopy is the best technique to study the bonding structures of carbon films. It is a widely used non-destructive way to characterize sp^3 to sp^2 bond ratio in carbon materials [114] [115]. Carbon films show typical features in their Raman spectra in the region of $800\text{-}2000\text{ cm}^{-1}$ where the G-peak and D-peak are located. The peak centered around 1580 cm^{-1} has been called the G peak (G denoting graphite) and the peak around 1355 cm^{-1} associated with the finite size has been called the D peak (D for disorder) [116].

Raman spectroscopy is based on the light scattering from the change of polarity due to lattice vibration. The polarity change causes an inelastic scattering of an incident photon. For amorphous carbon, the π states have lower energies than the σ states, so they are much easier to be polarized. This gives the sp^2 sites a 50 - 230 times larger Raman cross-section than sp^3 sites. Resonant Raman scattering refers to the polarization occurring by excitation of the electronic ground state into virtual energy states. The measurement using visible lasers can excite $\pi - \pi^*$ transitions in a graphitic ring, generating Raman scattering representing the breathing vibrations due to E_{2g} symmetry (G-peak) and disorder mode (D-peak) of graphite lattices [117]. A typical visible Raman spectrum of a-C film contains a skewed broad band that can be resolved into D-peak and G-peak of either Gaussian or Lorentzian distributions [118]. Because the Raman scattering cross-section of graphite ($5 \times 10^{-5}\text{ cm}^{-1}\text{sr}^{-1}$) is much larger than that of diamond ($9.1 \times 10^{-7}\text{ cm}^{-1}\text{sr}^{-1}$), the a-C film with higher sp^2 fraction generates higher Raman intensities and higher G-peak frequency [117]. Practically, the G-peak frequency and the intensity ratio of the D-peak and G-peak, I_D/I_G , are of most interest.

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It has been found that the films with high sp^3 fraction tend to have lower G-peak frequency and I_D/I_G . I_D/I_G varies inversely with the in-plane grain size of the graphite. UV laser at 244 nm (5.1 eV) can excite both $\sigma - \sigma^*$ and $\pi - \pi^*$ transitions and is very useful for sp^3 -rich carbon like ta-C films. In a UV Raman spectrum, both the D mode and G mode are still present and strong. This is consistent with their high polarisability.

Raman scattering analysis on all carbon films in the project was performed using a Raman spectroscopy (Renishaw System) excited with He-Ne laser operated at wavelength of 633 nm (visible range).

3.4.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is also called ESCA (Electron Spectroscopy for Chemical Analysis). It utilizes X-ray (with energy $E_{\text{photon}} = h\nu$) generated from ultra pure Al or Mg targets by sputtering to excite the sample which thus emits photoelectrons from atoms near the surface. A small fraction of the photoelectrons from the top surface is therefore collected by the analyzer for kinetic energy (KE) analysis. Based on energy conservation, binding energy (BE) is obtained as $BE = h\nu - KE$. By referring to standard binding energy data, the electrons are identified as from specific orbits of certain elements. XPS is not only able to identify elemental composition of samples, but also the stoichiometry. Atomic concentration as low as 0.2% is detectable using XPS for elements heavier than He. In addition, it measures thickness for ultra thin film within a few atomic layers. Combined with ion sputtering, it does depth profiling for elements of interest. XPS works under ultra high vacuum conditions, and is surface sensitive. Its detection thickness range is from 1 to 10 nm.

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In the study, an X-ray photoelectron Spectroscopy system using a Kratos-Axis spectrometer with monochromatic Al K α (1486.71 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer was employed to characterize the atomic composition and bonding characteristics of the multilayer films. Chamber works under a vacuum of 1.8×10^{-9} Torr.

3.4.3 X-ray Diffraction (XRD)

X-ray diffraction is a useful and non-destructive technique for phase identification and quantitative analysis of crystalline materials. Phase identification is achieved by comparing the measured x-ray diffraction pattern with reference patterns in a standard database. A crystal lattice is a regular three-dimensional arrangement of atoms in space, e.g. cubic, rhombic, etc. The atoms are arranged so that they form a series of parallel planes separated from one another by a certain distance, which varies according to the structure of the material. For any crystal, planes exist in a number of different orientations, each with its own specific spacing d .

When a monochromatic x-ray beam with a wavelength λ is projected onto a crystalline sample at an incident angle of θ , diffraction occurs only when the distance traveled by the beam reflected from successive planes differs by a whole number n of the wavelength. By changing the angle θ , Bragg's law is satisfied by different d spacing. Plotting the angular positions and intensity of the resultant diffracted peaks of radiation produces a pattern, which is a characteristic of the sample. Different peaks will be observed with respect to different phases in the sample material. Bragg's law is explained in the Fig. 3-10 and given as:

$$n\lambda = 2d \sin\theta$$

Fig. 3-10 Bragg's law explanation

The width of the peaks in a diffraction pattern is an indication of the average crystalline size. Smaller crystallites give rise to wider peaks, while the peak width decreases as crystallite size increases. Peak broadens also as a result of d spacing variation induced by micro-strain. In general, XRD measurement shows the information of phase type, preferred orientation, and crystallite size.

PANalytical X'Pert X-ray diffraction (XRD) with a Cu tube anode ($\lambda = 0.15406$ nm) at 45 kV and 40 mA was used for phase identification. Symmetric θ - 2θ scans have been conducted ranging from 10° to 120° with a step size of 0.1° .

3.4.4 X-ray Reflectometry (XRR)

Reflectometry is the X-ray technique in which the reflectivity curve of a material is measured. The technique is also called Grazing Incidence X-ray Reflectivity (GIXR), or simply, "reflectivity". Surface layer characteristics, such as thickness, roughness and density, can be determined from the reflectivity curve of a material. A reflectivity profile shows the response of a material during specular reflection, this scattering effect depends upon the change of the average electron density across an interface and not upon the periodic nature of the electron density as described by the crystal

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structure. It is a response that occurs for non-crystalline and crystalline materials alike. In this respect it is quite different from X-ray diffraction.

A reflectivity curve is a plot of the intensity of specularly reflected X-rays (Y axis) versus the angle of incidence with respect to the surface (X axis). It is assumed that the angle of incidence is equal to the angle of detection with respect to the surface. During reflectometry these angles are scanned synchronously (a coupled $\Omega/2\Theta$ scan) from an angle close to zero up to a few degrees. From zero up to the critical angle for total external reflection the wave barely penetrates into the material, this means that very little intensity is absorbed. The critical angle for total external reflection depends upon the electron density of the surface layer. Above the critical angle the wave penetrates into the material. The penetration depth increases rapidly with the angle. Absorption increases, and the proportion of specularly reflected radiation decreases. This results in a rapid drop in intensity in the reflectivity curve.

The critical angle is measured as the start point of this rapid fall in intensity. Being able to fix this position accurately depends upon the nature of the material and the instrumental optics. The shape of the profile immediately before the critical angle, i.e. at total external reflection, is determined by the size of the sample, its flatness, and instrumental parameters (for example: beam size). This region is ideally a plateau, but for very small or non-ideal samples it may rise to a peak. The intensity drop at the critical angle may be less than ideally sharp if the electron density is inhomogeneous at the surface, for example if the surface is rough or the electron density graded, or the materials involved have a large absorption value. The sharpness of the critical edge is also dependent upon instrumental factors such as the wavelength spread and divergence of the incident beam.

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As the angle of incidence increases the penetration depth increases, a proportion of the incident beam is specularly reflected at every interface, within the penetration depth, in which the electron density of the material changes. Waves reflected back outwards towards the surface the material might be re-reflected back towards the bulk. Oscillations in the reflected amplitudes are created, that are related to the angle of incidence, and the depths of the interfaces with respect to each other and the surface. The oscillations interfere and even from as few as two thin layers a complicated interference pattern can evolve. As the angle of incidence increases the absorption increases and the specularly reflected intensity is eventually reduced below the background and no useful reflectivity information can be obtained beyond this point.

In this project, XRR is employed to measure film density, film thickness with high resolution, and qualitatively study film stack interface roughness. PANalytical X'Pert X-ray diffraction (XRD) with a Cu tube anode ($\lambda = 0.15406$ nm) at 40 kV and 40 mA was used for 2θ scan. Symmetric θ - 2θ scans can be operated in a small range (a few degrees) with a step size of 0.005° .

3.4.5 Secondary Ion Mass Spectroscopy (SIMS)

SIMS is a surface sensitive analytical technique that makes primary ion beam (a few keV energy) bombardment on a sample surface followed by mass spectrometry of the emitted secondary ions. The primary ion energy is transferred to sample atoms via atomic collisions and a so-called collision cascade is generated. Part of the energy is transported to the surface allowing surface atoms to overcome the surface binding energy. The interaction of the collision cascade with surface molecules results in the escape of even large and non-volatile molecules with or without fragmentation. Most of the emitted particles are neutral in charge, but a small proportion is positively or

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negatively charged. The mass analysis of the emitted ions provides detailed information on the elemental and molecular composition of the surface. TOF-SIMS is a combination of SIMS with Time of Flight mass analysis (TOF). TOF mass spectrometry is based on the fact that ions with the same energy but different masses travel with different velocities. Basically, ions formed by a short ionization event are accelerated by an electrostatic field to a common energy and travel over a drift path to the detector. The lighter ones arrive before the heavier ones and a mass spectrum is recorded. Measuring the flight time for each ion allows the determination of its mass. This cycle is repeated with a repetition rate which depends on the flight time of the highest mass to be recorded. SIMS is destructive method in nature because particles are etched from the sample. In this project, ToF-SIMS was used to obtain information on the in-depth distribution of elements. This dynamic SIMS mode was applied to analyze compositional depth profiles of thin films. The SIMS system used in experiments was the ToF-SIMS V system manufactured by ION-TOF GmbH (Münster, Germany). Primary ion bombardment was done with 25 KeV Bi⁺ ions from a liquid metal ion gun and was rastered over an area of 100 x 100 μm^2 . The sputter gun uses Ar⁺ ions with 500 eV energy rastered over a 500 x 500 μm^2 area. Depth profiling was carried out with interlace mode. The apparatus is pumped down to a vacuum of 1×10^{-8} Torr prior to operation of spectrometer. A picture showing the layout of the ToF-SIMS instrument is given in Fig. 3-11.

Fig. 3-11 ToF-SIMS V system manufactured by ION-TOF GmbH, Münster, Germany

3.4.6 Transmission Electron Microscope (TEM)

TEM is a microscopy technique whereby an electron beam is transmitted through an ultra thin specimen, interacting with the specimen as it passes through it. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen. TEM allows researchers to determine the internal structures of materials at atomic level. TEM samples need to be specially prepared to a thickness which allows electrons to transmit through, like light is transmitted through materials in a conventional optical microscopy. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms. Magnifications of 350000 times can be routinely obtained for many materials, whilst in special circumstances; atoms can be imaged at

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magnifications greater than 15 million times. For solid samples, phase determination as well as defect and crystalline orientation are typical outcomes. Microstructural characterization can be readily determined using various combinations of imaging and electron diffraction techniques. Images obtained from a TEM are two-dimensional sections of the material under study, but applications which require three-dimensional reconstructions can be accommodated by these techniques. The energies of the electrons in the TEM determine the relative degree of penetration of electrons in a specific sample, or alternatively, influences the thickness of material from which useful information may be obtained. Because of the high spatial resolution obtained, TEMs are often employed to determine the detailed crystallography of fine-grained materials. TEM is a complementary tool to conventional crystallographic methods such as X-ray diffraction. A schematic picture of TEM optics is represented in Fig. 3-12. The TEM used in the project is the model CM300 manufactured by Philips.

Fig. 3-12 Schematic of the optics of a transmission electron microscope

3.5 Thickness, Surface, Electrochemical and Magnetic Properties

3.5.1 Film Thickness Measurement

Carbon film thickness was measured with an n&k 1500-D Manual-Load Analyzer manufactured by n&k Technology, Inc. The spectroscopic ellipsometer was setup and calibrated for a full media stack (Cr/Co/Carbon) with predetermined n (refractive index) and k (extinction coefficient) values. The instrument relies on the mechanism that the reflection at a dielectric interface depends on the polarization of the light. The transmission of light through a transparent layer changes the phase of the incoming

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wave, which is determined by the refractive index of the material. Based on broadband spectrophotometry in conjunction with the Forouhi-Bloomer dispersion equations, n&k Analyzers provide real-time, nondestructive measurements for carbon films. It can be used to measure layers as thin as 1 nm and as thick as a few microns. In the experiments, 4 points at the MD (middle diameter) position of the disk were measured per surface and the average value was calculated.

XRF from Spectrace QuanX was used to measure thickness for metal films (Cr, magnetic, and Ru). The Spectrace QuanX is a compact high performance Energy Dispersive X-ray Fluorescence (EDXRF) system. The analyzer uses an X-ray tube excitation source and a solid-state detector to provide spectroscopic analysis of elements ranging from sodium to uranium. The sample is presented to the spectrometer on the sample stage. As shown in Fig. 3-13, the X-ray tube excitation source shines X-rays up onto the sample at 45 degree angle.

