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Structure and Properties of Amorphous Diamond-Like Carbon Films Produced by Ion Beam Assisted Plasma Deposition

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The microstructure and tribological properties of carbon film produced by ion beam assisted plasma deposition in a plasma source ion implantation (PSII) chamber with energies varied from 0 to 30 keV are examined. The process is illustrated schematically, and Raman spectra as well as TEM images and corresponding diffraction patterns of carbon films are shown.

Keywords
diamond-like carbon film, plasma deposition, tribological test

1. Introduction

THERE is increasing interest in the production and properties of diamond-like carbon films. These films are typically amorphous and have potential applications like protective coatings for magnetic and optical disks, wear-resistant coatings for abrasive applications, as well as semiconducting materials.[1-6]

Carbon has two crystalline forms, graphite and diamond. Graphite is the thermodynamically stable structure at room temperature, possesses a layered structure, with atoms strongly bonded within a basal plane (sp^2-hybrid bond), and the planes weakly bonded to one another (Van der Wals forces). In diamond, each carbon atom is surrounded by four other carbon atoms to form covalent bonds (sp^3-hybrid bonds) in a tetrahedral structure. Many investigations have been undertaken to characterize the microstructure of amorphous carbon using techniques such as Raman spectroscopy,[7,8] Electron Energy Loss Spectroscopy (EELS),[9,10] and transmission electron microscopy. These studies show that both sp^2- and sp^3-bonded atomic sites are incorporated in diamond-like carbon films, and their physical and chemical properties depend strongly on deposition techniques and film growth conditions, which result in different microstructures.

Diamond-like carbon can be produced by a variety of ion beam and plasma techniques such as low energy carbon ion beam,[11-13] dual beam,[14] ion plating techniques,[15] and rf sputtering,[16,17] or rf and dc plasma deposition of a hydrocarbon gas or other alkanes.[18,19] All of these techniques involve energetic ions with energies less than several kiloelectron volts. This article examines the microstructure and tribological properties of carbon film produced by ion beam assisted plasma deposition in a plasma source ion implantation (PSII) chamber with energies varied from 0 to 30 keV.

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2. Experimental

The process is illustrated schematically in Fig. 1.[20] The plasma is generated by either filament or glow discharge, which ionizes the methane gas. Permanent magnets on the chamber walls confine the primary ionizing electrons. The target is pulse biased to a negative potential, in the present case, from 0 to –30 keV. The energized ions generated during the pulse either deposit on the surface, sputter the deposited film, or are implanted into the surface depending on the bias voltage. This experimental setup allows for investigation of a wider range of ion energies.

Table 1 shows the process parameters of four batches of carbon films. Plasmas were generated by filament discharge, except for the second batch which was produced by glow discharge. The pressure of the second batch was 50 mtorr, whereas other batches were at pressures of 0.4 mtorr. In Batch 1, samples were grounded without bias in the chamber to allow diffused hydrocarbons to deposit. The structure and properties of samples produced in this batch have been compared with other samples produced using different bias voltages. Targets of the second batch were biased at –2 keV, and the film grows from both neutral hydrocarbons and ion-plated ions. The third batch used –12 keV bias. For the fourth batch, the target was biased at –30 keV. As a result, a carbon implanted region plus a 300-Å carbon film formed on top of the implanted surface.

Table 1 Processing conditions

Batch No.	PSII pulse bias, keV	Pressure, mtorr	Plasma	Thickness, nm
1	0	0.4	HF	200
2	–2	50	GD	150
3	–12	0.4	HF	60
4	–30	0.4	HF	30

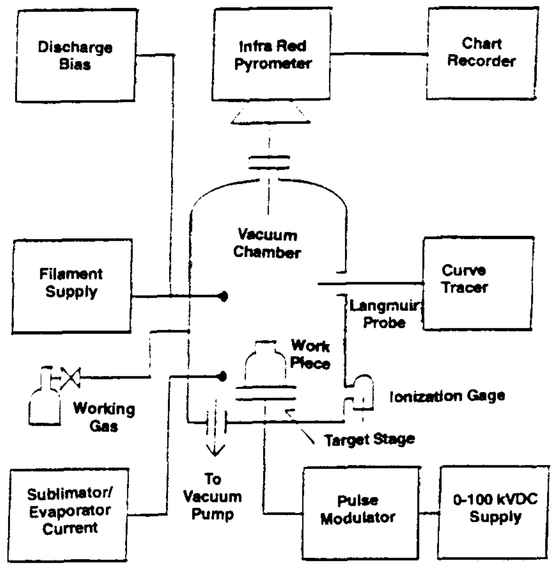

Fig. 1 Schematic of the plasma source ion implantation (PSII) chamber.

