CHAPTER 3 EXPERIMENTATION AND METHODOLOGY

This chapter will present experiment methods for investigate the effect of thermal stress to the changes of ta-DLC film properties. The equipments, tools and materials used in this work will be described in detail along with the processes or experimental methods underlying each section. The experiment for this work is divided into 3 main parts as following: 1) ta-DLC films deposition, 2) thermal heating condition, and 3) ta-DLC films characterization.

3.1 ta-C films deposition [13]

The setup for ta-C films deposition consists of the single vacuum chamber equipped with two RF ion beam sources: 21 cm diameter large area etch source, 18 cm diameter deposition source with dished ion beam focusing grids for ion beam sputtering, and FCA source with 90 degree curvilinear magnetic solenoid filter. Automated substrate fixture has tilt, and rotation capabilities. Size of the square pallet is 9x9 in. The pallet (substrate carrier) with mounted in the center 2 in. diameter in situ monitor is being loaded into the chamber using load-lock unit. The base pressure of the system prior to deposition was less than $3x10^{-7}$ Torr. In situ process control is being performed by two multi-wavelength J.A.Woollam ellipsometers for separate monitoring Si-Si_3N_4 and ta-C deposition. The full process typically includes 3 steps: (1) surface cleaning by Ar ion beam etching; (2) Si-Si_3N_4 sputtering deposition for adhesion improvement; (3) ta-DLC film deposition.

3.1.1 Surface cleaning by Ar ion beam etching

The purpose of this step is to remove the organic and other contaminations e.g. oxides. Ion beam etching was performed with a 120V Ar+ ion to clean the sample surface before ta-DLC deposition.

3.1.2 Si-Si3N4 sputtering

The carbon films have a poor adhesion to the magnetic materials, e.g. NiFe. To prevent the carbon films delamination in the magnetic material area, the thin interface layer is needed to provide stronger chemical bonding to the magnetic material as well as to the carbon films. That prevents the delamination of carbon and pores formation in the areas that are most sensitive to the oxygen, water penetration, and in turn to the corrosion process. Ion beam deposition was performed with a 550V Ar^+ ion to sputter the Si-Si_3N_4 material prior to ta-DLC deposition.

3.1.3 ta-DLC deposition

The ta-DLC films were deposited from a filtered beam of C^+ ions produced by a cathodic carbon arc; see the schematic diagram of the FCA system for ta-DLC deposition in Figure 3.1 [1]. The cathodic arc discharge (I_{arc} = 70 A, V_{arc} = 23 - 25 V) between the grounded graphite cylinder cathode and anode generates a relatively high flux of C^+ ions providing a reasonable ta-DLC deposition rate. The arc discharge plasma was filtered by 90 degree curvilinear magnetic solenoid in order to remove the neutral

species and macroscopic particles (MP), leaving a beam of high-density plasma stream. A relatively high magnetic field (around 60 mT at 8 A coil current) was used for magnetic filter to provide the deposition by mainly C^+ ions. A specially designed baffle trap assembly was installed into the duct to enhance the MP filtering efficiency. For a further MP reduction, the positive bias potential 0–30 V could be applied to the filter bend (duct) [1,13-14]. To increase the effective area of deposition, the deflection magnetic coil was placed around the exit of the plasma duct. It provides the proper shift of the plasma beam at the substrate carrier plane. Fixture tilt angle can be varied from 0 degree (ion beam is normal to the substrate surface) up to 90 degree.

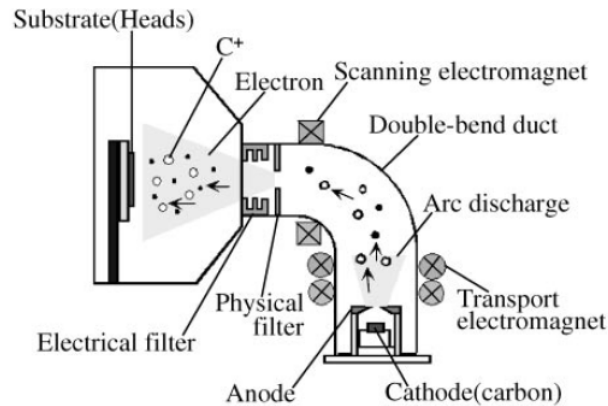

Figure 3.1 Schematic diagram of the FCA system for ta-C deposition [1]

3.1.4 Deposition tool

The following images are the deposition tool that used in the films preparation. Samples were prepared using Veeco's DC-FCA tool (model DLC-350V FCA). Pre-deposition surface etching, adhesion material film deposition and ta-DLC film deposition were made within a single chamber which equipped with two RF ion beam sources and FCA source with 90º curvilinear magnetic solenoid filter. Ion beam etching was performed with a 120V Ar+ ion to clean the sample surface before adhesion and ta-DLC deposition. 1.0 nm of Si-Si3N4 was then deposited to act as an adhesion layer prior to the DLC coating.