Fig. 3-13 X-ray spectrometer optics for film thickness measurement

X-ray photons from the X-ray tube penetrate the layers of the disk and excite the elements in the sample by the photoelectric effect, causing inner orbital (K-shell) electrons to be ejected from the atom. The excited atoms switch back to the ground state and in the process emit X-ray photons with the energies that are characteristic of each element. These characteristic X-ray photons from the elements in the sample are

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emitted in all directions. The spectrometer contains a lithium drifted silicon (Si(Li)) X-ray detector that is mounted at 45 degrees from the sample (90 degrees from the X-ray tube) to detect the X-ray photons emitted from the sample. The Si(Li) detector determines the energy of each X-ray and a spectrum of emissions is produced. In general with XRF techniques, the intensity of the analyte peak, which is proportional to the concentration of that element, is integrated into the film thickness.

3.5.2 Atomic Force Microscope (AFM)

The surface topography and film roughness were measured using a Digital Instrument (Dimension 3000) AFM. It uses a silicon nitride (Si_3N_4) probe scanning across the sample surface at ambient. The system works by vibrating the cantilever with constant amplitude and frequency. The amplitude and phase change correlate with the change of the sample surface feature. By detecting amount of vibrational amplitude change, the response of the sample surface to the tip vibration is displayed as an image. A feedback loop is used to maintain a constant interaction between the probe and the sample. The position of the probe and the feedback signal are electronically recorded to produce a three dimensional map of the surface. Scanning was well controlled through piezoelectrically induced motion. Three-dimensional imaging was accomplished and root mean square roughness (RMS or R_q) was calculated based on 4 locations each of which were measured a $1 \times 1 \mu\text{m}$ area scanned at the tapping mode. The 4 points are located as indicated in Fig. 3-14.

Fig. 3-14 AFM measurement points

3.5.3 Scanning Electron Microscope (SEM)

SEM is a tool allowing us to do sample surface imaging at sub-micron scale, composition identification, and element quantification. It utilizes electron beam, which is a result of acceleration of electrons generated at a hot filament, to bombard the sample surface. Beam size and focus are controlled by magnetic lenses. Backscattered and secondary electrons created by the bombardment will be detected and analyzed for element recognition and topographical imaging respectively. Detection of X-ray generated during the process is used for composition analysis. Variations in darkness on the image distinguish among different elements.

SEM system works under vacuum condition which normally requires a base pressure of 10^{-6} to 10^{-7} Torr. Vacuum protects filament, prevents beam disturbance from residue gases, and ensures minimum contamination. SEM requires samples to be electrically conductive. Otherwise, charging effect results. For non-conductive samples, thin coatings (Au, Ag, or C) and/or conductive tapings are the practice to minimize electron charging.

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In operation, filament current is normally $< 75 \mu\text{A}$ to maintain it at good condition and extend its lifetime. Usually 20 kV is used as the electron acceleration voltage. Working distance has to be kept at 12-20 mm range, in order to prevent sample damage without compromising the sharpness of picture. By experience, to obtain well-taken image at certain magnitude, samples are first focused at larger magnification then zoomed back to the required scale.

In this project, a JEOL JSM-5600LV SEM instrument was used for surface morphology scan.

3.5.4 Water Contact Angle Goniometry

Water contact angle (WCA) is used to measure the surface energy of a solid sample. The smaller the angle, the higher the surface energy. Deionized water (DIW) is usually used as the liquid in the measurement. If the contact angle of a surface by water is smaller than 90° , it is called hydrophilic. Otherwise, it is called hydrophobic.

In the contact angle measurement, one drop of water with a controlled volume (10-20 μl) is placed on the sample surface. Release of the water droplet is of importance in the experiment since the weight of the droplet could affect the measurement accuracy by changing its own shape. To minimize the error, water is dispensed in a receding way for hydrophilic surface, and an advancing manner for hydrophobic surface. Sample surface needs to be fresh and clean enough so that is free of contamination by foreign materials or adsorption of gases which might greatly change the surface energy, in order that the contact angle reflects the true sample properties. Besides freshness and cleanliness of sample surface, roughness and pre-treatment of surface such as coating affect the contact angle as well.

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In the experiment, the water contact angle was measured using a ramé-hart Contact Angle Goniometer Model 100. All measurements were conducted by applying 10 μ l of DIW droplets onto the fresh film surfaces of prepared samples. 4 different locations of every sample were measured to get the average value.

Fig. 3-15 ramé-hart water contact angle goniometer

3.5.5 Linear Sweep Voltammetry (LSV)

Linear Sweep Voltammetry (LSV) was carried out to study overcoat anti-corrosion performance using an Autolab Potentiostat/Galvanostat (PGSTAT30) with a PC interface. The software used for the experiment parameters and subsequent analysis of the results was the General Purpose Electrochemical System software (GPES) version 4.97. A custom made test cell for media corrosion with an exposed sample surface of 0.727 cm^2 was used for the test. The test cell was shielded by a faraday cage against external electronic interferences during the experiment. The counter electrode used was a platinum counter electrode as it was inert and does not react with the test environment. The reference electrode used was a silver/silver chloride reference electrode. The experiment was carried out in a controlled temperature environment at 23°C .

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The test cell was rinsed thoroughly with de-ionized water prior to the experiment and then air dried for 15 minutes. The sample was then mounted onto the test cell and screwed tight. The test cell was filled with 0.2 M sodium chloride electrolyte to increase conductivity. The test cell was then connected to the electrodes and then placed into the faraday cage.

Fig. 3-16 The test cell installed and connected to electrodes

The system was allowed to become steady for 3000 seconds before scanning for a Tafel plot. After equilibration, scanning commenced at a slow rate of 0.01 V/s to give the system sufficient time to stabilize at each potential.

The samples were scanned at three different locations and the Tafel plots obtained were analyzed using the GPES software. The averages of the results were taken and compared.

3.5.6 Magnetic Property

A non-contact Rotating Disk Magnetometer (RDM) is used to characterize the magnetic properties of the thin film recording media. The measurement system is calibrated using the magnetization reversal curves obtained by the combined use of a recording head sensor and a calibrated electromagnet. The RDM system is able to measure coercivity (H_c) and MrT (product of remnant magnetization and thickness) of magnetic films with approximate 180 individual points per circumference. The data presented in the context are the average values of the 180 points for every sample.

Chapter 4 Process study of ruthenium film deposition

4.1 Introduction

Ruthenium (Ru) has been proposed as the carbon diffusion barrier in magnetic recording application due to the facts that: 1) it is denser than most other metals; 2) it provides anti-corrosion protection; 3) it is chemically inert at ambient and moderately high temperatures; 4) it is easier to get than some other metals, i.e. Rh, Ir, Os which are denser than Ru; and 5) manufacturing processes for Ru films have been long used in the hard disk industry. Fig. 4-1 compares the densities of some of the bulk metals.

Fig. 4-1 Metal density versus atomic number

One of the objectives of the project is to deposit highly dense Ru films of smooth surface morphology which provides a base for the conformal coverage of carbon films.

Chapter 4 Process study of ruthenium film deposition

The properties of Ru film deposited by magnetron sputtering at varied deposition conditions such as power density on target and argon pressure are studied in this chapter, in order to understand and achieve sustainable process window. Film density, roughness and crystalline structure are characterized. Chemical Vapor Deposition (CVD) was not considered due to difficulties in handling the precursor which is normally metal-organic material. Other factors include byproduct contamination, and the fact that sputtering has been an accessible technique employed in hard disk industry for many years.

4.2 Crystalline structure

In general the bulk and surface properties of metallic thin films rely on their crystallographic structures. Understanding of the crystalline constitution and texture orientation will help explain the observed physical, chemical, electrical, magnetic, thermal, optical properties as a function of various deposition parameters. Such information, in addition, helps to elucidate the relationship between the crystallographic formation and the thin film growth dynamics.

The crystalline phases of the Ru samples (all with a thickness of 25 ± 1.5 nm) deposited with varied sputtering pressures were identified as the XRD peaks plotted in Fig. 4-2 by the conventional θ - 2θ scan. It was found that there is a minimum (100) peak intensity (at 38.35°) for films deposited at 5 mTorr. With increasing deposition pressure the (100) peak attains higher intensity. On the other hand, there was a slight drop in the intensity of (002) peak corresponding to c-axis orientation which is located at about 42.25° (c-plane is parallel to the substrate surface). Peak (101) with negligible intensity appears at about 44.05° , and no peak attributable to any other phase was observed for all the samples. As the pressure was further increased to the 80-100

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mTorr range, the (100) crystal orientation of the Ru film was well established with high intensity. A (100) preferred orientation is assumed at higher pressure.

Fig. 4-2 XRD patterns for Ru film deposited at varied working pressures

The preferred orientation of the grains inside the Ru film can be defined as follows according to Lee's relation [119]:

$$T_{hkl} = \frac{I_m(hkl) / I_0(hkl)}{\frac{1}{n} \sum_{i=1}^n \frac{I_m(hkl)}{I_0(hkl)}} \quad (4-1)$$

where T_{hkl} is the coefficient of texture, $I_m(hkl)$ is the measured relative intensity of the reflection from the (hkl) plane, $I_0(hkl)$ is that from the same plane in a standard reference sample (powder), and n is the total number of reflection peaks from the sample. In the case of Ru samples studied, $n = 3$. Only planes (100), (002), and (101) are considered.

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Fig. 4-3 Coefficient of texture as a function of sputtering pressure

Fig. 4-3 shows the coefficient of texture (CT) defined by the equation (4-1) for Ru samples sputtered at varied Ar pressure. The value of CT corresponding to the plane (002) decreased from 2.27 at 5 mTorr to 0.71 at 100 mTorr. Therefore, the (002) orientation remained dominant at lower sputtering pressures, which is preferred to obtain a more closely packed film structure. The possible reason for c-axis orientation degree loss at higher pressures might be that the deposited atoms have altered their direction, energy, momentum and mobility due to the decrease in the mean free path of the atoms at elevated pressures. Kawamura observed that with an Ar and N₂ gas mixture, the preferred crystalline orientation of Ru film was influenced by the N₂ concentration [120]. The degree of c-axis orientation was suppressed at higher N₂ concentration when films were sputtered at low temperature. No compound formation between Ru and N was detected, and the c-axis orientation remains when the films were prepared at high temperature at which N incorporation is negligible. Although

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pure Ar was used as sputtering gas in our case, it can be expected that the inclusion of gases (e.g. Ar) in the films would suppress c-axis orientation of Ru crystals. In our study, the excessive incorporation of Ar in Ru film at higher pressures is similar to the case when N was purposely introduced in the structure. The c-axis orientation may have become unfavorable and suppressed in the Ru films, which were slightly strained due to excessive Ar incorporation. Another possible mechanism, namely the preferential adsorption of Ar on (002), could explain the suppressed growth of the (002) at higher pressures. Park et al. also found that the (002) peak intensity decreases as the Ar pressure increases. A lower pressure is favorable for film grown along the (002) orientation [121].

It can be further understood based on sputtered film structure zone model illustrated by Thornton in Fig. 4-4. Thornton in 1970's had constructed a schematic zone model which defines the sputter coating structure by extending Movchan and Demchishin's findings [122]. The basic features were essentially independent of the substrate material, and the model is now widely used by scientists to explain their results. As shown in Fig. 4-4, film surface structure was classified in term of four zones as a function of T/T_m and argon pressure, where T and T_m are substrate temperature and melting point of coating material respectively. Based on Thornton's zone model, the granular structure of sputtered metal films depends on the kinetics of the arriving species and the surface migration of the atoms on the substrate.

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Fig. 4-4 Structure zone model for sputtered films of metals [122]

In our experiment, as all the Ru samples were deposited without external substrate heating, the value of T/T_m should be estimated at the range of 0.1-0.3 with regards to 2250 °C of T_m for Ru. The film structure should develop from Zone T to Zone I according to Fig. 4-4 as the deposition pressure increases. More porous structure consisting of crystallites separated by voids is promoted at higher pressures. At higher pressures, adatoms have little surface mobility due to energy loss in the “vapor” phase. Therefore initial nuclei tend to grow in the direction of available coating flux, causing intergrain shadowing effect. The shadowing effect aggravates as more adsorbed argon accumulates at the grain boundaries. In addition, adsorbed argon on surface limits the adatom mobility at high argon pressures [123]. Intergrain boundaries become rich of voids rather than true grain boundaries due to argon incorporation, so that coatings are underdense, although individual crystallites have near bulk density. The growth morphology which is affected significantly by intergrain shading will be further discussed later.

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Fig. 4-5 XRD patterns for Ru film deposited at varied sputtering power density

The results of XRD θ - 2θ absolute scan of Ru films deposited at varied sputtering power density are illustrated in Fig. 4-5. In all samples, the diffraction peaks corresponding to the (100), (002), and (101) orientation were observed with increased intensity for peak (002). The dependence of the film crystallinity on the sputtering power can be explained by the kinetic energies of sputter-ejected species. As applied discharge power is low, less ion bombardment occurred and resulted in a low kinetic energy of the ejected atoms arriving at the substrate. This leads to a reduction of adatom diffusion for atomic arrangement and hence tends to form poor crystalline structure.

