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Influence of thermal heating on diamond-like carbon film properties prepared by filtered cathodic arc

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ABSTRACT

Tetrahedral amorphous diamond-like carbon (ta-DLC) films were deposited on magnetic recording heads using the filtered cathodic arc method. The deposited film thickness was on the order of several nanometers. The DLC films were then annealed to 100 °C–300 °C for 30 and 60 min, and the structure of the ta-DLC films was investigated using Raman spectroscopy, where the gross changes were observed in the Raman D and G peaks. Detailed interpretation concluded that there was sp^2 clustering as a function of temperature, and there was no sp^3-to-sp^2 conversion after heating up to 300 °C. Furthermore, X-ray photoelectron spectroscopy suggested that oxidation of both the ta-DLC film and the adhesion layer occurs at 300 °C. Additionally, more film wear was observed with heating as measured by a nanoindenter.

1. Introduction

The tetrahedral amorphous diamond-like carbon (ta-DLC) film of less than 10 nm can be reliably produced by filtered cathodic arc (FCA) technology. FCA ta-DLC film has a high percentage of sp^3 bonded structure and a very high density (~3.0 g/cm^3), thus allowing the film to be thinned down to within a few nanometer range and yet retain sufficient mechanical and corrosion protection capabilities [1,2]. In addition, the advancement in other technologies which are commonly employed together with the FCA-based deposition tool such as electrostatic filter to reduce macroparticle contaminations and in-situ ellipsometer for film thickness control also allows the ta-DLC film to be reliably produced utilizing the FCA for several critical applications [3]. The FCA ta-DLC film has been employed as a protective overcoat film for magnetic head in order to meet the stringent corrosion and wear resistance requirements of hard disk drive (HDD) applications [2,4–6].

Understanding thermal stability of ta-DLC film is crucial for HDD application especially when the film thickness is typically less than 10 nm. The thermally induced property changes to the protective overcoat on the magnetic head will not only influence corrosion and wear protection capability but also the head–disk interaction dynamics [6].

Previous thermal stability studies of 500–1500 nm DLC films made by RF-plasma assisted chemical vapor deposition (CVD) showed a transformation of sp^3 to sp^2 structure via Raman spectroscopy when such films were heated above 200 °C in air [7–9]. In addition, Choi et al. concluded that during the annealing step, oxygen can be adsorbed onto the DLC film surface to form carbon dioxide and eventually causing a film mass loss as the oxidized film material evaporate out from the surface [8]. Furthermore, Li et al. [9] and Chiu et al. [10] also observed the oxidation of carbon material after the annealing via X-ray photoelectron spectroscopy (XPS).

On the other hand, ta-DLC film has a much more stable thermal behavior. Kamiya et al. observed that ta-DLC film of 150–400 nm can be structurally stable when heated up to 500 °C [11]. In a different study using 100 nm FCA deposited ta-DLC films and heated to 400 °C, Raman spectroscopy showed that sp^3 content remained relatively constant with only an increase of microscopic sp^2-bonded clusters volume [12]. Furthermore, at a thickness of 70 nm, Tay et al. observed only some degree of graphitization in ta-DLC films when annealed in air at 400 °C [13].

In current HDD application, the thickness of ta-DLC film is on the order of only a few nanometers. At such reduced thickness, it is of interest to know whether the superior thermal stability of ta-DLC film is still retained. Since the operating temperature in HDD enclosure does not exceed 300 °C, the scope of this study is limited to such temperature range. The structure of ta-DLC film and chemical bonding were characterized by Raman spectroscopy and XPS. The wear resistance was investigated using a nanoindenter operating at a constant loading force.

2. Experimental details

2.1. Film deposition and thermal heating treatment

Pre-deposition surface etching, adhesive material film deposition, and ta-DLC film deposition were conducted within a single chamber equipped with two RF ion beam sources and an FCA source with a

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90° curvilinear magnetic solenoid filter. In-situ process control of growing film thickness was performed using two multi-wavelength ellipsometers for separate monitoring of Si–N sputtering and ta-DLC deposition. Tantalum coupon was used as witness coupon for in-situ thickness endpoint during deposition [2]. Ion beam etching was performed with a 120 V Ar^+ ion beam to clean the sample surface before DLC deposition. Following this step, 1 nm of Si–N material was sputtered prior to ta-DLC coating to serve as an adhesion layer. The ta-DLC films were deposited from an FCA to a thickness of approximately 1.5 nm on the magnetic recording head, which consists of alumina titanium carbide (AlTiC) and another stacked thin film material (e.g., NiFe, Al_2O_3) as the magnetic recording device. Deposition temperature for this study is less than 50 °C as measured by the temperature dot.

The as-deposited ta-DLC films were isothermally annealed in an oven at 100 °C, 200 °C, and 300 °C for 30 min or 60 min in an air atmosphere. For each annealing process, the temperature was increased at the rate of 20 °C/min.

2.2. Film characterization

The structure of the DLC films was investigated by Raman spectroscopy. Raman spectra of ta-DLC films were collected on a Raman spectrometer (Renishaw inVia Reflect) using a 514.5 nm 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 50× objective lens. The scan range was from 1100 to 2000 cm^{-1}. The Raman spectra were fitted using a Gaussian profile to obtain smooth curves and by applying Gaussian functions corresponding to the G and D peaks. In addition, Raman spectra were collected at 325 nm and 785 nm to better distinguish between the sp^3 and sp^2 bonding characteristics.

