Application of a Large Area Inductive Ion Source to Diamond-Like Film Deposition

P. Bletzinger* and A. Garscadden*, Richard L.C.Wu** and William Lanter**

* Wright Laboratory, Wright-Patterson AFB, OH 4543 3-7919
** UES Inc., Dayton, OH 45432

For large area, non-planar surface thin film deposition a system using a 20cm diameter ion gun and a 4-axis substrate scanner has been developed. The advantage of ion beam deposition is a wide range of available control parameters like ion energy, current density, source rf power and gas composition. We have investigated the influence of these parameters on DLC film characteristics such as adhesion to substrate, wear resistance, optical transmission and dielectric strength. In order to have on-line control and some predictive capability over film characteristics, we have measured the ion beam composition with an on-line mass analyzer. Initial correlations between operating parameters, ion beam composition and film characteristics will be presented.

In order to achieve deposition of diamond-like coatings (DLC) over large areas methods such as immersion into large RF-plasmas have been used [1]. Control of deposition parameters like ion energy and ion composition in such systems is limited. In order to achieve detailed and reproducible control over these parameters we have applied a large area (20cm diameter) inductively excited ion gun capable of ion currents of up to 5.4 mA/cm^2 at ion energies from 50 to 3000 eV in conjunction with a 4-degrees of freedom substrate table to allow coatings of up to 1000 cm^2 area over non-planar surfaces (Fig. 1) [2]. The ion source is similar to the transformer coupled plasma sources used in semiconductor etching reactors which can produce plasma densities of 10^{12} cm^{-3} and higher. It has no filaments or electrodes which reduces problems of operating lifetime and plasma contamination. The ion source uses a very high energy density (up to 1kW 13.56 MHz rf power into a volume of 2.7 liters) plasma at pressures $\geq 10^{-4}$ Torr. Ions are extracted and focussed with a standard two-grid system and maximum ion currents reach 5.4mA/cm^2. From measurements of the ion beam current densities with a Faraday cup we infer electron densities in the source of 10^{12} - 10^{13} cm^{-3}. This indicates a very high degree of ionization and results in efficient dissociation of the molecular species. For on-line analysis a quadrupole mass analyzer has been installed which provides measurements of ion species and their abundance. The ion beam composition was investigated as a function of ion energy, gas composition and rf power. In Fig. 2 the mass peaks of CH_2^+, CH_3^+ and CH_4^+ are shown as a function of rf power normalized to the CH_3^+ peak. CH_4^+ and CH_3^+ decrease relative to CH_2^+ as the rf power increases. CH_3^+ is the most abundant ion up to 400W of rf power; at higher powers, CH^+ and C^+ become the most abundant species. Apparently, dissociation increases monotonically with increasing rf power. From 149 to 209 W rf power and for a gaseous mixture Ar/CH_4 3:17sccm, the total current increased from 160 to 230 mA, the CH_3^+ current decreased from 3.9 to $2.3*10^{-7}$ and the intensities of Ar^+ and ArH^+ increased. If CH_3 is the radical most responsible for DLC film growth, then there may be an optimum rf power for maximum growth rate. Note that there are also sizeable amounts of $C_2H_n^+$ (n=2-5) ions, especially at higher ion energies (see Fig. 4). As another example, in an Ar/CH_4 mixture, the ratio of the ion intensities of CH_n^+/CH_3^+ (n=0,1,2,4,5) and $C_2H_n^+/CH_3^+$ (n=2,3,4,5) was measured as function of the Ar/CH_4 ratio at constant rf power of 200 W. The ratio of CH_4^+/CH_3^+ decreases and the ratio of CH_2^+/CH_3^+ increases as the ratio of Ar/CH_4 increases (Fig. 3). The ratio of $C_2H_n^+/CH_3^+$ was found to be nearly constant. Increasing amounts of argon then also increase the degree of dissociation. When increasing amounts of hydrogen are added to the Ar/CH_4 mixture, the predominant ion is CH_3^+, the relative ion intensity of CH_4^+ increases and that of CH_2^+ decreases. The selective use of Ar, while helpful in stabilizing the ion source discharge, is also useful in cleaning and preparing the substrate prior to deposition. The intensity ratio of selected radicals ions and CH_4^+ to CH_3^+ as a function of ion energy is shown in Fig 4 for a gas flow rates of $Ar/CH_4/H_2$ of 3/17/17 sccm. At energies above 800 eV CH_4^+ has decreased by more than a factor of 2 while CH_5^+ and $C_2H_5^+$ have increased to about 50% of CH_3^+. If the amount of H_2 flow is doubled, then CH_4^+ remains at 50% of the CH_3^+ reference ion intensity while CH_5^+ and $C_2H_5^+$ increase to 60-70% at energies above 1 keV. Ion energy also has a large effect on the DLC properties. With increasing ion energy, the hydrogen content in the film decreases. This was established by simultaneous Rutherford backscattering spectroscopy and proton recoil detection analysis of six films deposited on silicon substrates under the conditions shown in Table 1. It is interesting to

Table 1. Deposition conditions and elemental analysis of 6 DLC samples.