By plotting the coefficient of texture as in Fig. 4-6, it was found there is a slight increase of CT value for the plane (002) as sputtering power density increases from 2.34 to 9.34 W/cm². Obviously (002) preferred orientation is promoted at higher

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sputtering power. This is result of the fact that when the discharge power is increased, the number of particles generated by sputtering and the probability that these particles arrive at the substrate increase. At higher deposition rate, the number and kinetic energy of the depositing molecules have been considered as major factors determining the adatom mobility and formation of the nucleated clusters, which in turn determine the crystallinity, microstructure and surface morphology of the films. If we refer to the results of pressure impact discussed earlier, it can be explained that Ar incorporation in Ru film is reduced at higher sputtering power due to more energetic bombardment, which helps to sustain (002) preferred orientation of Ru films.

Fig. 4-6 Coefficient of texture as a function of sputtering power (Ar pressure was fixed at 40 mTorr)

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4.3 Surface morphology and density

As mentioned, Ru diffusion barrier for carbon has to exhibit multiple properties, such as smooth surface morphology and dense structure. The impact of sputtering conditions on film surface morphology and density is then examined using XRR and AFM techniques.

In the X-ray energy range, the refractive index (RI) of a solid material is usually smaller than that of the air. Thus, at small grazing angles, an X-ray beam traveling in the air is fully reflected by the solid surface [124]. A typical XRR scan is performed in specular condition for Ru films prepared at varied Ar pressures as indicated in Fig. 4-7, and the XRR curves are obtained by plotting the scattered X-ray intensity against the scattering angle, 2θ . Due to total external reflection, at very low incidence angles the scattered intensities are almost constant and form a plateau. The plateau ends with a shoulder due to the fact that the X-ray beam is no longer totally reflected off the solid surface as the reflection angle increases. The incidence angle beyond which total reflection intensity is cut off by half of the plateau value is in most cases referred as the critical angle of total external reflection, θ_c . In the X-ray region, θ_c is generally in the range of tenths of a degree and is directly related to the mass density, ρ , as described by the following equation [125-126]:

$$\frac{\theta_c^2}{\rho} = \frac{r_e \lambda^2 Z N_A}{\pi A} = B \quad (4-2)$$

where r_e is the classical electron radius (2.82×10^{-15} m), λ the X-ray wavelength, Z the atomic number, N_A the Avogadro's number, and A the mass number. B is a constant for a given material and irradiating beam. θ_c is the experimental parameter used for

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determining ρ by XRR. Film density ρ is directly calculated from Equation (4-2) after that θ_c has been assessed from the XRR curve. Information of film surface roughness can be estimated from the XRR reflection pattern as well.

Fig. 4-7 XRR reflection curves for Ru films deposited at varied sputtering pressures

Fig. 4-7 shows XRR measurements of samples deposited at argon pressures ranging from 5-100 mTorr. More rapid damping of the interference fringes is observed in the XRR data, which arises when deposition pressure becomes higher. It illustrates the film roughness increases as the ion energy is weaker for high pressure deposition. The reflection edge is slightly shifted to smaller angles for films deposited at higher argon pressures, indicating lower density films at higher pressures. Apparently, films deposited at higher pressures showed more porous and rougher structures.

Fig. 4-8 Film density as a function of the working pressure

Film density measured based on the critical angle for films deposited at different pressures are plotted in Fig. 4-8. In low Ar pressure range, the kinetic energy of the sputtered Ru atoms is not reduced by collisions with the vapor phase (Ar, Ru) due to longer mean free path. The angular spread of the impinging material flux onto a substrate also decreases with decreasing pressure because the sputtered atoms undergo less collision with Ar and are thus less scattered, and the energies of particles are distributed in the range of 0.1–10 eV [127]. This energy promotes surface diffusion and more pronounced peening effect, which, in turn, results in the formation of a denser film. As the Ar pressure increases, the flux angular distribution gets wider, and the average energy of the deposited atoms decreases. As voids form in Ru films due to the lack of diffusion, they are never filled-in since geometric shadowing screens the flux of arriving atoms. In this case, porous structure forms, and the grain boundaries are rich in Ar inclusion as discussed previously.

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The roughness variation detected by XRR in Fig. 4-7 due to change in sputtering pressure is also reflected in the AFM results as shown in Fig. 4-9. Though the two techniques are based on significantly different ways of measurement, the same trend of roughness was seen. The AFM images showed that the particle size proportionally increased as Ar pressure increased. The root mean square (RMS) roughness was calculated and summarized in Fig. 4-10. The root mean square roughness can be described by:

$$R_{rms} = \sqrt{\frac{1}{N} \sum_{i=1}^N (z_i - z_m)^2} \quad (4-3)$$

where z_m is the height of a reference plane and N is the number of data points with a relative height z_i .

RMS increased from 0.32 nm at 5 mTorr to 0.50 nm at 100 mTorr. The roughness change may be associated with the shadowing effect and structural transformation in preferred orientation. The RMS roughness measured using AFM is believed to have lower values than the actual, probably due to the large size of the tip used to probe the surface. The tip is approximately 10 nm in diameter, therefore it cannot probe into the deep, narrow crevices on the surface. As a consequence the AFM will always give a lower roughness when lateral correlation distance is small.

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Fig. 4-9 AFM surface scans for Ru film deposited at varied working pressures: (a) 5 mTorr, (b) 20 mTorr, (c) 50 mTorr, (d) 80 mTorr, (e) 100 mTorr

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Fig. 4-10 Surface roughness as a function of sputtering pressure

Fig. 4-11 XRR reflection curves for Ru film deposited at varied power densities

Fig. 4-12 Film density as a function of sputtering power density

XRR scans for Ru films prepared at varied sputtering power are indicated in Fig. 4-11. The vanishing of the interference pattern at larger angles indicates an increase in the surface roughness of the sample sputtered at lower power over that of the sample sputtered at higher ones. Also the total reflection edge is slightly shifted revealing a lower film density at lower power. In Fig. 4-12, the dependence of film density of different samples on sputtering power is given based on calculations using equation (4-2). It is apparent that both the density and the roughness of the Ru films are affected by the sputtering power. It is remarkable that higher power resulted in higher film density and lower roughness, though the impact is not so significant as compared to Ar pressure. The trend presented in Fig. 4-12 shows the film density increased from 11.72 to 12.35 g/cm³ when power increased from 2.34 to 5.61 W/cm². However, there was no further increase in film density when power density was above 5.61 W/cm². It is believed that the film density is very close to the bulk density of Ru (12.37 W/cm²) at

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the highest power densities. For process control purpose and because of hardware limitation, power density of 6 W/cm² or below is preferred.

It has also been found that the microstructures and surface morphology of the films are strongly dependent on the energy of the sputtered particles arriving at the substrate [128] [129]. The films deposited at lower sputtering power are exposed to lower energetic atmosphere which resulted in a rougher surface. The AFM images and RMS roughness measured for samples sputtered at varied power densities are shown in Fig. 4-13 and Fig. 4-14. The power density effect on surface roughness is consistent with the XRR decay pattern in Fig. 4-11. As examined by AFM, the RMS roughness was measured to be approximately 0.5 nm with a power density of 2.34 W/cm², and remained constant up to a power density of 3.74 W/cm². However it is reduced from 0.5 to 0.38 nm when the power density is raised up to 9.34 W/cm². The AFM surface morphology shown in Fig. 4-13 suggested that Ru films deposited at 2.34 and 3.74 W/cm² of power densities are with bigger particle size and less densely packed. This is due to the fact that fewer energetic particles strike the substrate surface at lower power. Therefore, the mobility of atoms deposited on the substrate is small. A denser structure with much smaller particle size started to develop as the sputtering power density increased to 4.67 W/cm². As discharge power is further increased, film surface morphology changed little. The effect from power density can be explained by surface diffusion which is affected by sputtering power. Sufficient diffusion energy induced at higher power prevented shadowing effect from being observed, leading to a smoother film surface. This situation is not observed for other films, e.g. Cu, which is likely due to different grain growth mechanisms [130]. The crystalline structure of Cu films is significantly influenced by sputtering power, while that of the Ru films was only slightly affected.

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Fig. 4-13 AFM surface scans for Ru films deposited at varied power densities: (g) 2.34

W/cm², (h) 3.74 W/cm², (i) 4.67 W/cm², (j) 5.61 W/cm², (k) 7.01 W/cm², (l) 9.34

W/cm²

Fig. 4-14 Surface roughness decreases with increasing sputtering power density

4.4 Summary

Ruthenium (Ru) films deposited at varied Ar pressures and sputtering power densities were characterized. Ru thickness for all samples was control at 25±1.5 nm. There was no extra substrate heating during deposition. XRD examination showed lower pressure down to 5 mTorr is preferred to achieve higher degree of c-axis orientation. Excessive Ar incorporation at grain boundaries at higher pressures are believed to suppress Ru crystalline growth along (002) orientation. On the other hand, higher power density encourages Ru c-axis orientation, though the effect is not as significant as pressure within the process window studied. Both XRR and AFM analysis indicated smoother surface morphology obtained at lower Ar pressure and higher power density. Higher roughness induced at high Ar pressure and low sputtering power is believed to be due to lower diffusion energy and surface mobility of adatoms. Film density measurement

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based on XRR oscillation showed more porous structure at higher Ar pressure and lower power density. Voids formation at such conditions is associated with shadowing effect when Ru atoms have reduced kinetic energy. It is apparent that Ar pressure lower than 10 mTorr and power density above 5.61 W/cm^2 are desirable to achieve both dense structure and smooth morphology.

Chapter 5 Interaction between Carbon and Magnetic Films

5.1 Introduction

In Chapter 2, it was mentioned that carbon diffusion into the magnetic layer causes degradation of overcoat. Detrimental effect due to formation of magnetically “dead” layer is also reported. Carbon diffusion reduces M_s (Saturation Magnetization), and may enhance the decoupling of magnetic grains to give low media noise. The effect of overcoat diffusion is stronger for thinner magnetic films and thus overcoat diffusion will play an important role in media of low remanent magnetization and thickness product (MrT). Thiele et al. [131] studied the reactions between Co-based alloys and carbon overcoat at their interfaces. They observed a drop in magnetic coercivity up to 200 Oe for carbon (3.5 nm) coated media. The creation of magnetically “dead” layer is consistent with reported results by Leng [132]. Detrimental effect of carbon diffusion into the magnetic layer on the overcoat tribological properties has already been observed [133]. Carbon overcoat became more porous, leaving magnetic film more susceptible to corrosion and wear.

In this chapter, the impact of carbon deposition on magnetic property of CoCrTa films is studied. Interaction between Ta-containing alloy CoCrTa and carbon was further understood by using pure Ta films. The effect of Ru as a diffusion barrier was compared to the carbon overcoat scheme with direct contact with CoCrTa film. Ru was chosen due to its extremely high density among a few other candidates. The role of Ru interlayer was investigated. Film structures were characterized by means of AFM, SEM, XPS, XRR, XRD, and Raman spectroscopy.

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5.2 Carbon on CoCrTa Magnetic Films with Ru Interlayer

5.2.1 Magnetic Property

Fig. 5-1 shows the remanent magnetization and thickness product or MrT (normalized) of magnetic films. Without an Ru interlayer MrT variation is large. With an Ru interlayer MrT becomes more uniform. Fig. 5-2 plots the impact of annealing on magnetic properties of the films. Without Ru interlayer, the film was more susceptible to plasma damage during carbon deposition. It was worse at higher substrate bias. MrT values of magnetic films without Ru interlayer changed quite a lot after N₂ annealing, while there were only minor changes for those with an Ru interlayer. There are two possible factors that may cause such an effect: one is the enhanced reactions between carbon and magnetic alloys at elevated temperatures, and the other is due to N₂ diffusion into the sub-layers. The details of the mechanisms will be discussed with XPS results below. The slight change of MrT for films with Ru interlayer might be caused by the ultra-thin thickness of Ru films and the non-uniformity nature of sputtering deposition.

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Fig. 5-1 Normalized MrT of α -C:H coated CoCrTa films with and without an Ru interlayer

Fig. 5-2 Comparison of the MrT as a function of substrate bias for CoCrTa films with and without an Ru interlayer

5.2.2 Surface Energy and Morphology

Fig. 5-3 Water contact angle measurements

Fig. 5-3 shows the water contact angle results of all the samples. There is not much differences between C/Ru and C films in terms of Contact Angle (CA) values. Within the substrate biases varied from 0-160 V, there is very limited change for water contact angle. The results are different from what was observed by S. Zhang et al. [134]. In their work, α -C:N films prepared by sputtering were studied. Different carbon deposition method and incorporation of nitrogen in their study might be the reason for the differences. However, the values of CA drop by $\sim 20\%$ after N_2 anneal at 200°C for 30 minutes, resulting less hydrophobic carbon surface with higher surface energy. The observed change is supposed to be roughening effect of N_2 anneal which induces grain growth of magnetic layer underneath. On the other hand, the role of H species also needs to be considered. The bounded hydrogen species are displaced and might

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desorb from the film at higher temperature, through which the film surface is activated via hydrogen abstraction.

