Effect of N Doping on Structure and Properties of DLC Films Produced by Plasma Beam Deposition

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***Abstract*—A novel plasma beam source for the deposition of DLC films is described. Wide ranges of ion energy (130-250 eV) and C_2H_2/N_2 flow conditions have been used to investigate the effect of N doping on the structure and properties of DLC films. The resulting films are characterized by their chemical composition, Raman spectra, electron spin density, mass density, and hardness, which critically depend on the N content. The addition of N causes the *sp*^{2} carbon content in the DLC films to increase and results in lower density and hardness. The film density also decreases with increasing ion energy at high N concentrations. Carbon films with maximum density and hardness of 2.1 g/cm^3 and 25 GPa, respectively, can be produced using the plasma beam source.**

***Index Terms*—Diamond-like carbon, plasma beam deposition, protective coating, density**

I. INTRODUCTION

CONTINUATION of the rapid increase in the recording density of magnetic disk drives necessitates the reduction of magnetic spacing between the head sensor and the magnetic medium. This can be partly achieved by reducing the thickness of the protective carbon overcoat on disks, which is mostly deposited by sputter deposition today. Recent studies have shown that various energetic carbon deposition techniques, such as plasma-enhanced chemical vapor deposition (PECVD) and ion beam deposition (IBD) using hydrocarbon gases, can produce amorphous diamond-like carbon (DLC) films that are more wear and corrosion resistant than those produced by conventional sputtering methods [1], [2]. Hence, ultra-thin DLC films produced by these deposition techniques could potentially replace sputtered carbon overcoats without compromising the wear and corrosion resistance.

Weiler et al. [3] have recently reported the preparation of highly dense DLC films using a novel plasma beam source [4], [5]. They found the properties of CH_x films produced from the C_2H_2 precursor to markedly vary with the ion energy in the range of 75-150 eV/C atom. A maximum density of 2.9 g/cm^3, as determined by electron-energy-loss spectroscopy (EELS), can be attained at an optimum ion energy of 92 eV/C atom [3]. Moreover, other studies have shown the addition of nitrogen can significantly increase the durability of conventional sputtered carbon films [6]. With the application of magnetic disk overcoat in mind, we report the effect of nitrogen doping on the properties of DLC films produced by a novel plasma beam source.

II. EXPERIMENTAL

A. *Plasma Beam Source*

The schematic diagram of the plasma beam source is illustrated in Fig. 1. The source generates a capacitively coupled RF discharge between its powered electrode and grounded electrode through a 27.12-MHz power supply. A magnetic field is used to confine the plasma and to maximize the plasma ionization. The powered electrode is a large, hollow cylinder. The grounded electrode is a tungsten grid, through which the plasma beam is extracted. The high mobility of electrons and the large area of the powered electrode allow the plasma to acquire a relatively high bias potential, which accelerates ions through the plasma sheath and the extraction grid. To maintain charge neutrality of the plasma, same amount of electrons also pass through the grid during each RF cycle to form a quasi-neutral plasma beam [5].

The plasma beam source is mounted on a BPS Circulus M12 disk processing system. Acetylene and nitrogen are used as the source gases. The background pressure in the chamber is maintained at 0.3 mTorr during deposition. The ionic composition of the plasma, as measured by quadrupole mass spectrometry, mainly consists of $C_2H_x^+$ and N_2^+. The ion energy distributions in Fig. 2, as measured by a Faraday cup 10 cm away, show that the plasma beam is relatively monoenergetic. The ion-neutral ratio in the plasma beam is estimated to be 0.8 from the measurements of ion current density and deposition rate. Fig. 3 shows the ion energy to increase linearly with the RF power for a fixed C_2H_2/N_2 ratio. The ion energy can also be changed by varing the area of the powered electrode, which effectively changes the capacitance of the plasma sheath and hence the plasma potential.

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B. Film Preparation and Characterization

Amorphous CH_x and CH_xN_y films with a nominal thickness of 15 nm were deposited on p-type Si (100) substrates for most characterization work. The ion energy of the plasma beam was varied from 130-250 eV (65-125 eV per C or N atom) by changing the RF power. The N content in the films was controlled by varing the C_2H_2/N_2 flow ratio.

