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Influence of Ion and Neutral Flux on the Properties of Diamond-Like Carbon from Pulsed Glow Discharges of Acetylene

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Abstract

The deposition rates, composition, and mechanical properties of diamond-like carbon (DLC) coatings deposited using pulsed glow discharges of acetylene (C_2H_2) have been studied as a function of deposition bias and gas pressure. The data show that a -4 kV bias is one order of magnitude more efficient than a bias of -8 kV for depositing DLC via plasma immersion ion processing (PIIP). Sputtering is the suspected cause for the reduced deposition efficiency at -8 kV. A methodology for comparing the magnitudes of the ion and neutral flux is used to show that neutrals dominate the deposition process under all conditions tested. The necessary data is shown to prove that the coating hardness is independent of gas pressure when the ion flux, J_i , is less than 10% of the total flux, J_d . If J_i/J_d is greater than 10%, then increasing the gas pressure reduces the coating hardness to levels below 15 GPa. The implications of these results regarding sheath thickness, deposition rates and throughputs for large area processing (many m^2) are discussed

Keywords: **diamond-like carbon, DLC, thin film, hardness, plasma deposition**

Introduction

Deposition of tribologically important coatings, such as DLC, continues to be of interest to both the scientific and industrial communities. The use of PIIP, and other variations of pulsed plasma depositions, for the deposition of adherent DLC coatings have been recently reviewed [1]. While PIIP is easily used to deposit various kinds of DLC, the process is not yet optimized even though attempts to coat many m^2 simultaneously have been successful [2-3]. The following experiments were performed for the purpose of narrowing in on optimum conditions for DLC deposition onto large and complicated surfaces.

Experimental Details

All the DLC coatings evaluated in this work were deposited using the PIIP facility at Los Alamos National Laboratory [4]. The acetylene (C_2H_2) plasma was generated using a pulsed glow discharge process, as this process is the most easily scaled to treat large areas (many m^2). The acetylene gas is referred to as “welding grade,” and contains small amounts of acetone to prevent polymerization during storage. The coatings were deposited onto various substrates, but typically silicon, on an 840 cm^2 stage cooled to with water at 20°C was used. No attempt was made to measure the temperature of the sample or the sample stage. The bias voltages were -4 and -8 kV , the pulse width ranged from 15 to $75\text{ }\mu\text{s}$, the pulse frequency ranged from 0.6 to 4 kHz , and the C_2H_2 pressure ranged from 0.67 to 4 Pa (5 to 30 mTorr). The thicknesses of the coatings, which ranged from 60 nm to $1.3\text{ }\mu\text{m}$, were measured using standard surface contact

profilometry. The chemical compositions of the coatings were determined using standard Rutherford Backscattering Spectrometry and Elastic Recoil Detection techniques [5]. The hardness and elastic modulus of the coatings were determined by nanoindentation. Reported results are an average of six to ten individual measurements.

Results and Discussion

Measured parameters and results from the coatings are listed in Table 2-3. Fig.1 shows the results of deposition rate plotted against the average deposition power, $\langle P \rangle = \langle I_p \rangle V f / A$, where $\langle I_p \rangle$ is the average current during the pulse, V is the pulse bias, f is the duty cycle, and A is the stage area. The deposition rates vary from 0.07 to 3.9 $\mu\text{m/hr}$. The lines are a linear fit through the data points for depositions at -4 kV and -8 kV biases. The slopes of the -4 kV and -8 kV lines are 10.8, and 1.2 $(\mu\text{m/hr})/(\text{W}/\text{cm}^2)$, respectively. It is speculated that the deposition rate for the -8 kV bias is reduced because of sputtering. Sputtering yield has a high dependence on energy [6], especially at the low ion energies (<1 keV) expected when the operating pressure is high enough to account for numerous ion-neutral collisions in the sheath. Regardless of the reason, a -4 kV bias is about 10x more efficient than -8 kV. This result has positive implications for scaling up the deposition process as a lower bias implies a smaller sheath, and thus higher packing densities for components in a PIIP chamber, as discussed below.

The mechanical properties of the coatings are shown in Table 3 and Fig. 2. Note that $H/E = 0.1$ as required for covalent solids [7], and that coating hardness ranges from 5 (equivalent to steel) to 25 GPa (equivalent to ceramics).

The hydrogen (H) content of the coatings are plotted against the coating hardness in Fig.3 and listed in Table 3. Note that there is no clear dependence of hardness on H-content. However, it can be said that the H-content ranges between 20 and 40 at%, as is typical for DLC coatings.