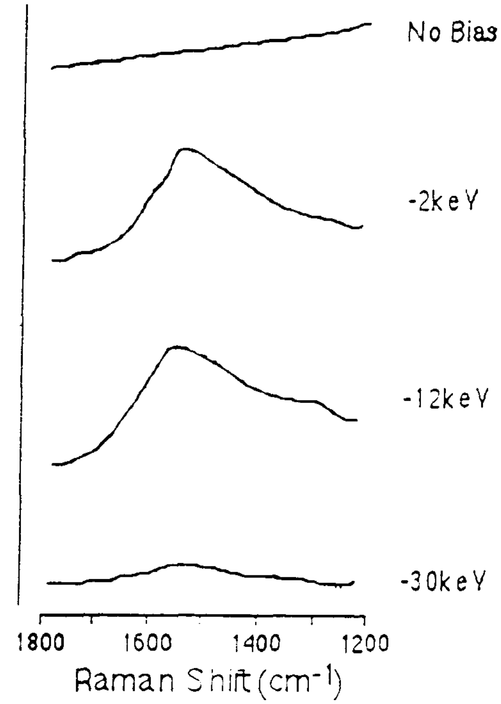

Fig. 2 Raman spectra of four films produced at different conditions.

The coefficients of friction of the carbon films were studied using a pin-on-disk wear tester without lubrication. All the samples were polished under the same conditions and finished with a 0.5 μm diamond paste. Surface roughness before deposition was about 200 Å and less than 100 Å after deposition. A 3-mm ruby ball was used as the stylus. The disks were rotated at 54 rpm with the pins positioned to produce a track diameter of 5 to 8 mm. The normal load was 50 g, and the humidity level in the laboratory was about 50%. The frictional force on the pin was measured with a load cell and normalized to the applied load to obtain the coefficient of friction. Structures of the films were also studied by Raman spectroscopy and transmission electron microscopy (TEM).

3. Results

Raman spectroscopy is a useful tool to study the microstructure of amorphous carbon films. Raman spectra from a single crystal of diamond has a sharp peak at 1332 cm^{-1}. Two peaks are observed at 1580 cm^{-1} (G band) and 1358 cm^{-1} (D band) in graphite. Increasing the number of sp^3-bond atomic sites leads to lower frequencies of G band instead of a mixture of the Raman peaks associated with diamond and graphite.[21] It was also found by Richter et al.[22] that frequency shifts in the G band are caused only by changes in the force constants and correspond to a certain sp^3-bond fraction. Raman spectra of carbon films produced at four different voltages are shown in Fig. 2. The film produced without bias does not show any peaks in the range, which suggests the formation of polymer-like material. Broad peaks in the range of 1200 to 1700 cm^{-1} were observed in all other samples. These broad peaks are composed of both G and D bands with different positions and intensities. A shift in the peak to lower frequency (1530 cm^{-1}) is observed for the sample produced with −2 keV bias compared with the −12 keV (1550 cm^{-1}) case and the −30 keV (1540 cm^{-1}) case, implying that samples produced at −2 keV have the highest number of sp^3-bond sites. The signal is weak from the sample biased to −30 keV because of the film thickness (only 300 Å).

Table 2 Coefficient of friction of amorphous carbon films

PSII pulse bias, keV	0	−2	−12	−30
Coefficient of friction	0.35	0.14	0.08	0.15

The microstructures of the carbon films were also investigated by TEM. Images and their corresponding diffraction patterns are shown in Fig. 3(a) to (h). The diffraction patterns taken from films of four conditions are not substantially different from each other, except for the one produced without target bias. All films are amorphous or quasi-amorphous. The morphologies are different for the four conditions used. The film produced without bias has spherical nucleation islands embedded in an amorphous matrix. Film produced with −30 keV pulsed bias has some areas (A) similar to that of the film produced without bias, whereas the rest appear to have totally amorphous (B) and network like structures (C). The −2 keV film has a totally amorphous feature, and the −12 keV film exhibited what resembled a fishscale morphology.