Figure 3.2 Deposition tool image

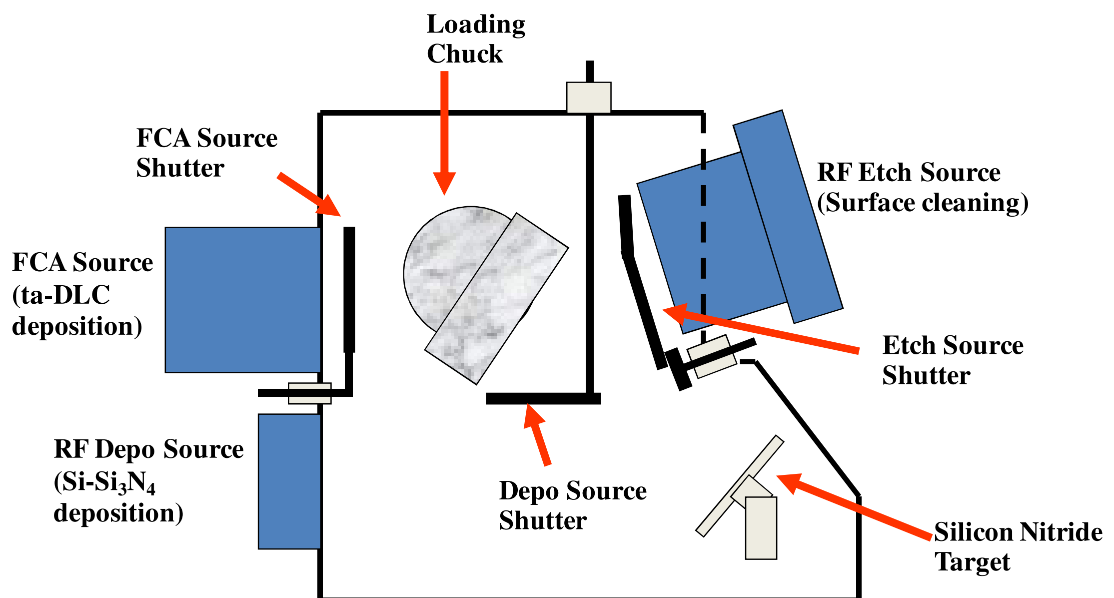

Figure 3.3 Deposition tool schematic

3.2 Thermal heating condition

The thermal stability of less than 2 nm ta-DLC films was investigated in this study. The thermal oven heating in the range of temperature at 100 ºC – 300 ºC was employed to study the thermal impact on ta-DLC as-deposited due to in present HDD application, the operating temperature do not normally exceed 300 ºC.

The films were isothermally annealed in oven at 100 ºC, 200 ºC, and 300 ºC under the air atmosphere for 30 and 60 min for all characterizations except corrosion test the time is varied from 30 min up to 180 min. For each annealing process, the temperature was increased with rate of 20 ºC/min. Table xx shows the thermal heating condition of each characterization plan. Table 3.1 shows the summary of thermal heating condition of ta-DLC films for each film characterizations.

Table 3.1 Thermal heating condition of ta-DLC films for each film characterizations

Substrate	Films characterization	Metrology
AlTiC	Film structure Optical property Surface roughness	Raman Ellipsometer AFM
NiFe	Chemical bonding Wear resistance Corrosion resistance	XPS Nanoidenter Acid dip test
Si coupon	Films density	XRR

3.3 ta-DLC films characterization

This section will describe the ta-DLC films characterization after deposition and after heat treatment. The interested film properties will be studied here are structure, chemical bonding, wear resistance, corrosion resistance, density, optical property and surface roughness

3.3.1 Film structure characterization by Raman spectroscopy

The structure of ta-DLC films was investigated by Raman spectroscopy. Raman spectra of ta-DLC films were collected on a Renishaw's inVia Reflect Raman spectrometer using 514 nm of Ar^+ ion gas laser. The Raman incident power at the sample surface was approximately 4 mW from the applied output power of 20 mW and 50X objective lens. The scan range was from 1100 to 2000 cm^{-1}. Raman spectra were fitted using Gaussian profile to obtain smooth curves and with Gaussian function corresponding to the G peak and D peak.