Fig. 5-4 Three-dimensional topographical images of α -C:H films scanned by AFM. a) As-deposited C film with $R_{\text{rms}} = 0.651$ nm. b) Post N_2 anneal (200 $^{\circ}\text{C}$, 30 minutes, 1 atm) C film, $R_{\text{rms}} = 0.949$ nm. c) As-deposited C/Ru film, $R_{\text{rms}} = 0.637$ nm. d) Post N_2 anneal (200 $^{\circ}\text{C}$, 30 minutes, 1 atm) C/Ru film, $R_{\text{rms}} = 0.771$ nm.

The study on overcoat surface topography and degree of surface roughness has been performed with AFM measurement. The AFM micrographs of carbon films that are as deposited and N_2 annealed are shown in Fig. 5-4. As seen from Fig. 5-4, the films appear to have good coverage and uniformity with the α -C:H surface morphology

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closely following the topography of the substrate which displays apparent texture lines even after being sputter coated. Carbon films without Ru interlayer show slightly greater roughness ($R_{\text{rms}}=0.651$ nm) compared to films with Ru layer ($R_{\text{rms}}=0.637$ nm). Film roughness R_{rms} increases for all films after N_2 anneal at 200°C and under 1 atm of N_2 pressure for 30 minutes. The results agree with the water contact angle measurement results shown in Fig. 5-3. The roughness change to $R_{\text{rms}}=0.949$ nm for C film is presumed to be caused by the grain growth of metal layers underneath. The phenomenon is more pronounced for samples without an Ru interlayer. The less change of surface roughness ($R_{\text{rms}}=0.771$ nm) for C/Ru sample after annealing is probably due to the fact that the dense structure of Ru suppresses the crystallization of magnetic layer to some extent, especially near the interface area.

5.2.3 Bonding Structure

The XPS core level spectra were analyzed by non-linear least square fitting performed after a Shirley background subtraction [135]. Spectra for C/CoCrTa and C/Ru/CoCrTa samples are compared before and after N_2 annealing. During the XPS scan, peak for N has never been detected from sample surface to the magnetic layer. The assumption of nitridation by and diffusion of N_2 is ruled out. It is believed that nitridation of carbon does not occur at temperatures up to 200°C . For metallic elements (Co, Cr, and Ta) considered here, the fact that nitridation is not observed might either because of not so high temperature or thick carbon overcoat which is dense enough to prevent the nitrogen from diffusing into the film.

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Fig. 5-5 XPS spectra of C $1s$ for (a) as-deposited carbon sample without Ru; (b) N_2 annealed carbon sample without Ru; (c) as-deposited C/Ru sample; (d) N_2 annealed C/Ru sample

From the spectra plotted in Fig. 5-5, there is only one distinguishable feature for C $1s$ detected at the sample surface, namely the 284.5 eV peak with a halfwidth of approximately 1.3 eV. This peak symbolizes C-C bonds for polymeric carbon [136] [137]. Its location does not shift after thermal treatment. When carbon sample is sputtered towards the interface area between carbon and magnetic layer, an additional peak is detected at the binding energy (BE) of 280 eV for both as-grown and annealed films. The peak is probably due to metal carbide formation. It signifies that carbide formation starts without thermal treatment subsequent to deposition as long as there is direct contact between carbon and the magnetic alloy (CoCrTa). However, the energy induced by ion bombardment during carbon deposition needs to be taken into account, especially when substrates are negatively biased at high voltage (160 V for C and C/Ru). The formation of carbide triggers a slight chemical shift of 0.3-0.6 eV to lower BE level for the C-C peak. The phenomenon is more significant for annealed sample as

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the carbide peak intensity increases. It demonstrates that carbon formation is aggravated at elevated temperature. Grain size of magnetic film grows at higher temperature which provides diffusion paths for carbon atoms at grain boundaries, leading to more carbide formation. In addition, the C-C peak broadens at the interface area compared to sample top surface. Ch. Linsmeier and Koumei Baba et al. have reported carbide formation at room temperature for a few elements, e.g. W, Ti, Be, Si, and carbon [138] [139]. The BE peak assigned to metal carbide is normally in the range of 281-284 eV [140]. The slight difference of observed BE in our experiment from reference data should be chemical shift caused by stoichiometry variation of the carbide.

Fig. 5-6 XPS Ta 4f core level spectra for (a) as-deposited carbon sample without Ru; (b) N₂ annealed carbon film without Ru; (c) as deposited C/Ru; (d) N₂ annealed C/Ru

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According to the literature [141] [142], the BE value for Cr_3C_2 is 282.8 eV and the value for TaC is 281.9 eV. The value for Co carbide is similar to Fe carbide (Fe_3C) which is 283.9 eV. Based on these reported data combined with the Ta 4f core level spectra in Fig. 5-6, and the fact that both oxygen and nitrogen level in the film is rather low, the peak at 280 eV (Fig. 5-5) can therefore be attributed to Ta carbide formation. As shown in Fig. 5-6, Ta 4f_{7/2} peak at 22.9 eV which matches with that of metallic Ta is observed for C/Ru sample. Meanwhile, the Ta 4f_{7/2} peak is shifted towards 23.1 eV for the sample without Ru interlayer. It indicates that Ru performs well in preventing intermixing between carbon and magnetic alloys.

5.3 Carbon on Ta with Ru Interlayer

Tantalum (Ta) and its nitride and carbide have many different applications in tooling industry and IC fabrication [143-146]. There exist two types of crystalline structure for Ta, i.e. body-centered-cubic (BCC) α -phase and tetragonal or hexagonal closed packed (HCP) β -phase. β -Ta has been widely used in hard disk industry as a buffer layer [147], seed layer [148], and alloying element to improve film crystallographic structure and magnetic properties [149, 150].

In the previous section, it has been demonstrated that Ta composition in magnetic film of ternary CoCrTa alloy forms carbide with carbon overcoat in absence of a barrier layer in-between. The formation of tantalum carbide is believed to affect the magnetic behavior of CoCrTa films. Here, the interaction between Ta and Diamond-like Carbon (DLC) films is studied using samples of DLC over pure Ta film. Ru is added as a barrier interlayer between Ta and DLC layers for comparison. Post sputter annealing is arranged in pure nitrogen gas at elevated temperatures. The role of Ru interlayer is investigated.

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5.3.1 Crystalline structure

The XRD profiles of the as-deposited and N₂ annealed C/Ta (TA01) and C/Ru/Ta (TA02) films were collected and shown in Fig. 5-7 and Fig. 5-8. In Fig. 5-7, peaks centered at 22.8°, 34.6°, 38.4°, 44.8° and 48.4° were attributed to the glass substrates (SiO₂). Four of them correspond to cristobalite structure of the glass with textures of (101), (201), (202) and (212) phases. The presence of diffraction peaks at 33.4° and 70.2° in the as-deposited samples indicates textures of Ta (002) and (004) orientation, showing existence of tetragonal Ta phase (β -Ta). The relatively higher intensity of the (002) peak compared to the broadened (004) peak implies that the samples are highly textured in the (002) orientation. Peak (006) at $\sim 118^\circ$ can not be shown as it is out of our scanning range (from 10 to 80°). The nonexistence of other peaks implied that there is very low level of texture exhibited by BCC α -Ta in the as-deposited TA01 and TA02 samples under the sputtering conditions studied. Lee et al. [151] reported highly (002) textured beta tantalum at sputtering pressures as low as 2 mTorr, which is very similar to our result. In addition, there were no diffraction peaks observed for the crystalline phases of tantalum oxide or tantalum carbide. This can be either due to the ultra-thin thickness of the compound films formed at the surface and interface which is undetectable by the instrument or due to their amorphous structures. Peaks for Ru are not seen due to its thickness of about only 1 nm. Absence of diamond and graphite peaks is due to the amorphous nature of the DLC film.

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Fig. 5-7 X-ray diffraction spectra for as-deposited and N₂ annealed TA01 samples versus carbon only films with glass substrate. Peaks for substrate SiO₂, α-Ta, β-Ta, and sub-stoichiometric Ta carbide are marked as ■, □, ▼, ○ respectively

In the structure without Ru intermediate layer, the Ta (002) peak shifted to lower diffraction angle after annealing at 300 °C, signaling a slight change in its crystalline structure. Also the full width at half maximum (FWHM) of the (002) peak became wider, and (002) plane to plane spacing enlarged in light of the lower diffraction angle which might be due to microstrain effect caused by heating induced partial phase change. It is believed that the one-way diffusion of carbon atoms into the Ta atomic network caused the slight distortion of Ta lattice. It is less likely that Ta diffused into carbon film because the atomic size of Ta is much larger than that of carbon (Atomic diameter of 0.4 nm for Ta and 0.14 nm for C). It was also observed that the intensity for peak at 38.4° increased almost 50% after annealing at 300 °C compared to the as-deposited state. It is likely due to the appearance of (110) peak of α-Ta at 38.4° which overlaps with the peak (201) of glass substrate. This illustrates onset of the phase

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transformation of Ta film from the beta to the alpha phase. The observation agrees well with the results by Robert Knepper et al. who found that the strongly oriented (002) β -Ta phase is progressively changed to a less well-oriented α phase between 300 and 375 °C [152]. The peak emerging at 69.9° (annealed at 300 °C) is either due to formation of tantalum carbide or to relocation of β -Ta (004) peak. Tantalum carbide with substoichiometry was observed for TA01 sample annealed at 400 °C and 500 °C as shown in Fig. 5-7. There is no tantalum nitride identified in all the samples, possibly because the carbon layer is thick enough to block the penetration of N₂ gas into the Ta layer.

Fig. 5-8 X-ray diffraction spectra for as-deposited and N₂ annealed TA02 samples with glass substrate. Peaks for substrate SiO₂, α -Ta, and β -Ta are marked as ■, □, ▼ respectively

In TA02 samples, as shown in Fig. 5-8, (002) and (004) peaks for β -Ta were still clearly defined after annealing at 400 °C. Even though the (004) peak faded away at 500 °C, (002) peak is still visible, with no sign of tantalum carbide. Nano-crystallites

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of β -Ta co-exist with α -Ta up to 500 °C in TA02 structure. The detected phase change is due to recrystallization of β -tantalum before transformation into α -Ta. The (002) grains became more randomly distributed in the phase change process. The non-drift of the (004) peak of β -Ta, together with the absence of TaC_x peaks, explains the effect of Ru interlayer as an effective barrier in impeding carbon diffusion into the lattice of the underneath Ta film. Compared to the C/Ta architecture, the film with Ru interlayer is more thermally stable. In addition, with the presence of the Ru interlayer, the phase transformation is slower, much favored in perpendicular recording media using β -Ta as a seeding layer.

5.3.2 Surface / Interface morphology and carbon bonding

The XRR scans of TA01 and TA02 films are presented in Fig. 5-9 and Fig. 5-10. Both as-deposited films exhibit strong interference fringes, indicating smooth surface and sharp interfaces. However, after annealing at 300 °C, reflection pattern for TA01 film undergoes significant change in terms of fringe shape and amplitude, indicating considerable increase in roughness at surface and interface. Extra modulations emerged as a result of intermixing at the TA01 interface. When TA01 samples are annealed at 400 and 500 °C, the interference fringes become more uneven. Aside from the increased roughness at surface and interface, the formation of an ultra-thin carbide layer at the interface leads to the scattering of the reflected x-ray and electron density change. The intermixing between carbon and tantalum layers is likely due to subplantation [131] of hydrocarbon ions into tantalum film during early deposition of carbon film, although the resolution is not well identified in XRR curve for as-deposited TA01 film. In comparison, there is basically no change in XRR reflection pattern for structure with Ru interlayer until annealing at temperatures higher than 400

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°C. In other words, the surface and interfaces in Ta/Ru/C are stable up to 400 °C. The decreased critical angle in TA01 as observed in Fig. 5-9 shows the density drop of Ta film which is transformed from HCP β phase to BCC α phase after annealing as observed in Fig. 5-7. The HCP is more closely packed than BCC structure because HCP has an Atomic Packing Factor (APF) of 0.74 while that of BCC has only 0.68.