Rutherford backscattering spectrometry (RBS) was used to determine the C and N contents, and forward recoil spectrometry (FRS) was used to determine the H content in the films. RBS and FRS spectra were obtained using a 2.3 MeV He^+ beam. The thickness and density of film samples were measured by X-ray reflectivity (XRR) [7]. The specular XRR data was acquired using a BEDE GXR1 X-ray Reflectometer. Beam divergence was less than 25 arc-seconds and the samples were aligned to within 5 arc-seconds in the scattering plane. Raman spectra were measured at room temperature using a Jobin Yvon 3000 Raman spectrometer equipped with an Argon ion laser (514.5 nm, 1 mW). The dangling bond density in the films was determined by electron spin resonance (ESR), the experimental details of which have been described elsewhere [8]. The hardness measurements were obtained from 120 nm thick films on Si substrates with a nanoindentor (MTS Nanoinstruments) operating in the continuous stiffness mode.

III. RESULTS AND DISCUSSION

The H concentration in the undoped CH_x films is in the range of 25-30 at.%, and does not vary significantly with the RF power and hence ion energy. The addition of nitrogen lowers the H content to 20-25%. As the N_2 flow rate increases, the film deposition rate decreases and the atomic N content in the films increases until saturation at 25%.

Raman spectra of DLC films are usually characterized by a *G* peak around 1560 cm^{-1} and a *D* (disorder) peak around 1360 cm^{-1} [9]. Fig. 4 shows the Raman *G* peak position of the CH_xN_y films to shift toward higher wave numbers with increasing N content up to 20%. According to Ferrari and Robertson [9], the *G* peak position of DLC films would move to higher wave numbers as the fraction of the sp^2 carbon bond increases. Hence, the Raman results here suggest that the structure of the CH_xN_y films becomes increasingly graphitic with N content.

Electron Spin Resonance, which measures the density of unpaired electrons or dangling bonds, can also be used to characterize the structure of carbon materials [3], [8], [10]. As observed by Yanagisawa in a variety of carbon materials including graphite, amorphous carbon, and diamond, the spin density increases with the sp^3 carbon content [10]. Fig. 5 shows the spin density of the films to decrease from 4×10^{20} cm^{-3} to 0.3×10^{20} cm^{-3} with increasing N. The ESR and Raman results both indicate that the CH_xN_y films are becoming more graphitic with N doping. In fact, a recent ^{13}C nuclear magnetic resonance (NMR) study has found a CH_xN_y film with 20 at.% N to contain little, if any, sp^3 carbon [11].

The mass density of the films, as measured by XRR, is shown in Fig.6. It decreases from 2.1 to 1.75 g/cm^3 as the N content increases from 0 to 23%. In contrast to the findings of Weiler et al. [3], at low N concentrations of 10% or below, the density is relatively independent of the RF power and hence ion energy in the range investigated here. Also, the maximum density observed in this study is 2.1 g/cm^3, compared with a maximum density of 2.9 g/cm^3 reported in [3]. Note however, that unlike XRR the EELS analysis used in [3] does not take the hydrogen content in the films into account and therefore might overestimate the density, as pointed out in the original work of Fink et al. [12]. As the N content exceeds 10%, the scatter in the data (Fig. 6) indicates that the density decreases with the RF power in the ion energy range of 130-210 eV.

Fig. 7 shows the film hardness to increase with density, reaching a maximum value of 25 GPa at 2.1 g/cm^3. Hence, it can be concluded that the addition of N causes the sp^2 carbon content in the DLC films produced by the plasma beam source to increase, which results in films with lower density and hardness. Mechanical properties and wear resistance of CH_xN_y coated magnetic disks have also been studied and are presented in a companion paper [13]. Interestingly, the wear resistance actually increases as the film hardness decreases.

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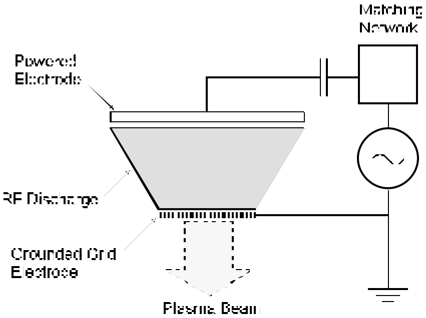

Fig. 1. Schematic diagram of the plasma beam source. The powered electrode is a large, hollow cylinder. The grounded electrode is a tungsten grid, through which the plasma beam is extracted.