A Raman spectrum of each sample will be saved and process spectrum fitting. All parameters such as position, intensity, line width and area under peak are investigated for structure and bonding of DLC films as-deposited and after thermal stress introducing.

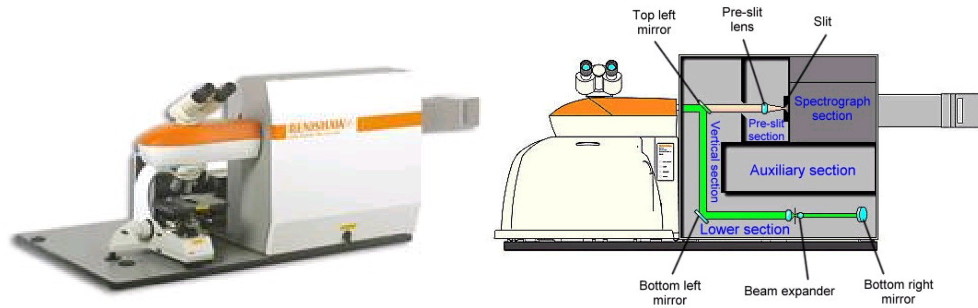

Figure 3.4 Image and Schematic of 514nm Raman System

In addition, Raman spectra were also collected at 325 nm and 785 nm in order to better distinguish between sp^3 and sp^2 characteristics.

3.3.2 Chemical bonding characterization by X-ray photoelectron spectroscopy (XPS)

XPS was used to characterize the bonding states of carbon atoms and silicon atom in the films in this study. XPS (PHI Quantera SXM Scanning X-ray) with an Al Kα monochromatic excitation source was employed with spot size of 200 µm; pass energy of 55eV (with step size of 0.1 eV); take-off angle of 45 degree; and sputtering ion gun setting at 1kV for 2x2 mm^2. The energy calibration of the system was done by measuring Ag $3d_{5/2}$ peak and the difference between Cu $2p_{3/2}$ – Au $4f_{7/2}$ peaks. Depth profiling use the ion gun provides a flux of positively charged argon ions with current density of 1-50 µA/mm^2 and energy of 0-5.5 keV.

Figure 3.5 Image of PHI Quantera II XPS Scanning Microprobe system

3.3.3 Wear resistance characterization by Nanoidenter

The wear resistance of ta-DLC film was measured by nanoindentation (Hysitron Inc.) using cube corner tip probe after deposition and after heat treatment. The wear pattern were created by raster scanning with 4 passes in a 6x6 µm track at fixed force at 4 µN.

Figure 3.6 Image of Hysitron TriboIndenter

3.3.4 Corrosion resistance characterization by acid dip test

Part corrosion test was performed by dipping the part into hydrofluoric acid (HF) which controlled pH at 3.54 +/- 0.05 for 30 min. The 2 min of deionized (DI) water rinsing was done to clean part after acid dipping then using N_2 blow dry. The samples were analyzed by Scanning Electron Microscopy (SEM) at 10kX magnification to count the percentage of corroded parts. The area of interest is at metal magnetic device which is NiFe layer.

For this corrosion testing, the condition of thermal annealing is different from other test to establish trend of corrosion as function of temperature time. The deposited film was then thermally stressed with predefined number of heating cycles. One heating cycle consisted of heating samples to 200 ℃ and 300 ℃ for 30, 60, 120, 180 min and then air-cooled to room temperature.

3.3.5 Optical property characterization by ellipsometer

The optical property of DLC films are measured by spectroscopic Ellipsometer model M2000F that manufactured by J.A.Woollam Inc. The system was spectroscopic wavelength 280nm to 800nm using Xenon lamp as a light source. Ellipsometer use technique that measurement of the change in polarization upon reflection from the sample and the output polarization is measured. The schematic was shown in Figure3.5. The values that instrument measure and report was called experiment data that consist of two data such as PSI (a change in reflection) and Delta (phase shift)