Fig. 5-9 XRR curves for TA01 films deposited on glass substrate before and after N₂ annealing at 300 °C, 400 °C, and 500 °C

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Fig. 5-10 XRR curves for TA02 films deposited on glass substrate before and after N₂ annealing at 300 °C, 400 °C, and 500 °C

In an amorphous carbon layer, the intensity ratio of the D-peak to G-peak in a Raman spectrum (I_D/I_G) is used to determine the degree of graphitization as the D-peak arises from the graphitic grain boundaries and impurities, for instance, substituted N or H atoms and sp^3 carbon [153]. Moreover, the widths of the peaks also provide essential information about the crystallinity of the films. Amorphous materials produce broad, diffuse peaks, while crystalline materials give well-defined sharp peaks. Raman spectra obtained from as-deposited and annealed TA01 and TA02 films are shown in Fig. 5-11 and Fig. 5-12 respectively. As-deposited films all show a relatively flat pattern, indicative of limited amount of crystalline structure of carbon or a nearly amorphous microstructure. The peaks at around $1560\text{--}1590\text{ cm}^{-1}$ with strong background corresponds to G-peak of graphite and a broad shoulder at a lower frequency of $1370\text{--}1375\text{ cm}^{-1}$ is commonly recognized as D-peak. The Raman spectra

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acquired from the as-deposited DLC films and the annealed films at elevated temperatures show obvious differences. After annealing in N₂ atmosphere from 300 °C to 500 °C, the spectra evolve from an almost flat curve to one with well isolated and sharp G-peak and D-peak. The G peak is attributed to the stretching-vibration mode of any pair of sp² sites, whether in C=C chains or in aromatic rings [154]. The designated D peak positioned at 1335, 1338, 1367, and 1370 cm⁻¹ can be interpreted by the scattering of disorder activated optical zone-edge phonons [155]. Up to 300 °C, the Raman spectra of the annealed TA01 films do not show evident changes as compared to that of the as-deposited film. However, as the annealing temperature increased to above 400 °C, the G peak position shifts slightly upwards and the D peak intensity increases. Compared to the as-deposited films, the annealed films beyond 400 °C give rise to higher G-peak frequency and better resolved D and G peaks. This is a good indication of graphitization of the films during heating, signifying a severe degradation of the structural property of the films, i.e. the decrease of the sp³ content, weakened diamond-like feature and the increase of graphite-like component.

Fig. 5-11 Raman spectra of as-deposited and annealed TA01 samples

Fig. 5-12 Raman spectra of as-deposited and annealed TA02 samples

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As for TA02 sample, the same trend was observed as the annealing temperature increases. However, there is no clear segregation of D-peak and G-peak up to 400 °C. Graphitization became more evident only at 500 °C. The results indicate that the carbon film in TA02 has a higher thermal stability than that in TA01. Graphitization is the growth of graphitic domains in either size and/or number. The enhanced Raman intensity with graphitization is because the cross-section of Raman scattering due to diamond ($9.1 \times 10^{-7} \text{ cm}^{-1} \text{ sr}^{-1}$) is much smaller than that due to graphite ($5 \times 10^{-5} \text{ cm}^{-1} \text{ sr}^{-1}$) [156]. The results in Fig. 5-12 show that as annealing temperature increases, the sp^3/sp^2 bonding ratio decreases or the film graphitization increases. However, the carbon film in TA02 structure tends to maintain their sp^3 state.

Fig. 5-13 I_D/I_G ratio plotted as a function of annealing temperature

The intensity ratio of I_D / I_G was plotted in Fig. 5-13. The intensity ratio increases as the annealing temperature is raised, which is consistent with the results reported by Sam and Nakazawa [157-158]. Dischler et al. [159] found that hydrogen is effused

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from hydrogenated carbon films at a temperature around 350–400 °C, causing more sp^2 bonding. Conway et al. [160] investigated the structural changes by thermal annealing using Raman spectroscopy and temperature programmed desorption. They found that the I_D/I_G ratio started to increase slightly before the main part of the hydrogen evolution. Similar results for the hydrogenated films prepared by PECVD have been reported [161]. According to their studies, the relocation of carbon atoms would be caused by the effusion of hydrogen from the films, and the effusion of hydrogen from the films is enhanced at higher temperatures. Interestingly, introduction of Ru layer in our study causes the intensity ratio drops by 7-15%. It is likely that the effusion of hydrogen thus the disruption of carbon networks by atomic hydrogen were hindered in TA02 structure. More thermal energy which favors the clustering of sp^2 -bonded carbons into ordered aromatic rings is needed for TA02 samples. The amount of sp^2 fraction in TA02 which is accompanied by the hydrogen effusion changes less with annealing temperature in comparison to TA01 samples.

Fig. 5-14 Arrhenius plots of I_D/I_G for post deposition annealing of TA01 and TA02

Graphitization process of carbon films in TA01 and TA02 structures can be further explained based on the activation energy of the process involved. $sp^3 \rightarrow sp^2$ transformation and sp^2 clustering are believed to be the two stages for the graphitization process. Since the $sp^3 \rightarrow sp^2$ transformation process is a process of atomic bond breaking and reformation, it is rate-limited by the atomic jumping frequency and temperature [162]. The activation energy can be estimated by $kT \ln(v\tau)$ where k is Boltzmann constant, T is temperature in Kelvin, v is atomic jumping frequency, and τ is the time taken to realize the transition. Typically, v is about 1×10^{14} Hz. The obvious D-peak and G-peak segregation starts at 400 °C for both TA01 as shown in Fig. 5-11 and it starts at 500 °C for TA02. For the sake of convenience, the temperatures prior to the peak segregation points are taken as the transition temperatures for estimation. For simplicity, τ is taken as one second, the activation

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energies for the $sp^3 \rightarrow sp^2$ conversion are estimated as 1.63 eV for TA01 and 1.92 eV for TA02 after annealing. The activation energies of sp^2 clustering can be extracted from the Arrhenius plot of I_D/I_G ratio ($\ln[I_D/I_G]$ vs $1/T$) in Fig. 5-14. The plot is generated based on data obtained at deposition temperature from 300 to 500 °C. The activation energy calculated is 0.042 eV for TA01 and 0.044 eV for TA02. Apparently, the evolution for sp^2 clustering process is comparable for both TA01 and TA02. Therefore, carbon graphitization at elevated temperature is impeded with the introduction of Ru because sp^3 to sp^2 transformation is made more difficult, while sp^2 clustering is not affected in the presence of Ru.

The surface morphology of TA01 and TA02 samples after annealing at 500 °C is compared in Fig. 5-15. The as-deposited films do not demonstrate any significant surface morphology under SEM. However, after annealing, surface feature becomes obvious. Interlocked twister structure is observed for both carbon films. The one without Ru interlayer experiences more change in surface roughness and pattern size. The SEM morphology agrees well with the roughness measurement done by AFM in section 4.4.2 where roughness in carbon films with Ru interlayer are less susceptible to thermal impact.

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Fig. 5-15 SEM morphology of samples a) TA01 and b) TA02 annealed at 500 °C for 20 s

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5.4 Summary

In summary, a study on Ru as an inter layer for a-C:H overcoat in magnetic recording films has been presented. With an Ru interlayer, magnetic performance of the films is more consistent in terms of remnant magnetization measurement. The surface roughness of as-deposited C/Ru films is comparable to films without an Ru sub layer. However, after N₂ annealing, surface roughness of films without Ru barrier changes more than the ones without Ru. Although N₂ diffusion is not found in the experimental conditions, XPS analysis reveals that TaC_x formation is observed at the carbon and metallic alloy interface while it does not occur for samples with an Ru film.

The as-deposited carbon films are amorphous with or without a Ru interlayer. In TA02 structured films, phase transformation of Ta from β to α structure is impeded up to 400 °C, which otherwise happens at 300 °C without the Ru barrier layer. Crystalline carbide is only observed for structures without Ru interlayer, but not when Ru barrier layer is in place. In TA02, no obvious intermixing between Ta and C was observed, and the surface and interface integrity was maintained well even after annealing at 400 °C. Graphitization of carbon in TA01 sample was observed at 400 °C. In TA02, however, the degree of graphitization was less severe. The results indicate that the carbon films in TA02 structure have better thermal stability than in TA01 structure.

Chapter 6 Diffusion of Carbon

6.1 Introduction

The fact that carbon can readily diffuse into the magnetic films and cause its performance degradation has been noticed. Its interaction with magnetic films was discussed in Chapter 5. Co alloy films became magnetically more stable with insertion of thin Ru barrier. Ru film, which is preferably deposited at low sputtering pressures (<10 mTorr) and high power densities (>5.61 W/cm²), was selected due to its high density and chemical inertness. There has been no report on the details of diffusion of carbon in magnetic film so far. It is therefore essential to understand the diffusion characteristics of carbon in magnetic films in order to interpret the results in Chapter 5. Understanding of the impediment of carbon diffusion by Ru barrier is of utmost importance as well. In the present Chapter, the diffusion of carbon into Co-Pt-TiO₂ composite films, which is widely used in perpendicular magnetic recording structure, is investigated by Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) technique. Carbon diffusion into pure Ru film is studied as well. Diffusion profiles were determined, and the diffusion kinetics of carbon is analyzed quantitatively. All samples studied were described in Chapter 3. The stacks for the sample MAG03, MAG04, and RU01 were represented in Fig. 3-8.

6.2 Carbon Diffusion Kinetics

Fig. 6-1 shows the change in normalized magnetic coercivity (H_c) of the Co-Pt-TiO₂ films (Sample MAG03) corresponding to Ru film thickness. The coercivity decreases as Ru film thickness is reduced. The drop of coercivity is caused by the carbon

diffusion in Co-Pt-TiO₂ structure, and the impact of carbon diffusion increases as its thickness increases [91]. The dead layer formation at the interface area is believed to be less evident with introduction of Ru barrier, which also decreases the downshift of H_c. As the deposition pressure for Co-Pt-TiO₂ films goes up, H_c down-shifts more, owing to more diffusion of carbon into more porous Co-Pt-TiO₂ at higher argon pressure. The change in the chemical environment of the alloying elements in the structure leads to change in the magnetic properties of the Co-Pt-TiO₂ films.

Fig. 6-1 Magnetic coercivity (H_c) of Co-Pt-TiO₂ films coated with Ru and C layers of varied thickness. Co-Pt-TiO₂ films were sputter-deposited at Ar pressures of 50, 80, and 120 mTorr. Total thickness of Ru and carbon films was fixed at 4 nm

The faster diffusion of carbon in Co-Pt-TiO₂ films prepared at higher sputtering pressures is associated with the film properties such as density and surface roughness. Co-Pt-TiO₂ films deposited at varied Ar pressures were analyzed using X-ray Reflectometry (XRR). The oscillation curves were obtained as in Fig. 6-2, and critical angles correlated to film density were measured as in Fig. 6-3. The fast damping

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pattern and small critical angle presented at higher Ar pressure indicated more porous structure which provided more “short circuit” diffusion paths to carbon.

Fig. 6-2 XRR oscillation curves of Co-Pt-TiO₂ films of single layer deposited at varied sputtering pressures

Fig. 6-3 Critical angles of Co-Pt-TiO₂ films measured by XRR

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To understand the results observed in Fig. 6-1, SIMS compositional depth profiling for carbon was carried out on sample MAG04 and RU01. The elemental depth profile of carbon in its own bulk region and sub-interface area in Co-Pt-TiO₂ and Ru films was established in Fig. 6-4 and Fig. 6-5. Sub-plantation of carbon into Co-Pt-TiO₂ was detected in the as-deposited sample as shown in Fig. 6-4. Carbon was driven further into the bulk area of Co-Pt-TiO₂ after annealing at 50 to 200 °C. The profiles clearly revealed long penetration “tails” due to diffusion. Thickness loss in carbon layer was seen for sample MAG04 annealed at 200 °C, which is believed due to carbon oxidation by the oxygen released from Co-Pt-TiO₂ layer underneath. The interface structure in sample RU01 was intact after annealing up to 200 °C (Fig. 6-5). Very limited amount of carbon atoms was detected in the sub-interface area in sample RU01. There was no thickness loss which means with Ru interlayer the carbon layer is thermodynamically stable. This may be attributed to the higher graphitization activation energy when Ru barrier layer is present. The graphitization process with and without Ru barrier has been discussed in details in chapter 5. Results obtained in Fig. 6-4 and Fig. 6-5 suggested that carbon is ready to penetrate into magnetic Co-Pt-TiO₂ film of porous structure during deposition, and diffuse into the sublayer under external driving force, i.e. thermal treatment. Based on the etch rate of 0.05 nm/s in Co-Pt-TiO₂ for our SIMS setup, carbon diffused up to 14.4 nm deep into Co-Pt-TiO₂ in as-deposited sample MAG04. In contrast, carbon concentration remained low at the sub-interface area in sample RU01. Carbon diffusion in Ru was very little from 50 to 200 °C.