The coefficients of friction for four films are summarized in Table 2. All of the numbers were recorded after 30 min of wear. The recorded traces of the friction tests are shown in Fig. 4. The lowest friction value occurred in samples produced at −12 keV bias. The friction value of samples produced at −2 and −30 keV

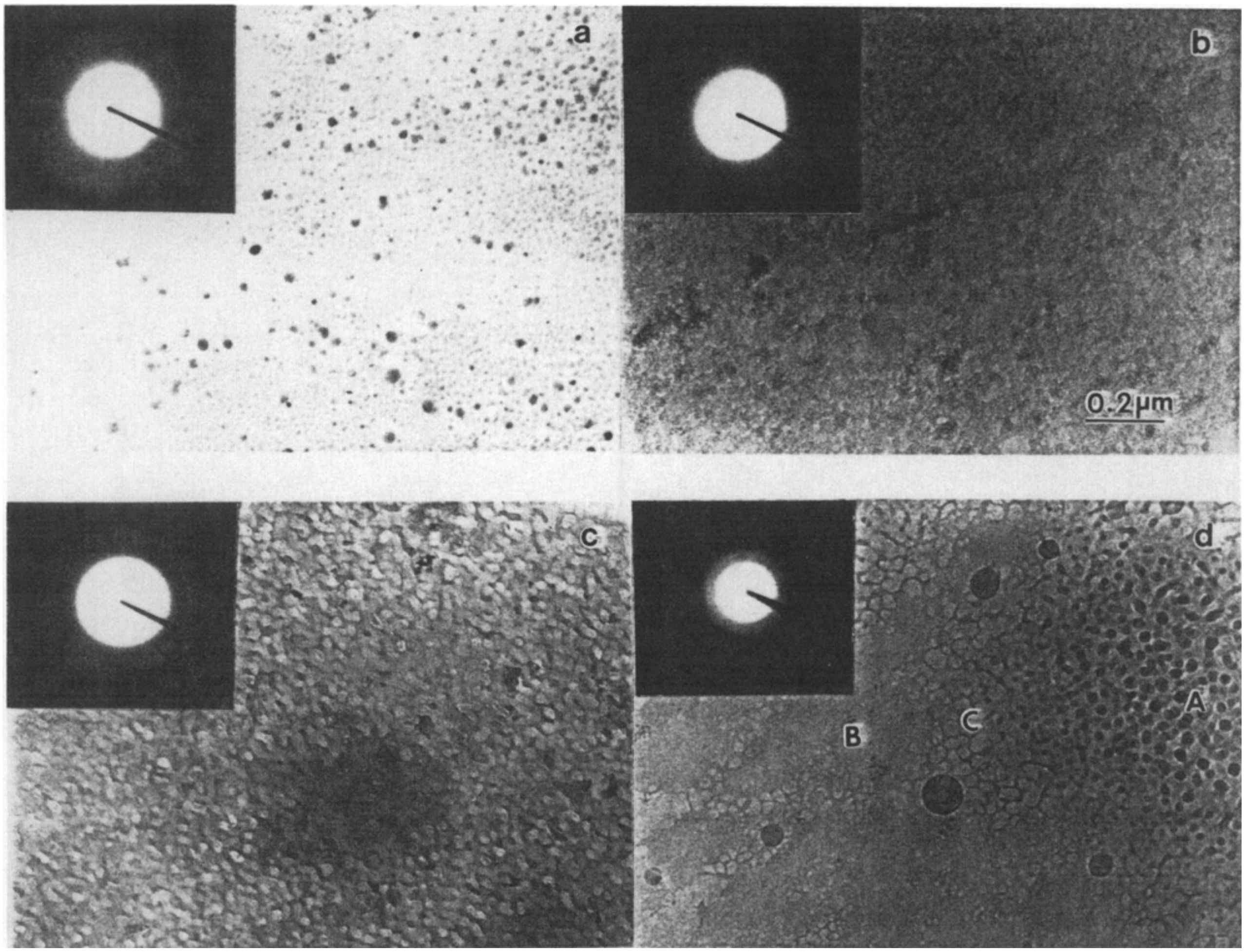

Fig. 3 TEM bright-field images and corresponding diffraction patterns of carbon films produced at (a) no bias, (b) –2 keV, (c) –12 keV, and (d) –30 keV.

are comparable. Samples produced with no bias exhibited the highest friction value.