It is well known that not all of the material deposited from a plasma process is made up of ions. While it is difficult to directly measure the neutral flux onto a surface in a plasma environment, it is simpler to estimate the ion flux. The total amount of material deposited can also be calculated by combining the results of ion beam analysis. We define the ion flux, J_i , to be

$$J_i = \frac{\langle I_p \rangle f \eta}{Ae},$$

where $\langle I_p \rangle$ is the average current during the pulse, f is the duty cycle, η is the number of carbon atoms per ion (assumed to be two for $C_2H_2^+$), A is the area being coated and e is the electronic charge. The average flux of material, from both ions and neutrals, J_d , is calculated from

$$J_d = \frac{(Nt)}{T} = J_i + J_n,$$

where (Nt) is the atomic areal density measured from ion beam analysis, T is the total deposition time, and J_n is the deposition flux due to neutral atoms and molecules that are not subsequently sputtered from the surface. A plot of J_d vs J_i is shown in Fig. 4 and the values are listed in Table 3. Note that the trends in Fig. 4 are nearly identical to those shown in Fig. 1. This is not

surprising as the deposition rate is proportional to J_d , and the average deposition power is proportional to J_i . However, it is instructional to plot the data as in Fig. 4 because it makes the point that in all cases, $J_d > J_i$ which indicates that neutrals always play a role in the deposition. In fact, J_d is always greater than $2J_i$, which means that deposition by neutrals, namely J_n , always dominates coating growth.

Regarding mechanical properties of the DLC coatings, the coating hardness is essentially independent of bias, duty factor, and deposition rate. These plots are not shown in Fig. 5-7.

Fig. 8 shows the dependence of DLC coating hardness on the J_i/J_d ratio. The hardness is practically independent of J_i/J_d when J_i/J_d is less than 0.1. However, increasing the gas pressure when J_i/J_d is more than 0.1 can decrease the hardness by about 50%.

These results have consequences for PIIP scaleup that should be considered carefully. For instance, a commercial operation would meet the following goals:

- Maximize coating thickness per unit power consumed
- Maximize packing density of components
- Minimize dependence on operational parameters (e.g. pressure and voltage)

From Fig. 1, the highest deposition rate utilizing the lowest power occurs for 4 Pa (20 mTorr) gas pressure and a pulse bias of -4 kV. From Fig. 5, J_i/J_d for high hardness DLC under these conditions is less than 0.1, so the coating properties should be independent of local variations in

bias and pressure that might occur during deposition. The packing density of components is maximized when the sheath thickness is minimized. The sheath thickness is proportional to $(V/n)^{1/2}$ and the pulse width, τ , so using a lower bias, a higher ion density (or gas pressure) and a shorter pulse width will minimize the extent of a sheath. Assuming an ion density of 10^9 cm^{-3} and a C_2H_2^+ ion, the calculated sheath thickness for -4 and -8 kV bias is 9 and 13 cm, respectively for a 15 μs pulse.

Summary & Conclusions

DLC coatings deposited via pulsed glow discharges of acetylene have been compared as a function of bias, pressure, and duty cycle. The most efficient process parameters are -4 V, 4 Pa (20 mTorr) pressure, and a duty cycle between 0.05 and 0.1. Under these conditions, components can be as little as 18 cm (twice the sheath thickness) apart. The DLC coatings will be deposited at rates up to 3 $\mu\text{m/hr}$ and have a hardness of approximately 15 GPa.

There is no obvious relationship between the coating hardness and a combination of process parameters (e.g. pressure, bias, or duty factor). There is obviously another parameter that is not accounted for in the preceding analysis. While the gas composition is constant (acetylene), perhaps the ion and/or neutral species change drastically within the parameter ranges reported. Indeed, qualitative comparisons of RGA spectra taken during each deposition experiment show no change with bias or duty factor, but do show an increase in the concentration of particles with mass 2 and 50 amu. Molecular hydrogen is likely responsible for the signal at 2 amu, and some polymeric combination of carbon and hydrogen are responsible for the signal at 50 amu (i.e.

C₄H₂ radical, C₄H₄ and derivatives). The increase in concentrations of these particles correlates weakly with a decrease in the coating hardness.

While the sample stage was actively cooled with 20°C water, the temperature of the sample stage was not measured and could have varied, especially when using a – 8 kV bias. The effect of temperature on DLC properties, especially hardness, is complicated but could be responsible for the increase in hardness using –8 kV and 4 Pa (20 mTorr) as seen in Fig. 8.

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Figure Captions

Figure 1. Plot of measured deposition rates against the average deposition power for -4 kV (diamond symbols) and -8 kV (square symbols) bias. The open symbols are for data at 0.67 Pa (5 mTorr) acetylene gas pressure. The gray symbols are for 1.3 Pa (10 mTorr), and the solid symbols are for 4 Pa (20 mTorr) gas pressures.