Fig. 6-4 SIMS depth profile for carbon films coated on the top of magnetic film

Fig. 6-5 SIMS depth profile for carbon films coated on the top of Ru layer

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In our experiment, both Co-Pt-TiO₂ and Ru films are polycrystalline. Our conditions match the type B diffusion kinetics of Harrison's classification when the samples were annealed at low temperatures, and with relatively short annealing time. As seen in Fig. 6-4, diffusion profile of carbon consists of two well defined regions: one is the near-surface area dominated by lattice-diffusion and the other deep penetrating grain-boundary diffusion tail. This diffusion profile is very similar to what was generalized by Harrison's in his kinetics classification. The lattice diffusion or bulk diffusion is believed to occur due to atomic defects in crystals, such as vacancies and interstitials. Those defects appeared more easily and frequently at the interface area because the top layers of Co-Pt-TiO₂ adjacent to carbon film were subject to plasma damage during carbon deposition. The diffusion at the second zone of a long penetrating "tail" can be explained by the granular structure of Co-Pt-TiO₂ as shown in an in-plane Transmission Electron Microscope (TEM) image in Fig. 6-6. The Co-Pt-TiO₂ deposited at 80 mTorr showed a distinct granular structure with clearly segregated grain boundaries. In the image, Co-Pt-TiO₂ film shows a well isolated and uniform granular structure. The averaged grain size was about 10 nm. From the TEM image, the distinct grain boundaries of Co-Pt-TiO₂ film provide high-diffusivity channels for carbon diffusion, because the mobility of atoms along grain boundaries is usually much higher than in the lattice [112]. This explains the compositional depth profile of carbon in Fig. 6-4 where after anneal, grain boundary tail is clearly appreciable. However, the carbon diffusion profile in Fig. 6-5 suggests otherwise when Ru layer is present. The gradient of the line in Fig. 6-10, which determines the type of diffusion mechanism involved in sample RU01, is almost flat. It is therefore believed that the diffusion in Ru was confined to the surface [163]. The insignificant amount of carbon in Ru is explained by its grain structure as measured by XRD in Fig. 6-7. There was a

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minimum (100) peak intensity (at 38.25°). The intensity of (002) peak corresponding to c-axis orientation at about 42.05° was comparably small as well. There is no preferred orientation. All these suggest a nano-crystalline structure of Ru that impedes the carbon diffusion across the Ru film. Tan and others [164], however, observed amorphous Ru film as-deposited using ion beam sputtering. With a structure of grains in nanometer size, the Ru film in sample RU01 is believed to be dense. Carbon diffusion would then become more difficult. Improvement of barrier effect through grain size reduction for copper metallization using TaN film has been demonstrated by Takeyama et al. [165]. Carbon diffusion in Ru is believed to be interstitial, not substitutional, because there is no carbide formation detected and Ru atomic size is almost twice of carbon.

Fig. 6-6 In-plane TEM image for Co-Pt-TiO₂ film deposited at 80 mTorr

Fig. 6-7 X-ray diffraction spectra for Ru film deposited at room temperature (2 kW, 5 mT) with glass substrate. Peaks are marked as ■ for SiO₂ (substrate) and ▼ for Ru

Fig. 6-8 Fitted carbon SIMS depth profile for as-deposited and annealed carbon-Co alloy bi-layer structure

Fig. 6-9 Fitted carbon SIMS depth profile for as-deposited and annealed carbon-ruthenium bi-layer structure

Using the solution of the Fick's Second Law of diffusion to fit the data presented in Fig. 6-4 and Fig. 6-5 based on constant surface concentration [166], after time t at temperature T , the carbon profile in the layer is:

$$c / c_s = 1 - \operatorname{erf}(x / 2 \sqrt{Dt}) \quad (6-1)$$

where x is the distance from the surface, c and c_s are the concentrations of carbon at location x nm into the film and at the surface, respectively, and D is the diffusion coefficient. The results were plotted in Fig. 6-8 and Fig. 6-9 for carbon in Co-Pt-TiO₂ and carbon in Ru. The values of $2\sqrt{Dt}$ were obtained based on the fitting results for samples annealed at varied temperatures, and listed in Table 6-1.

Table 6-1 Diffusion length and diffusion coefficient values for different samples

Temperature, °C	C diffusion in Co-Pt-TiO ₂		C diffusion in Ru	
	Diffusion length, nm	Diffusion Coefficient D , nm ² /s	Diffusion length, nm	Diffusion Coefficient D , nm ² /s
25	3.4	0.0963	2.2	0.0403
50	4.1	0.1401	2.2	0.0403
100	4.6	0.1763	2.3	0.0441
150	5.4	0.2430	2.4	0.0500
200	6.3	0.3308	2.6	0.0542

Based on data in Table 6-1, the Arrhenius diagram was plotted in Fig. 6-10. The linearity of the curves agrees well with the thermal dynamic description of diffusion coefficient D . The Arrhenius equations for C diffusion in Co-Pt-TiO₂ and Ru were therefore obtained as:

$$D \text{ (nm}^2\text{/s)} = 2.2596 \exp (-7721 \text{ Jmol}^{-1} / kT) \quad (6-2)$$

and

$$D \text{ (nm}^2\text{/s)} = 0.0898 \exp (-2079 \text{ Jmol}^{-1} / kT) \tag{6-3}$$

respectively, where k is Boltzmann’s constant. The pre-exponential factor D_0 in eq.(6-2) is one to two orders of magnitude higher than that in eq. (6-3), indicating the readiness of carbon diffusion in Co-Pt-TiO₂ and the effectiveness of Ru as a diffusion barrier.

Fig. 6-10 Arrhenius diagram obtained from curves fitted based on diffusion from constant surface concentration model

6.3 Summary

In this chapter, we focus on the diffusion behavior of hydrogenated amorphous carbon into Co-Pt-TiO₂ and Ru films. Impact of carbon on Co-Pt-TiO₂ composite film and its diffusion in Co-Pt-TiO₂ and Ru films were studied using Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS). Magnetic coercivity drop was observed for Co-Pt-TiO₂ composite films coated with Ru and carbon hybrid overcoat at varied thickness ratios. The poisoning effect was reduced with increasing Ru thickness, and

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more porous structure of Co-Pt-TiO₂ is more inclined to the changes in carbon thickness. ToF-SIMS analysis of carbon compositional depth profile showed that carbon can readily diffuse in Co-Pt-TiO₂ film. In contrast, its diffusion in Ru film is limited to the sub-surface area even after argon annealing up to 200 °C. Carbon diffusion in Co-Pt-TiO₂ is dominated by grain boundary diffusion and it is limited to sub-surface in Ru. This explains the poisoning effect of carbon diffusion in magnetic Co-Pt-TiO₂ films and that Ru is a reasonable choice as carbon diffusion barrier. Based on Harrison's grain-boundary diffusion classification, carbon diffusion in Co-Pt-TiO₂ film belongs to type B kinetics regime. Curve fitting for carbon diffusion profiles according to constant interface concentration diffusion model indicated the diffusion length and diffusion coefficient of carbon in Co-Pt-TiO₂ are much higher than those in Ru film, which further justifies why Ru is able to work as a barrier impeding carbon diffusion. Activation energy for carbon diffusion in Ru is much lower than that in Co-Pt-TiO₂ film.

Chapter 7 Characteristics of Hydrogenated Carbon Films with Ru Interlayer

7.1 Introduction

It has been demonstrated, in previous chapters, that Ru barrier layer is effective in preventing carbon diffusion into magnetic films, thus maintaining stable magnetic performance of the underlying structure. Understanding of the properties of hydrogenated diamond-like carbon (DLC) films and kinetics of its deposition, which are influenced by both the process parameters and the characteristics of the substrate on which they are deposited, is essential. In our study, DLC films have been deposited, using C_2H_2 source gas, on aluminum substrates with Ru interlayer in a commercial hot filament PECVD deposition system. Influence of various process parameters such as substrate temperature, and C_2H_2 flow rate on deposition kinetics has been assessed. Optimization of process parameters to obtain the maximum DLC film deposition rate with optimized properties will be carried out. Corrosion behavior of DLC films with Ru interlayer was characterized by linear sweep voltammetry. The feasibility of dual-layer overcoat structure in combination of Ru and DLC was evaluated.

7.2 Carbon Growth Kinetics with Ru Interlayer

7.2.1 Temperature Effect on Film Growth and Properties

Substrate temperatures was evaluated up to 350 °C beyond which the structure and composition of C:H films are believed to significantly change [167]. The deposition rate as a function of substrate temperature was plotted in Fig. 7-1. It was observed that the deposition rate decreased with increasing temperature. The trend is similar to that

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reported by Kessels et al. [168]. For plasma deposition of hydrocarbon films, there are three general stages during the process, i.e. the reactions in the plasma (gas molecule dissociation, ionization etc.), the plasma-surface interaction and the subsurface reactions in the film [169]. With C_2H_2 precursor, it is assumed that C_2H and H are the major radicals in the plasma contributing to film growth [168]. It is known that dissociation reaction of C_2H_2 gas is exothermic and thus inversely affected by temperature. At higher substrate temperatures, the amount of C_2H immediately above the substrate surface, which is the product of C_2H_2 dissociation, is reduced. Furthermore, the growth rate decreases with increasing substrate temperature due to a less efficient incorporation of neutral radicals based on the adsorbed layer model [170]. The etching rate through erosion by atomic hydrogen, which increases with increasing substrate temperature, also plays an important role in film growth rate observed in Fig. 7-1. Substrate temperature impact on film growth rate can be further understood by calculating the activation energy of the process concerned. The natural logarithm of film deposition rate with C_2H_2 CVD process as a function of inverse Kelvin temperature is shown in Fig. 7-2. The apparent activation energy (E_a) of 914.6 Jmol^{-1} was derived from the Arrhenius plot in Fig. 7-2 based on Arrhenius equation below.

$$k = Ae^{-E_a/RT}$$

where k is the carbon film deposition rate, A is the pre-exponential factor, R is the gas constant, and T is Kelvin temperature. The E_a value obtained here is considerably lower than the results reported by others [171]. The discrepancy might be attributed to the differences in the precursor selection, filament temperature and the range of surface temperatures applied in our studies. It showed that the hydrocarbon film deposited on Ru-coated surface in our study is weakly activated by heat.

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Fig. 7-1 Carbon film deposition rate at varied substrate temperatures

Fig. 7-2 Arrhenius plot of deposition rate vs. 1000/T for carbon films deposited by hot filament PECVD with -120 V of substrate bias

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Hydrogenated carbon films with Ru interlayer were analyzed with XRR. A three-layer model (C/Ru/NiP) was used to fit the data. Dependence of film density on substrate temperature was shown in Fig. 7-3. The density of a-C:H film is an indication of the network coordination, and whereby the mechanical performance. The film density is also a good indicator of sp^3 fraction in hydrogen-free carbon films [169]. However, in the case of a-C:H film, it is much more complicated due to hydrogen incorporation. As CH_x groups in the film occupy a lot of space, they reduce the film density. The substrate temperature appears to have a similar effect on a-C:H as the bias. The reduction in H content is believed to be caused by substrate heating which drives off hydrogen as temperature is increased, resulting in an increase in density. Reduction in film thickness was observed by Katsuhiro for post argon annealing of hydrogenated DLC films [172]. Film density increase was accompanied with loss of H_2 as indicated in the weakened C–H absorption strength for films annealed at higher temperatures in his study.

Fig. 7-3 Film density at various substrate temperatures

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The film roughness varies with substrate temperature, as measured by AFM and shown in Fig. 7-4. At higher substrate temperature rougher film structure with larger cluster size was obtained. It is believed that surface diffusion occurs more easily than bulk diffusion, since the activation energy is lower. Surface diffusion can be promoted either by the energy associated with arrival of impinging ions which remain within the surface layers or high substrate temperature [173]. Diffusion in the surface layers of α -C:H films tends to produce clusters with highly sp^2 concentration, i.e. graphite phase at higher substrate temperature. Such clusters therefore form preferentially on the surface and produce roughening effect. The observed effect on surface roughness is consistent with results in the literature [174] [175].

Fig. 7-4 Surface roughness and AFM micrographs of carbon films deposited at varied substrate temperatures

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The I_D/I_G ratio and G-peak positions were summarized in Fig. 7-5. The I_D/I_G ratio and G-peak wavenumber increased with deposition temperature. Increase in the I_D/I_G ratio indicates the increase of number of sp^2 clusters and its size enlargement in DLC films [176]. The G-peak position in the Raman spectrum provides the information about the sp^2/sp^3 ratio [177] [178]. The G-peak position for DLC films in the study traveled to a higher wavenumber with increasing temperature, meaning an increase in the sp^2 bonding fraction in the structure. Therefore, the Raman spectrum showed that higher thermal energy caused the DLC structure to be transformed into the graphite structure. Increased temperature also led to release of hydrogen contents in DLC films and to a transition from sp^3 to sp^2/sp^3 carbon hybridization. Some tetrahedral bonds in the films have been broken and transformed to trigonal structure. This development also causes increase in the number of sp^2 clusters (or graphitization). The result is shown in Fig. 7-5, in sync with the surface roughening effect shown in Fig. 7-4. Therefore, proper selection of energy range and substrate temperature may minimize the graphitization and preserve sp^3 carbon bonding structure.

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Fig. 7-5 I_D/I_G ratio and G-peak positions extracted from Raman data as a function of substrate temperature.

Fig. 7-6 XPS spectra of hydrogenated DLC films deposited at 60, 180, and 300 °C

The carbon films were characterized by XPS for sp^3 and sp^2 bonds. *C1s* spectra of the films prepared at different temperatures were shown in Fig. 7-6. The XPS core level

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spectra were analyzed by non-linear least square fitting after a Shirley background subtraction. The peak position in the *C1s* envelope shifts toward lower binding energy with increase in deposition temperature, corresponding to the shift of binding energy from 285.1 eV to 284.9 eV and then 284.4 eV when temperature changed from 60 °C to 180 °C and 300 °C. The core level *C1s* XPS spectra of the a-C:H films in Fig. 7-6 can be decomposed into two components. The first component is centered at approximately 284.4 eV corresponding to sp^2 C-C bonds, and the second is at 285.8 eV which is meant sp^3 C-C bonds. The temperature dependent sp^2 and sp^3 structure evolution observed is consistent with the Raman analysis demonstrated in Fig. 7-5. Higher deposition temperature resulted in an increase in the graphitic fraction in the film and the clustering of the sp^2 bonded carbon. This indicates the phase transition from diamond-like to graphite-like structure as a function of temperature.