Wear depths were also measured by a profilometer. All wear depths were not measurable after 30 min (1620 cycles) of wear, except the one produced without bias, which was about 2000 Å. Samples after wear were examined by scanning electron microscopy (SEM). No transfer layer was found on the worn surfaces of the carbon film or pin material. Grooves along the sliding direction were found in both disks and pin surfaces, which suggested an abrasive wear mode.

4. Discussion and Conclusions

Raman spectroscopy shows that the film produced without bias is polymer like. The film grew mostly by absorbing diffused neutrals and ions in the energy of plasma potential. To obtain better quality diamond-like carbon films with a low coefficient of friction, a bias voltage needs to be applied to enhance the effect of bombarding ions. It was suggested by Catherine[23] that hot carbon atoms undergo reactions by insertion into C-H bonds and result in the formation of unsaturated C-C bonds. The effect of a primary implant is multiplied by the formation of secondary hot carbon atoms by knock on processes of the primaries with the substrate. A large number of secondary hot carbon atoms are concentrated in a very small volume, and direct interaction of unsaturated structures with other cold or hot carbon atoms may occur. They may provide the pathway for ring formation, which is in agreement with the most recent network models of diamond-like carbon.[24-26] The difference that might result from using different bias voltages is the number of secondary projections induced by a primary carbon atom, projected range, and surface sputtering effect, etc. In the present case, the highest fraction of sp^3-bonds was found in a sample produced at –2 keV bias voltage. It seems that the combined effect of ion projection and resulting secondary knock on are likely to produce the highest fraction of sp^3-bond carbon films at this energy.

However, the lowest coefficient of friction was found in the samples produced at –12 keV bias voltage. There is no previous report by other researchers about how the fraction of sp^3-bonds affects the behavior of wear and friction. This study suggests that the coefficient of friction of amorphous carbon film is not controlled by a single factor such as sp^3-bond fraction. A higher

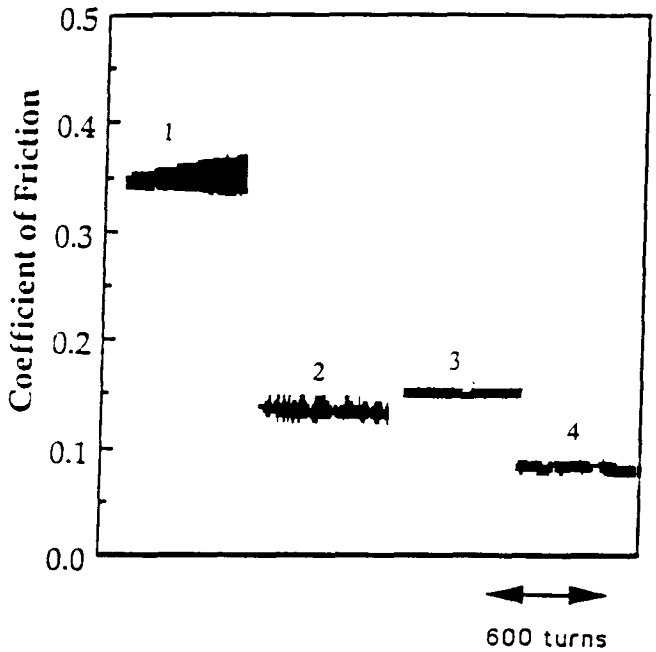

Fig. 4 Traces of coefficient of friction of carbon films produced at different conditions. Trace 1, no bias; Trace 2, –2 keV; Trace 3, –30 keV; Trace 4, –12 keV.

fraction of sp^3-bond does not yield a lower coefficient of friction. A number of researchers[4,6] reported that a transferred carbon film was found on the worn counterface. This transfer film appears softer than the initial diamond-like film—a mechanism that produces an extremely low coefficient of friction. Their counterfaces were mostly hard steel balls, which differ from the current pin material (Al_2O_3). The cohesive strength between steel and carbon film is different from that between Al_2O_3 and carbon film. Therefore, it is reasonable to find a dissimilar wear mode. In the present case, wear basically occurred in an abrasive mode. The sliding is probably accounted for by shearing at the interface of the sliding surface. The mechanical properties of the carbon film therefore could determine the shear strength and consequently the coefficient of friction. Further work still needs to be done to investigate how the mechanical properties of these carbon films produced by different bias voltages affect the coefficient of friction.

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