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Wettability, nanoscratch resistance and thermal stability of filtered cathodic vacuum arc grown nitrogenated amorphous carbon films

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ABSTRACT

Composition, structure, surface energy, nanoscratch resistance and thermal stability of nitrogenated amorphous carbon films grown by filtered cathodic vacuum arc (FCVA) are studied in this paper. X-ray photoelectron spectroscopy and electron energy loss spectroscopy studies reveal that by controlling the nitrogen flow rate and substrate bias carbon films with different bonding structures and composition are formed. Higher nitrogen flow rate results in higher nitrogen content of the film and the stability of C≡N bonds. Increasing the nitrogen content of the films (0 to 16 at.%) increases the polar surface energy (10 to 22 mJ/m^2) of the films while the dispersive surface energy does not change significantly. Thermal stability of the films strongly depends on the composition and bonding structure. The films deposited at higher substrate bias (300 V) and containing higher nitrogen content undergo graphitization at lower annealing temperatures. There is no significant difference in the scratch resistance of the films at small scratch loads (up to 35 μN). Further increase in the scratch load results in larger scratch depth in the film deposited at high nitrogen flow rate (40 sccm).

1. Introduction

The ability of carbon to form bonds with sp^1, sp^2 and sp^3 hybridization makes amorphous carbon (a-C) an interesting material with diverse properties [1,2]. Detailed studies have been performed to investigate the mechanical and physical properties of the a-C films as well as the mechanisms responsible for the stability of different hybridizations and nanostructures in carbon films [3,4]. The high sp^3 hybridization which can be achieved by controlling the deposition conditions confers a-C and a-C:H outstanding hardness and scratch resistance [3,5].

Noticeable mechanical properties and ultra-smoothness of the a-C films make them remarkable candidates for specific applications such as hard disk drive (HDD) media and head overcoat [6]. a-C film grown by filtered cathodic vacuum arc (FCVA) is used as HDD head overcoat [7]. Bilayer of hydrogenated and nitrogenated amorphous carbon (a-C:H and a-C:N) grown by chemical vapour deposition (CVD) and sputtering respectively is applied as the HDD media overcoat [8]. a-C and a-C:H grant outstanding scratch resistance to their underlying head and media layers. a-C:N is used to enhance the bonding of the lubricant to the media overcoat by increasing the surface energy [9].

In order to overcome the problems associated with superparamagnetic effects in the conventional CoCrPt based media, heat assisted magnetic recording (HAMR) is proposed. HAMR enables the application of magnetic alloys with higher thermal stability (such as FePt based alloys) and is considered as the emerging technology in HDD technology [10]. A diode laser heats up the media to temperatures close to its curie temperature. Heating of the media facilitate the writing of high coercivity FePt alloys. Addition of a heating source adds on new challenges to HDD overcoat reliability [11]. High temperature performance and stability of overcoat are new significant issues that should be addressed carefully [12]. Our previous results show that FCVA grown a-C and CVD grown a-C:H have noticeable thermal stability while the sputtered a-C:N undergoes a significant structural changes upon HAMR laser irradiation [13]. Therefore, looking for new candidates that fulfil the media overcoat requirements (such as scratch resistance and high surface energy) and possess high thermal stability is of noticeable importance.

Nitrogen doping has diverse effects on the microstructure and properties of carbon films [14,15]. As it is reviewed by Ferrari et al. [16], carbon and nitrogen form nine different bonding configurations with sp^1, sp^2 and sp^3 hybridizations which in turn result in wide range of properties. Depending on the deposition conditions, carbon nitride films can be classified in four groups: 1) Mainly sp^2 bonded a-C films grown by atomic plasma sources such as sputtering [17]; 2) moderately sp^3 bonded a-C:N films grown by FCVA and pulsed laser deposition [18,19]; 3) moderately sp^3 bonded ta-C:H:N films grown by chemical vapour deposition (CVD) [20]; and 4) high sp^3 bonded films grown by high density plasma sources such as electron cyclotron resonance (ECR) [21]. In this paper we have studied the structure and properties of FCVA grown a-C:N films. Growth of films with higher sp^3 hybridization through the application of energetic FCVA plasma may result in films

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with good scratch resistance and thermal stability suitable for HAMR overcoat. Despite interesting works on hardness, the nanoscratch resistance of the a-C:N films has not been investigated in detail. Moreover, nitrogen incorporation increases the total surface energy of the carbon films although the exact mechanism for surface energy enhancement is not very well understood [22]. In this paper, the wettability of the films is studied as a function of film composition to examine the effect of surface energy on the wettability of the surfaces. Thermal stability of the films is another crucial parameter which needs to be studied for applications such as HAMR overcoat.

2. Experimental

Carbon films were grown by an off plane double bend DC FCVA. Nitrogen gas was purged in the chamber during the deposition. FCVA uses a high current low voltage arc between the target (cathode) and another graphitic bar (anode) to form the plasma. The deposition is done at room temperature. The target is a 99.99% carbon rod. The nitrogen flow rate varies in the range of 0–40 sccm. The deposition chamber is first pumped down using combination of a rotary and turbo pumps. The base deposition pressure was 1.0×10^{-6} Torr. Purging 40 sccm N_2 in the chamber increases the pressure to 3.5×10^{-4} Torr. The arc current was kept at 80 A while a negative DC substrate bias of 0–300 V was applied to the substrate to control the deposition energy. Deposition was done on (100) silicon coupons. Deposition rate decreases with increasing the nitrogen flow rate. The deposition duration was varied accordingly to grow films with desired thickness for different tests.