7.2.2 C₂H₂ Gas Flow Effect on Film Growth and Properties

The deposition rate derived from the film thickness measured by XRR and deposition time for each sample varied with C₂H₂ flow rate are given in Fig. 7-7. Deposition rate increased almost linearly when C₂H₂ flow rate increased from 20 to 45 sccm, while it started to saturate when the flow rate was at 50 sccm, beyond which it was not studied due to the capacity constraint of Mass Flow Controller (MFC). The results suggested that the DLC films formation were chemically restricted by the supply of ion species. When C₂H₂ flow rate is high enough, the mean free path of the particles in the chamber becomes shorter. Ionic species which contribute to film deposition might be blocked and/or recombined to neutral C₂H₂, resulting in a saturated or lower deposition rate. Similar trend was reported by Miyakawa et al. who studied the dependence of DLC deposition rate on C₂H₂ flow rate by means of filtered arc deposition technique [179].

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A reduced mass density of DLC films from 1.89 to 1.44 g/cm³ measured by XRR was also noticed as C₂H₂ flow rate increased from 20 to 50 sccm. The result could be both explained by energetic impingement of ionic particles and H incorporation into the films. Increased gas flow raises the chance of collisions between atoms and ions in plasma, which results in more ion scattering and broadens the ion energy distribution. It leads to the loss of the effective energy of the impinging ions on the growing films. Increased C₂H₂ flow implies a reduction in the plasma density and an increase of H incorporation in the films as well. Rossnagel et al found film density varied inversely with gas pressure. The variation can be attributed to the ion fraction being higher at low gas pressures [180]. The reduction of C₂H₂ gas flow to certain level favors the formation of high density and low-hydrogen content DLC films without compromising the deposition rate. The range within 30-40 sccm will be advised as the optimal conditions to achieve high density without compromising manufacturability for the setup in our study.

Fig. 7-7 Deposition rate and film density dependence on C₂H₂ gas flow

The dependence of sp² and sp³ contents on C₂H₂ flow rate was studied. Similarly, intensity ratio of the D and G peaks (I_D/I_G) and G-peak positions extracted from Raman spectra were plotted as a function of C₂H₂ gas flow shown in Fig. 7-8. The G-peak positions and the I_D/I_G ratio showed a clear minimum, and varied with the C₂H₂ flow. As the C₂H₂ gas flow increased from 20 to 40 sccm (first stage), the G peak and I_D/I_G ratio decreased. As it increases further beyond 40 sccm (second stage), the trend reversed. It has been reported that the position of the G peak and I_D/I_G intensity ratio are important factors determining the film structure. The increase of G shift and I_D/I_G ratio when C₂H₂ flow rate is higher than 40 sccm reveals the decrease of sp³ fraction and increase of sp² fraction. The hardness of the films which is corresponding to I_D/I_G ratio is expected to decrease when C₂H₂ is higher than 40 sccm. Studies by Wei have suggested a correlation of carbon film hardness with thickness [181]. The phenomenon in Fig. 7-8 can be explained by the role of hydrogen in the films. It is generally

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accepted that hydrogen in a-C:H was to promote sp^3 bonding, but a too high H content produces many $=CH_2$ groups and a poorly cross-linked network which is on the other hand affected by ion bombardment [182]. Dehydrogenation to produce such cross-linked network driven by energetic ions is believed to be hindered at higher gas flow rate. In our experiment, sp^2 fraction organized in aromatic rings decreased for low flow rates as indicated by I_D/I_G ratio. The down shift of G-peak can be explained by the change of the sp^2 configuration from mainly rings to short chains (olefins). When C_2H_2 flow rate exceeded 40 sccm, the film tends to have polymer-like structure. More free hydrogen atoms are able to exist as clusters between the planes and in the voids. High hydrogen concentration enhances the formation of a polymeric CH_n ($n>1$) structure, which changes the bonding constraints of sp^3 -bonded carbon by binding more H carbons. The increase of I_D/I_G and shift of G peak position to higher values could be attributed to the simultaneous decrease of C–C sp^3 (and/or C=C sp^2) bonds and increase of C–H bonds, because the probability of broken bond passivation by hydrogen atom should be higher for high hydrogen concentration in the films. The disruption of the C–C sp^3 and C=C bonding by atomic hydrogen leads to the disordering of the films [183]. As a result, the hardness of the DLC film was reduced as the structural integrity of the films was weakened due to the presence of a large amount of H. Hydrogen effusion experiments have shown that H-rich a-C:H films present an increased density of voids, which will influence the network connectivity and hardness [184]. Gas flow below 40 sccm is preferred to obtain a film with adequate mechanical performance in our study.

Fig. 7-8 I_D/I_G ratio and G-peak positions extracted from Raman data as a function of C_2H_2 gas flow for carbon deposition

XPS analysis on films deposited at varied C_2H_2 flow rates as shown in Fig. 7-9 further confirmed the observation in Fig. 7-8. The binding energy of $C1s$ shifted towards higher value from 284.7 eV to 284.9 eV when C_2H_2 flow increased from 20 to 40 sccm, and then shifted back to 284.6 eV as flow rate further increased to 50 sccm. The perceived change illustrated that the sp^3 content in the film bonding structure depends directly on the increasing C_2H_2 flow. Reduction of sp^2 content was observed when C_2H_2 increased from 20-40 sccm, and sp^2 content increases or saturates when C_2H_2 flow rate increases further.

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Fig. 7-9 XPS spectra of hydrogenated DLC films deposited at varied C_2H_2 flow rate of 20, 35, 40, and 50 sccm

The film surface morphology affected by C_2H_2 gas flow was studied by AFM measurements and shown in Fig. 7-10. It demonstrated that the increase of C_2H_2 flow from 20 to 45 sccm promotes film with rougher surface structure. An increase of C_2H_2 led the DLC films to be grown under less ion impingement from positively charged ions such as $C_2H_2^+$. The ion-atom interactions induced by the impingement of these ions on the growing film surface were complicated and resulted in films grown with more randomly oriented coarse clusters. The results indicate that the films produced at gas flow lower than 40 sccm are more suitable, because low friction coefficient related to lower values of roughness is expected to enhance mechanical performance of the coating.

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Fig. 7-10 Surface roughness dependence on C₂H₂ flow rate and AFM micrographs of DLC films deposited at C₂H₂ flow of 20, 35, and 45 sccm

7.3 Carbon Anti-corrosion with Ru interlayer

7.3.1 Theoretical Background

7.3.1.1 Tafel Equation and Extrapolation

Corrosion normally occurs at a rate determined by equilibrium between two opposing electrochemical reactions, one of which is known as the anodic reaction. The opposite reaction is called the cathodic reaction, during which a solution species is being reduced and electrons are being removed. The flow of electrons from these two reactions is balanced and no net electron flow and hence current occurs when these two reactions are in equilibrium [185] [186].

The corrosion rate can be predicted from the polarization curve by considering following two facts [186]:

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- 1) A single potential value will be obtained following measurement of a material immersed in solution, implying that all reactions are occurring at the same potential.
- 2) By the conservation of charge in the absence of any applied potential or current, all the electrons produced in oxidation reactions are consumed in the reduction reaction.

The corrosion rate can be found if the corrosion current I_{corr} can be determined [187]. However, I_{corr} cannot be measured directly by any measuring techniques. I_{corr} is usually estimated from current versus voltage data with the polarization scan centered upon the open circuit potential or the corrosion potential. The measured data is then fitted to a theoretical model for the corrosion process. One such model the Tafel equation which is based upon the assumption the rate of both the anodic and cathodic processes are under the control of the kinetics of electron transfer reaction at the surface as shown below [186]:

$$I = I^0 e^{(2.303)(E - E^0) / \beta}$$

Where I is the current, I^0 is the exchange current which is reaction dependant constant, E is the electrode potential, E^0 is the equilibrium potential And β is the reaction's Beta coefficient.

This equation governs the behavior of one reaction. In a corrosion system, there are two reactions, i.e., the cathodic and the anodic ones. Combining Tafel equations for both the anodic and cathodic reactions in a corroding system yield the Butler-Volmer equation [188] [189]:

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$$I = I_{\text{corr}} \left[e^{\left(\frac{2.303(E - E_{\text{corr}})}{\beta_a} \right)} - e^{-\left(\frac{2.303(E - E_{\text{corr}})}{\beta_c} \right)} \right]$$

Where, I is the measured current, I_{corr} is corrosion current, E_{corr} is the corrosion potential, β_a is anodic Beta coefficient, And β_c is the cathodic Beta coefficient.

The Butler-Volmer equation predicts that at $E = E_{\text{corr}}$ the current is zero as the two exponential terms cancel each other out. When E is close but not identical to E_{corr} , the overall current is determined by the two exponential terms. At potential sufficiently apart from the E_{corr} one exponential term will dominate and the other term will be negligible. In such a scenario, plotting the polarization curve in a logarithmic scale will result in a straight line and this plot of $\log I$ versus E is known as the Tafel plot [190]. From the Tafel plot as shown in Fig. 7-11, the linear portions of $\log I$ versus E can be extrapolated back to the point where it intersects at E_{corr} on the y-axis. The corresponding point at the x-axis is known as I_{corr} , the corrosion current [186, 187, 190]. The sharp point seen at E_{corr} where the current is zero is due to the characteristics of using a log scale which is difficult to plot on a finite piece of paper.

In order to improve the accuracy of extrapolation, two rules are commonly applied, the first of which is that no extrapolation should be done within 50 mV of the Corrosion Potential and the second rule is that at least one branch of the polarization curve should be linear on the semi logarithmic scale over one decade of current density [186].

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Fig. 7-11 Tafel extrapolation [190]

7.3.1.2 Corrosion Rate

By approximating the exponential terms in the Butler-Volmer equation with the first two terms of a power series expansion, we can relate the corrosion current to the polarization resistance (R_p) through the Stern-Geary equation as shown [191]:

$$I_{corr} = \frac{B}{R_p} ; \text{ Where } B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$$

The corrosion current can be related to the corrosion rate by combining the faraday laws with an electrochemical reaction of known stoichiometry.

Faraday's first law states that the mass of an element discharged at an electrode is directly proportional to the amount of electrical charge passing through the electrode.

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According to Faraday's second law, if the same amount of electrical charge is passed through several electrodes, the mass of an element discharged is directly proportional to the atomic mass of the element divided by the number of moles of electrons required to discharge one mole of the element from the material being discharged at the electrode.

The corrosion rate is then given by the following equation [186] [187]:

$$CR = \frac{(3272)(I_{corr})(EW)}{(SA)(d)}$$

Where, CR is the corrosion rate given in mm/year, EW is the equivalent weight of the material which is given by the atomic weight (g/mol) divided by the number of electrons involved in the reaction, SA is the surface area of the electrode (cm²), and d is the density of the material (g/cm³)

7.3.2 Corrosion Results and Discussion

The samples used for electrochemical analysis were prepared according to the description in section 3.3.6, and immersed in 0.2 M NaCl aqueous solution for corrosion test. Fig. 7-12 shows the characteristic potentiostatic polarization curve of the uncoated Al substrate. A corrosion current of 0.4639 μ A for the uncoated sample was measured. The DC cyclic polarization curves of samples with overcoat are collected in potentiostatic mode (controlled potential) and presented in Fig. 7-13. The curves were generated by first cathodically polarizing the samples at a rate of 0.458 mV/s from the corrosion potential to a lower limit of -0.3 V vs. SCE. For anodic polarization, the direction of potential change was simply reversed. As observed, the absolute value of the slope of extrapolated anodic current was higher than cathodic one

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for all samples. It means that the anodic polarization resistance is higher than cathodic polarization resistance. This can be understood as more substrate area was exposed to corroding solution after cathodic polarization test which is conducted prior to anodic one.

Fig. 7-12 Polarization curve for bare Al substrate without overcoat

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Fig. 7-13 Polarization curves for Al substrates coated with a) 3.5 nm of carbon only; b) 3.0 nm of carbon and 0.5 nm of Ru; c) 2.5 nm of carbon and 1 nm of Ru; d) 1.5 nm of carbon and 2 nm of Ru; e) 3.5 nm of Ru only.

The Tafel plots obtained in Fig. 7-12 and Fig. 7-13 were extrapolated, which yielded the corrosion current I_{corr} , the cathodic beta constant β_c and the anodic beta constant β_a . Other electrochemical parameters which were obtained directly from the polarization curve or by calculation based on previously described formulae are summarized in Table 7-1. For all the coated samples, both corrosion potential (E_{corr}) and corrosion current (I_{corr}) are significantly lower than those of bare sample, which indicates that the corrosion resistance of the Al substrate was improved with introduction of DLC, Ru, or DLC/Ru dual layer coatings.