Fig. 2. Graph of hardness versus elastic modulus of DLC coatings deposited by PIIP and measured by nanoindentation.

Fig. 3. Plot of $[H]$ versus coating hardness as measured by nanoindentation. The remainder of the coating composition is made up of carbon and trace amounts (<1 at% of oxygen).

Fig. 4. Plot of the deposition rates, in $\text{at}/\text{cm}^2/\text{s}$, for DLC deposited from PIIP at -4 and -8 kV bias. The grey area represents a region where $J_d < J_i$ and resputtering would be the dominate process. The lines represent a polynomial fit to the data sets.

Fig. 5. Plot of coating hardness as a function of bias and acetylene pressure.

Fig. 6. Plot of coating hardness as a function of duty factor, bias, and pressure.

Fig. 7. Plot of coating hardness as function of deposition rate.

Figure. 8. Plot of DLC hardness vs J_i/J_d and gas pressure. The grey symbols indicate a -4 kV bias, and black for -8 kV. Triangles are used for 0.67 Pa (5 mTorr) pressure, circles for 1.3 Pa (10 mTorr), and triangles for 4 Pa (20 mTorr).

Table 1. DLC deposition parameters of bias (V), gas pressure (P), pulse width (τ), frequency (f), and duty factor (F).

Run	V (kV)	P (Pa)	Pulse parameters		
			τ (μ s)	f (kHz)	F
1	4	5	30	4	0.12
2	4	5	75	3.33	0.25
3	4	5	4	15	0.06
4	4	10	4	15	0.06
5	4	10	75	3.33	0.25
6	4	10	15	0.667	0.01
7	4	20	75	3.33	0.25
8	4	20	30	4	0.12
9	4	20	30	4	0.12
10	4	20	15	4	0.06
11	4	20	15	0.667	0.01
12	8	5	15	4	0.06
13	8	5	30	4	0.12
14	8	5	75	3.33	0.25
15	8	20	15	4	0.06
16	8	20	15	4	0.12
17	8	20	30	4	0.12
18	8	20	75	3.33	0.25

Table 2. A list of results including the average current during a pulse ($\langle I_p \rangle$), the calculated average power ($\langle P \rangle$), the deposition rate (R), the coating thickness (t), and composition of the coating.

Run	$\langle I_p \rangle$ (A)	$\langle P \rangle$ (W/cm ²)	R ($\mu\text{m/hr}$)	t (μm)	[C] (at%)	[H] (at%)	[O] (at%)
1	0.01	0.006	0.17	0.21	71	29	
2	0.02	0.024	0.34	0.50	66	34	
3	0.06	0.017	0.09	0.15	75.5	24.5	
4	0.12	0.034	0.55	0.56	68	32	
5	0.08	0.095	1.05	0.35	68	32	
6	0.16	0.008	0.07	0.06	70	30	
7	0.24	0.235	3.40	1.3	65	35	0.5
8	0.32	0.183	2.10	0.85	64.5	34.5	0.5
9	0.35	0.200	1.40	0.64	65	35	0.5
10	0.45	0.128	1.50	1.2	61.5	38.5	0.5
11	0.55	0.026	0.45	0.24	65.5	34.5	
12	0.35	0.200	0.54	0.27	68	31	1
13	0.3	0.342	0.98	0.25	72	28	
14	0.2	0.476	0.90	0.3	71	27	2
15	1.4	0.800	2.10	0.6	68	31	1
16	1.0	1.141	1.20	0.3	73	27	
17	1.0	1.141	1.68	0.42			
18	1.2	2.854	3.90	1.3	73.2	25.7	1

Table 3. Results of the hardness (H), elastic modulus (E), ion flux (J_i), neutral flux (J_d) and their ratio (J_i/J_d).

Run	H (GPa)	E (GPa)	J_i (10^{15} at/cm ² /s)	J_d (10^{15} at/cm ² /s)	J_i/J_d
1	15.3	156	0.02	0.65	0.03
2	15	151	0.07	1.53	0.05
3			0.05	0.38	0.14
4	17	150	0.31	2.22	0.14
5	17	150	0.54	2.88	0.19
6	17.5	171	0.74	3.00	0.25
7	15	120	0.01	2.38	0.05
8	17	140	0.30	7.25	0.04
9			0.02	0.33	0.07
10	12	120	0.89	12.20	0.07
11	13.5	120	0.57	7.50	0.08
12	17	130	0.62	7.75	0.08
13	16	120	0.40	5.35	0.08
14	17	150	0.08	1.82	0.04
15	8.5	94	1.25	5.78	0.22
16	12.2	124	1.78	4.67	0.38
17	6	85	1.78	5.67	0.31
18	13	162	4.46	12.90	0.35

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8