The composition and bonding structure of the films were studied by X-ray photoelectron spectroscopy (XPS). A Tecnai TF20 transmission electron microscope (TEM) operated at 200 keV equipped with GIF Quantum 965 electron energy loss spectroscopy (Dual-EELS) was also used to study the bonding structure and composition of the films. The low-loss EEL spectrum was used to derive the mass density of the films by assuming that the films are hydrogen free and carbon and nitrogen contributes 4 and 5 valance electrons respectively [23]:

$$\rho = \frac{\varepsilon_0}{12\hbar^2 N_A e^2} M_C m^* E_p^2 \frac{11X_C + 13X_N + 1}{3X_C + 4X_N + 1} \qquad (1)$$

where ρ is the mass density, M_C is the carbon molar mass, m^* is the electron effective mass (which is considered as $0.87 \times m$ in this study), E_p is the plasmon energy and X_C and X_N are the carbon and nitrogen fractions of the film.

A Jipelec JetFirst200C Rapid thermal processing (RTP) was used to study the thermal stability of the films under air atmosphere. The heating rate was kept at 20 °C/s. The annealing time was 10 min and the samples were air-cooled after the annealing. The microstructure of the films was studied by visible Raman spectroscopy at 532 nm before and after annealing.

Surface energy of the films was studied by contact angle measurement. A rame-hart goniometer equipped with DROPimage software was used in this study. Ten measurements at 0.1 s intervals were performed after the droplet touches the surface. The probe liquids and their polar and dispersive surface tensions are shown in Table 1. Fowkes theory [24] was used to derive the surface energy of the films:

$$\cos\theta = \frac{2}{\sigma_l^P + \sigma_l^D}\left(\sqrt{\sigma_s^P \sigma_l^P} + \sqrt{\sigma_s^D \sigma_l^D}\right) - 1 \qquad (2)$$

where σ_l^P, σ_l^D, σ_s^P and σ_s^D are the polar and dispersive surface tensions of the liquid and the polar and dispersive surface energies of the solid respectively.

Table 1
Surface tension of probe liquids used for surface energy measurements.

Liquid	Dispersive component (mN/m)	Polar component (mN/m)	Total surface tension (mN/m)
DI water	21.8	51	72.8
Diiodomethane	0	50.8	50.8
Ethylene glycol	29	19	48

The nanoscratch resistance test was performed by a NanoScope Dimension 3000 AFM system (Digital Instruments, USA) using an indentation cantilever with a cube corner diamond tip (PDNISP-HS diamond tip from Bruker USA) mounted to the end of the cantilever. The diamond tip has a tip radius of less than 50 nm to ensure good imaging resolution and nanometer-scale scratches. In order to find the area of interest, the tapping mode is first engaged to scan the surface. The scratch mode is then selected to make a scratch on the surface. As the scratch is executed, the tip is forced by the piezo-scanner into the sample surface until a pre-set reaction force is reached. The tip is then moved laterally for the required distance (1 μm in our tests). The scratch was done in a single step and the scratch rate was kept at 1 Hz. As such the scratch rate is fixed at 2 μm/s. After the scratch, the tip is retracted from the surface to its initial position above the surface. Thereafter, the system is returned to the image mode and measures the scratch image by the same diamond tip under tapping mode.

The maximum force during the scratch is controlled by changing the trigger threshold (specified in volts), which is the cantilever deflection measured by the photodetector. The maximum force can be calculated by:

$$F = K \times T_{th} \times S \qquad (1)$$

where F, K, T_{th} and S are the force, spring constant, trigger threshold and deflection sensitivity respectively.

The spring constant of the indentation cantilever is 441 N/m and the sensitivity, which is used to convert the cantilever deflection in volts to nanometers, is measured to be around 193 nm/V.

The trigger threshold for nanoscratch tests were set to 0.2, 0.3, 0.4 and 0.5 V. The corresponding maximum forces were then calculated to be 17.2, 25.8, 34.4 and 43 μN.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the C1s and N1s edges of 10 nm thick carbon films deposited at 100 and 200 V substrate bias and at 0–40 sccm N_2 flow rates. The nitrogen content of the films derived from the XPS spectra is shown in Fig. 2. Regardless of the deposition bias, the nitrogen content of the films increases by increasing the flow rate and reaches a plateau at high flow rates. This can be mainly due to the high deposition pressure as a result of high nitrogen partial pressure in the plasma. As it can be observed in Fig. 1, the C1s and N1s edges become wider and asymmetric by nitrogen incorporation. The C1s edge of pure carbon film deposited at 100 V is shifted from 284.8 to 285.2 eV by 7.5 at.% nitrogen incorporation (the film deposited at 5 sccm N_2 flow). The full width at half maximum (FWHM) of the C1s edge increases from 1.6 to 2.1 eV as well. Broadening of the C1s demonstrates a more heterogeneous environment near the carbon atoms due to the formation of different bonds between carbon and nitrogen. Shifting of the C1s peak towards higher binding energies can be due to charge transfer from carbon to nitrogen which has higher electronegativity [25].

Pure carbon films consist of a carbon network with sp^2 and sp^3 hybridization. Diaz et al. studied the XPS spectra of pure carbon films in detail and suggested that the C1s spectra can be deconvoluted by two peaks at 284.3 ± 0.1 and 285.2 ± 0.1 eV attributed to sp^2 and sp^3