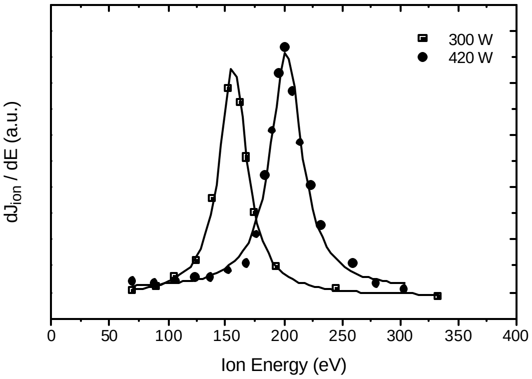

Fig. 2. Ion energy distributions at different RF power conditions. The FWHM is approximately 30 eV.

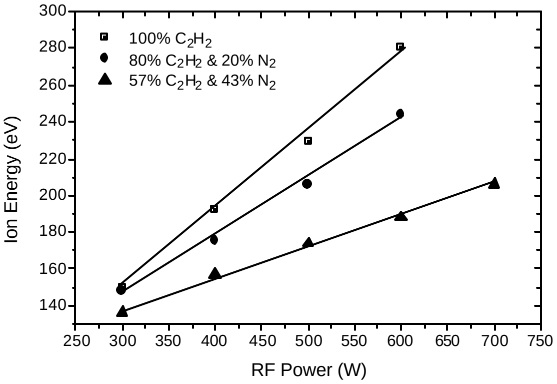

Fig. 3. Variation of ion energy with RF power for different ratios of N_2/C_2H_2 flow rates. The ion energy increases linearly with RF power.

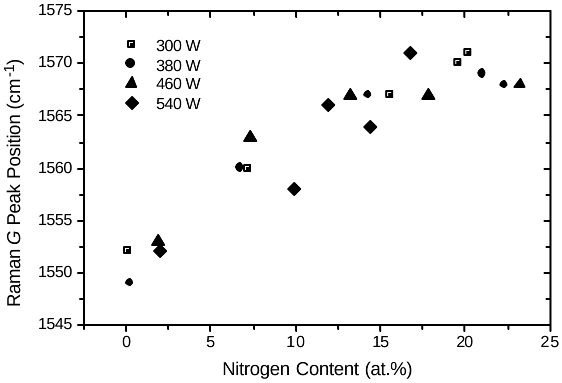

Fig. 4. Variation of Raman *G* peak position with N content in the DLC films. The shifting of the *G* peak position toward higher wave numbers implies the sp^2 carbon content is increasing with N.

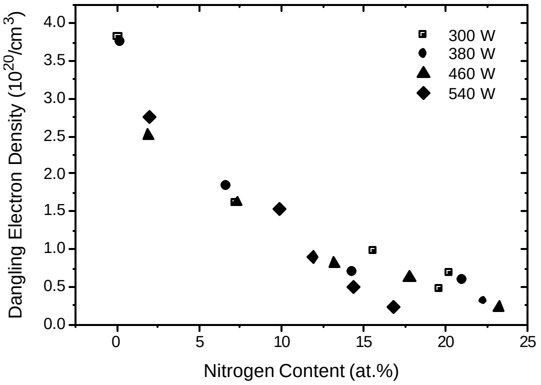

Fig. 5. Variation of electron spin density with N content in the DLC films at different RF power conditions.

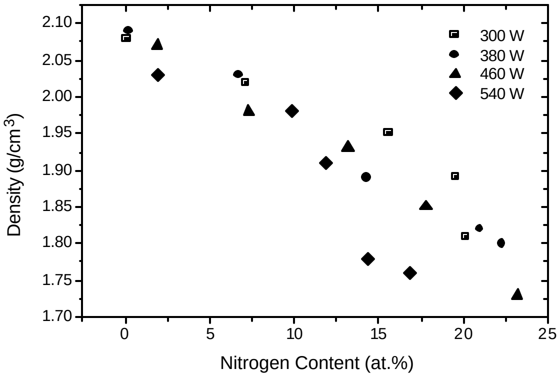

Fig. 6. Effect of N content on mass density of the DLC films as determined by XRR.

Fig. 7. Variation of hardness with density for DLC films.