XPS was used to characterize the bonding states of the carbon and silicon atoms present in the films examined in this study. XPS (PHI Quantera SXM Scanning X-ray) with an Al Kα monochromatic excitation source was employed, with a spot size of 200 μm, pass energy of 55 eV (with step size of 0.1 eV), take-off angle of 45°, and sputtering ion gun setting at 1 kV, over an area of 2 × 2 mm^2. The energy calibration of the system was performed by measuring the Ag $3d_{5/2}$ peak and the difference between the $Cu2p_{3/2}$ and $Au4f_{7/2}$ peaks. XPS spectra were fitted using Gaussian function after the background subtraction corresponding to the different bonding states of C and Si atoms. The C1s spectra were deconvoluted into five sub-peaks corresponding to the carbide, C – C sp^2 bond, the C – C sp^3 bond, the C – O bond, and the C═O bond or O – C═O bond. The Si2p spectra were deconvoluted into five sub-peaks corresponding to the Si – Si bond, Si – C bond, Si – N bond, Si – O bond, and Si═O bond.

The wear resistance of the ta-DLC films was measured using a nanoindenter (Hysitron Inc.). The nanoindenter uses a cube-corner-tip probe to produce a wear pattern after 4 passes in a 6 × 6 μm track at a fixed force of 4 μN.

3. Result and discussion

3.1. Film structure analysis

Raman spectroscopy is widely used as a non-destructive method to characterize the structural quality of carbon-containing compounds [14]. This method can distinguish the bonding type, domain size, and sensitivity to internal stress in the amorphous and nanocrystalline carbon films. Raman spectra are usually discussed in the context of short-distance, ordered sp^3 and sp^2 bonds [14–16]. To analyze the data quantitatively, the Raman spectra are fitted to two Gaussian peaks, which are defined as the D and G peaks. Previous studies have shown that the shift of the G and D peaks and the change of the D peak intensity in Raman spectra can provide information about the DLC film structure [16,17].

The Raman spectra shown in Fig. 1 exhibit an overall pattern for the as-deposited ta-DLC films and the films annealed at different temperatures and times. A shift in the Raman spectra of the DLC films to higher wavenumbers with increasing temperature can be observed. The experimental data show that the effects of the annealing temperature on the ta-DLC films can be divided into two stages. During the initial stage, up to 200 °C, there is only a slight change in the film structure. During the second stage, up to 300 °C, the structure is significantly altered, as shown in the Raman spectra. Fig. 2a–b shows the change in the D and G peaks as a function of annealing temperature and time. The D and G peaks of the as-deposited ta-DLC film are located at 1439 cm^{-1} and 1554 cm^{-1}, respectively. Han et al. also detected and identified similar D and G peaks wavenumbers of ta-DLC film on AlTiC substrate [18]. After annealing, both of the peaks shifted to higher wavenumbers. The maximum shift was observed at the highest annealing temperature, 300 °C, used in this study. The D and G peak positions for the ta-DLC film after annealing at 300 °C for 60 min were 1458 cm^{-1} and 1581 cm^{-1}, respectively.

The Raman peak intensity also changed after annealing. The D peak intensity increased from 385 counts after deposition to 804 counts after annealing at 300 °C as shown in Fig. 2c. The G peak intensity also increased from 620 counts to 885 counts after annealing to 300 °C, as shown in Fig. 2d. However, the ratio of the D to G peak intensity (I_D/I_G) increased from 0.580 after deposition to 0.881 and 0.910 after annealing at 300 °C for 30 and 60 min, respectively (Fig. 2e).

Fig. 2f displays the full width at half maximum (FWHM) of the G peak as a function of annealing temperatures and times. The FWHM of the G peak decreased from 168 cm^{-1} after deposition to 130 cm^{-1} and 128 cm^{-1} after annealing at 300 °C for 30 and 60 min, respectively.

The variation in the G peak position as a function of temperature is due to the high temperature, which initially causes sp^2 clustering into a modestly ordered aromatic [16,17]. Prawer et al. also suggested that an upward shift in the G peak position indicates sp^2 carbon aggregation into larger clusters with smaller nearest neighbor distances [19]. The increase of the D peak intensity also indicates an organization of the sp^2 sites into nanoclusters composed of sp^2 rings, which are formed due to clustering of the sp^2 film component [11,14,16,17]. Ferrari and Robertson have verified that the width of the G peak varies with disorder and used this finding to explain the in-plane correlation length or grain size of graphite. As the FWHM of the G peak decreases, there is a corresponding increase of the I_D/I_G ratio [14,16,17].

In this study, the Raman spectra were carried out at three excitation wavelengths of 514.5, 325 and 785 nm. Fig. 3 shows the G peak position of the as-deposited ta-DLC and the annealed films at different temperatures for 60 min as a function of excitation wavelength.

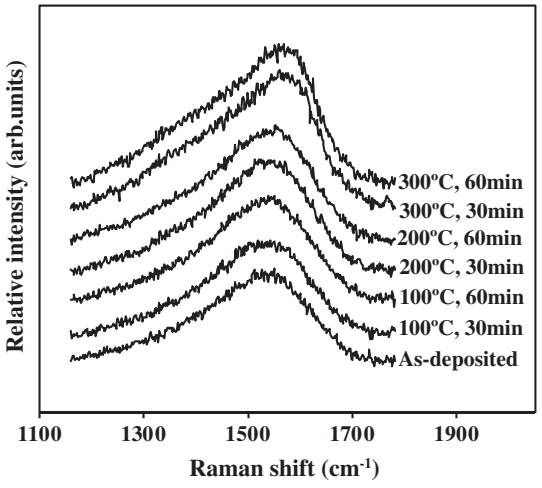

Fig. 1. Raman spectra of the as-deposited ta-DLC films and the films annealed at different temperatures and times.