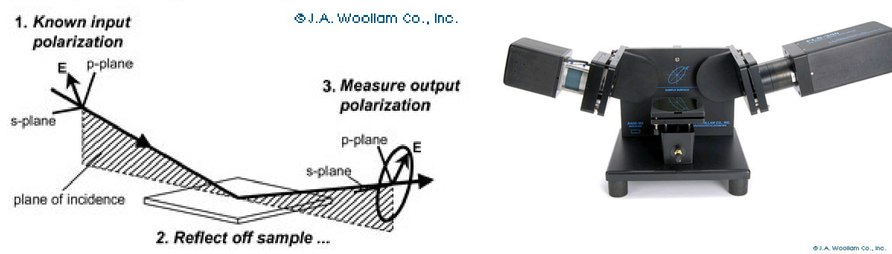

Figure 3.7 Schematic of Ellipsometry technique and image of system

As shown in Figure 3.6, the values from calculation (Gen. Data) were compared to experimental data (from measurement). Any unknown material properties would be varied to improve the match between experiment and calculation.

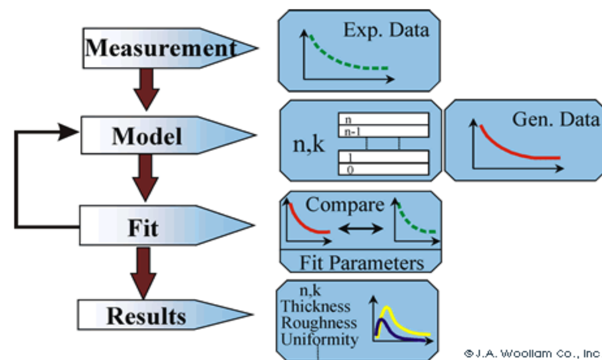

Figure 3.8 Determination of unknown value from Ellipsometry model

3.3.6 Films density characterization by X-ray reflectivity (XRR)

XRR (PANalytical XPert Pro MRD) was use to characterize the density of ta-DLC 200A deposited on Si substrate by scan 2 theta of 0-10 degrees for Carbon thickness and 0-7 degrees for all other layers. The setup of instrument during acquire scan is 40mA and voltage of 45 kV. For carbon layer acquisition, the step size 0.0080 degrees and a time/step 0.50 s; the total scan time 10 min 24 s; the scan range is from 0.1000 to 10.0040 degrees. Then use a 10 mm beam mask and a 1/32 divergence slit on the incident beam side and a Soller slit and 0.27 reflectivity slit on the receiving/detector side. Figure 3.6 shows the image of PANalytical XPert Pro MRD.

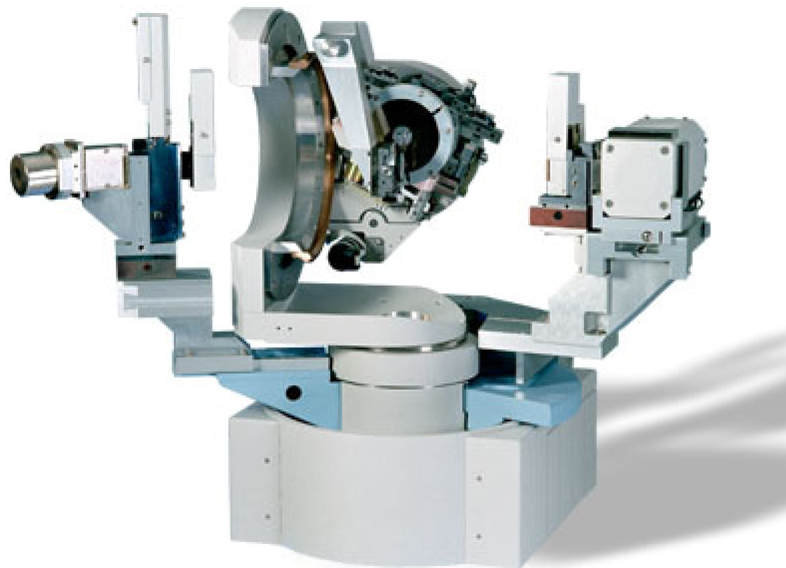

Figure 3.9 Image of PANalytical XPert Pro MRD

3.3.7 Surface roughness characterization by Atomic Force Microscopic (AFM)

Atomic Force Microscopy (Dimension 5000, Veeco Digital Instruments) was used to observe surface morphology and roughness. Silicon cantilever tip model NCHR from Nanoworld Inc was used for the tapping mode measurement. The shape of the tip is similar to polygon based pyramid and the typical tip radius of curvature is less than 8nm. The scan was 10x10 um^2 to obtain RMS (root mean square) roughness. Surface area of interest for this AFM scan is at AlTiC substrate.

Figure 3.10 Image of Atomic Force Microscopy system