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Table 7-1 Electrochemical parameters for the bare and coated Al samples tested in 0.2 M NaCl solution

Samples	E_{corr} (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	R_p (ohm)
Bare Al	-0.413	-0.638	38510
Carbon 0 nm, Ru 3.5 nm	-0.121	-0.292	538333
Carbon 1.5 nm, Ru 2.0 nm	-0.122	-0.00684	1584333
Carbon 2.5 nm, Ru 1.0 nm	-0.109	-0.00415	4215667
Carbon 3.0 nm, Ru 0.5 nm	-0.123	-0.00339	5358000
Carbon 3.5 nm, Ru 0 nm	-0.107	-0.00156	7720000

Fig. 7-14 Corrosion rate of samples with overcoat of varied thickness ratio (total thickness of carbon and Ru is 3.5 nm)

The corrosion current obtained by Tafel extrapolation can be converted into a more quantifiable form by means of the corrosion rate as discussed earlier. Corrosion rates in terms of thickness loss for coated samples are shown in Fig. 7-14. All the coated

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samples showed slower corrosion rate than bare sample whose corrosion rate was 6.95 $\mu\text{m}/\text{year}$. Among the coated samples, it was evident that the corrosion rate is inversely proportional to carbon thickness. Thicker carbon overcoat produced better anti-corrosion property. In Fig. 7-14, the sample with pure Ru coating (3.5 nm) has the worst performance even though it offers some anti corrosion protection to the substrate due to its poorer electrical conductivity than Al. Its corrosion rate was 3.19 $\mu\text{m}/\text{year}$ which is in the same order as bare sample. It is believed that the electrical conductance of Ru films deteriorates its anti-corrosion performance compared to samples with DLC coating. In addition, the CVD deposited carbon films provided better coverage than that of the Ru overcoat which is sputter prepared. Thereby the path in which dissolution takes place was better restricted on DLC covered substrate. Two orders of magnitude lower of corrosion rate was observed for all samples with DLC coating than bare sample. The samples coated with Ru and DLC bi-layer structure demonstrated the same order of corrosion rate as single DLC overcoat, though the performance dropped by 2-4 times when DLC thickness was reduced from 3.5 nm to 1.5 nm. Ru film itself was not adequate to fully replace carbon overcoat in terms of corrosion resistance. However, combined with the experimental results in previous chapters, it suggests a carbon overcoat scheme with ~ 1 nm thick Ru barrier is effective to minimize carbon diffusion, without compromising too much on its anti-corrosion property.

The trend observed in Fig. 7-14 can be further explained by the structure change of DLC as its thickness was reduced. It is believed that the carbon film mass density drops with more pinholes at reduced thickness. Yatsuzuka et al. has reported the thickness effect on area ratio of pinhole density in DLC films [192]. They found the area ratio of pinhole defects to substrate was decreased exponentially with increasing

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DLC film thickness. As a result, the corrosion resistance of DLC-coated specimens was improved with increasing film thickness.

7.4 Summary

A study of a-C:H films deposited on Ru interlayer using hot filament PECVD at varied substrate temperatures and precursor C₂H₂ gas flow has been presented. Film deposition rate is inversely affected by substrate temperature. Apparent activation energy (E_a) of 914.6 Jmol⁻¹ for the process was derived from the Arrhenius plot. Higher substrate temperature resulted in denser films and rougher film surface, which are believed to be mainly due to dehydrogenation process. Graphitization of carbon film occurs at higher temperatures as illustrated by the Raman spectroscopy. A process of temperature lower than 250 °C is preferred to obtain better film structure. Higher deposition rate was observed when C₂H₂ flow rate increased from 20 to 40 sccm. More porous film structure was detected at higher C₂H₂ flow due to more H incorporation and less ion impingement on growing film. Two stages of I_D/I_G ratio evolution pattern for Raman spectroscopy on carbon films were observed as C₂H₂ flow increased. Hydrogenation process is believed to be the key factor affecting the bonding structure of the films. Film surface morphology of higher roughness was noticed for samples prepared at higher C₂H₂ flow due to reduced peening effect. XPS analysis results confirmed the structure change of carbon films at varied deposition conditions.

Corrosion tests on Ru and DLC coated Al substrate were conducted in 0.2 M NaCl aqueous solution using potentiostatic polarization technique. Both Ru and DLC provided certain degree of anti-corrosion protection in terms of corrosion rate measured. Single layer of Ru is not able to offer sufficient electrochemical corrosion protection to Al substrate due to its electrical conductance and poorer surface coverage

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compared to CVD prepared DLC overcoat. The corrosion rate of samples with DLC overcoat and Ru interlayer is in the same order as that with single DLC layer. Degradation of anti-corrosion performance was observed to be proportional to the DLC thickness. The increase of pinhole density in DLC films as its thickness shrank, which is corresponding to film mass density drop measured by XRR, is believed to induce faster corrosion rate. A structure of DLC with 1 nm Ru interlayer is promising to maintain similar level of anti-corrosion property offered by DLC single layer, and to achieve minimum intermixing between magnetic and carbon films as discussed in previous chapters.

Chapter 8 Conclusions and recommendations

8.1 Conclusions

A novel film structure with a ruthenium (Ru) intermediate layer underneath the carbon overcoat in magnetic recording media has been investigated. The in-depth studies of interface behavior and effectiveness of Ru as a carbon diffusion barrier and protective layer for magnetic film are the most important results of this project. The conclusions are drawn in the following aspects.

Process study of Ru films prepared by magnetron sputtering shows that lower pressure is preferred to achieve higher degree of (002) (c-axis) orientation which is suppressed at higher pressure due to excessive Ar incorporation at grain boundaries. On the other hand, higher power density encourages Ru c-axis orientation, though the effect is not as significant as the pressure within the process window studied. Smooth surface morphology is obtained at low Ar pressure and high power density as measured by X-ray Reflectometry (XRR) and Atomic Force Microscope (AFM). Rough surfaces under high Ar pressures and low sputtering power is probably due to insufficient diffusion energy and surface mobility of adatoms. Film density measurement based on XRR curves showed denser structure at lower Ar pressures and higher power densities. Void formation under such conditions due to shadowing effect is minimized when Ru atoms have reduced kinetic energies. It is concluded that Ar pressures lower than 10 mTorr and power densities above 5.61 W/cm^2 are desired to achieve both dense structure and smooth morphology.

Magnetic properties of CoCrTa films are influenced by plasma ions bombardment on substrate during carbon deposition. The impact is more evident when the substrate is

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negatively biased at high voltages. With the introduction of an ultra-thin layer of Ru intermediate layer in-between the magnetic layer and the carbon overcoat, the magnetic performance of the film is more consistent. There is no remnant magnetization degradation even after N₂ annealing at 200 °C for 30 minutes. Surface topography studied by AFM indicates that the film structure with an Ru intermediate layer is thermally more stable with less Root Mean Square roughness change after N₂ annealing. X-ray Photoelectron Spectroscopy analysis shows tantalum carbide formation at the interface between CoCrTa and carbon overcoat in absence of Ru interlayer. A thin Ru barrier layer with ~1.0 nm is effective in preventing the intermixing between magnetic film and carbon overcoat.

With direct contact between β -tantalum films and carbon, Phase transformation of β -Ta to α -Ta started at 300 °C, and tantalum carbide phase was detected by X-ray Diffraction for samples annealed at 400 °C and 500 °C. Inclusion of a Ru interlayer between Ta and carbon films made beta phase of Ta film stable up to 400 °C and obstructed carbide formation. The stability of β -Ta up to 400 °C in C/Ru/Ta, together with the absence of TaC_x peaks, clarifies the performance of the Ru interlayer as a barrier in impeding carbon diffusion into the lattice of Ta film. Compared to the C/Ta dual layer structure, the β -Ta and carbon film with Ru in between them became more thermally stable.

Both as-deposited C/Ta and C/Ru/Ta films demonstrate sharp interference patterns in XRR. Film roughness at surface and interface in C/Ta stack increased considerably after N₂ annealing at 300 °C and the fringe shape and amplitude changed significantly. In contrast, there was almost no change in XRR reflection pattern for structures with Ru interlayer until samples were annealed at temperature of 400 °C. It indicates that

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the surface and interfaces in Ta/Ru/C stay intact even after N₂ annealing up to 400 °C. Incorporation of Ru intermediate layer helps to minimize the intermixing between tantalum and carbon films.

As-deposited hydrogenated carbon films present amorphous structure in both C/Ta and C/Ru/Ta constructions. Graphitization of carbon films were observed at elevated temperatures, which is an indication of reduction of the sp³ content and weakened diamond-like feature. However, carbon bonding in C/Ru/Ta structures tends to maintain their sp³ content. In C/Ru/Ta samples, the degree of graphitization of carbon is smaller than that of C/Ta, showing that the carbon films in C/Ru/Ta are thermally more stable than the C/Ta films. I_D/I_G increases with the annealing temperature. I_D/I_G for C/Ru/Ta is about 7-15% lower than that of C/Ta, which explains the consistently smaller amount of sp² fraction in C/Ru/Ta than in C/Ta.

Carbon diffusion causes degradation of magnetic coercivity of Co-Pt-TiO₂ composite films. With the introduction of carbon-ruthenium hybrid structure, the poisoning effect was reduced. Co-Pt-TiO₂ with more porous structure tends to be more sensitive to carbon diffusion. Second Ion Mass Spectroscopy depth profiling for carbon composition showed that carbon readily diffuses into Co-Pt-TiO₂ granular structure, while its diffusion in Ru is limited to sub-surface area at temperatures ranging from 50 to 200 °C. Carbon diffusion in Co-Pt-TiO₂ is dominated by grain boundary diffusion and that in Ru is believed to be limited to near surface areas. The diffusion of carbon in Ru is small even after argon annealing up to 200 °C. Based on Harrison's classification of grain-boundary diffusion, carbon diffusion in Co-Pt-TiO₂ film belongs to type B kinetics regime. Curve fitting for carbon diffusion profiles based on simplified constant surface concentration model indicated that diffusion coefficient of

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carbon in Co-Pt-TiO₂ ($D_0 = 2.2596 \text{ nm}^2/\text{s}$) is much higher than that in Ru ($D_0 = 0.0898 \text{ nm}^2/\text{s}$), even though the activation energy for carbon diffusion in Ru ($E_a = 2079 \text{ Jmol}^{-1}$) is much lower than that in Co-Pt-TiO₂ ($E_a = 7721 \text{ Jmol}^{-1}$) film.

The deposition rate of a-C:H films on Ru interlayer using hot filament Plasma Enhanced Chemical Vapor Deposition (PECVD) is inversely affected by the substrate temperature. Apparent activation energy (E_a) of 914.6 Jmol^{-1} for the process was derived from the Arrhenius plot. Higher substrate temperature resulted in denser films but rougher surface due to dehydrogenation. Graphitization of carbon film occurs at increased temperature, thus deposition at temperatures lower than 250°C is preferred. The deposition rate of carbon film increases with C₂H₂ flow rate, but the film becomes more porous due to more H incorporation and less ion bombardment, resulting in decreased film hardness. Hydrogenation is believed to be the key affecting bonding structures of carbon films deposited on Ru interlayer by hot filament PECVD process.

Potentiostatic polarization corrosion tests on Ru and diamond-like carbon (DLC) coated Al substrates conducted in 0.2 M NaCl aqueous solution showed Ru alone is not able to offer sufficient electrochemical corrosion protection to Al substrate due to its electrical conductance and poorer surface coverage compared to Chemical Vapor Deposition (CVD) prepared DLC overcoat. The corrosion rate of samples with DLC/Ru structure is in the same order as those with a single DLC layer. Degradation of anti-corrosion performance was observed as DLC thickness was reduced. The increase of pinhole density in DLC films at reduced thickness, which corresponds to film mass density decrease measured by XRR, is believed to induce faster corrosion rate. A structure of DLC with 1 nm Ru interlayer is promising to maintain similar level

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of anti-corrosion property offered by DLC single layer, and to minimize intermixing between magnetic and carbon films.

8.2 Recommendations

The following are left for future work:

- The properties of carbon films may vary with substrate material properties. Therefore, further investigation on mechanical performance of magnetic recording media with C/Ru overcoat is needed. The properties of carbon films such as hardness, wear resistance, and scratch resistance should be understood in terms of their chemical composition and structure.
- Electrical performance of magnetic recording media with new overcoat scheme (C/Ru) has to be demonstrated. An actual read/write recording test to evaluate Bit Error Rate performance of the media is necessary. The goal would be to determine how well the recording disk matches with read/write head as a complete recording device in terms of areal density.
- Compatibility between lubricant and the dual layer overcoat structure needs to be studied further. Flyability test with a magnetic recording head over the media surface is advised because it has great implications on the head-disk interface (HDI) tribology. Poor bonding and adhesion between carbon and lubricant layers could lead to destructive tribological performance of the disk drive and eventual disk failure. Therefore, it is necessary to study the HDI tribology in order to successfully implement the new overcoat method in magnetic hard disk.

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- This project focused on hydrogenated carbon prepared by CVD process. Sputter prepared carbon could be another topic for study. The impact of doping with nitrogen using reactive sputtering process should be investigated because carbon overcoat prepared by sputtering is also widely used in hard disk industry.

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