Gas Flow Rates (sccm)			Beam Energy (keV)	Total Current (mA)	RF Power (W)	Deposition Time (hr)	Concentration (atomic %)		
CH_4	Ar	H_2					C	H	Ar
17	3	0	0.7	150	156	3	56.5	41.7	1.75
17	3	0	1.5	270	149	5	61.1	37.8	1.0
17	3	17	1.5	190	149	4	61.9	36.8	1.4
17	3	34	1.5	270	169	2.2	62.5	37	0.4
14.4	20	0	0.1	390	199	1	63.9	34	2.1
14.4	20	0	0.3	410	199	1	62.3	36	1.7

note that the addition of hydrogen in the ion source did not affect the final hydrogen content in the deposited films. Note that the mass spectra were quite similar for all 1.5 keV ion deposition plasmas. When using argon in the gas mixture, consideration has to be given to sputtering effects, especially at the higher ion energies. A series of experiments were carried out to investigate then DLC deposition as a function of time at constant rf power for gas mixtures with and without hydrogen. When measuring the DLC thickness for eight time periods it was found that the film thickness increased linearly with time with zero thickness when extrapolating to time zero. This indicates that the deposition process starts immediately with no incubation period and possible sputtering process. The sputtering process appears to be much less important than the deposition process. The deposition rate for DLC film under the present experimental conditions is calculated to be 1400 Å/hr. Conducting wear measurements under UHV conditions, it was found that the wear rates increase with increasing ion energy. On the other hand, excellent adhesion to metal substrates was achieved with ion energies of 1.5 keV and greater. Also it was found that under the same plasma conditions ($Ar/CH_4/H_2$=3/17/17 at 1500 eV) the resistivity and dielectric constant of the deposited DLC films on silicon and glass were different. The average resistivity of DLC film on Si and glass were measured to be $1.0*10^9$ Ωcm and $2.8*10^{10}$ Ωcm respectively. The dielectric constant of DLC film on Si and glass were calculated to be 7.7 and 4.2 respectively. These examples show the very different operating parameters required not only for different processes but also for different phases of the same deposition process. More detailed investigations of the plasma properties and their influence on ion composition and deposition characteristics will be reported.

Acknowledgement

This work was done under Air Force contract F33615 - 92 - C 2205 with the plasma research group (WL/POOC-3), WPAFB, OH. The authors would like to thank Dr. K. Miyoshi of NASA Lewis for conducting tribological experiments and Ms. Sandra Carr of WL/POOC-1, WPAFB and Dr. P. Kosel of the University of Cincinnati for performing capacitor experiments.

References

1. P.Koidl, Ch.Wild, B.Dischler, J.Waynes and M.Ramsteiner, Materials Science Forum Vols 52 and 53, pp. 41-70, 1989.
2. R.L.C.Wu, W.Lanter, K.Miyoshi, S.L.Heidger, P.Bletzinger and A.Garscadden, "Uniform and Large Area Deposition of Diamond-Like Carbon Using RF Source Ion Beam". Proceedings of the 1994 Materials Research Society, Symposium A; Beam-Solid Interactions for Materials Synthesis, in press (1995).

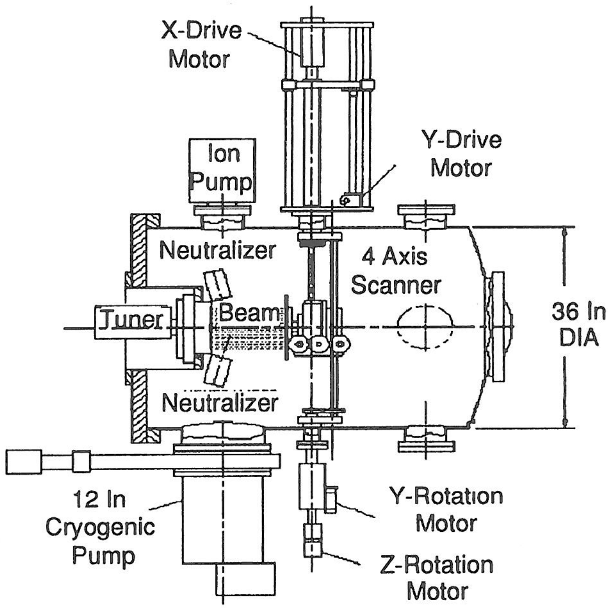

Fig. 1

Fig. 1 Schematic of deposition system

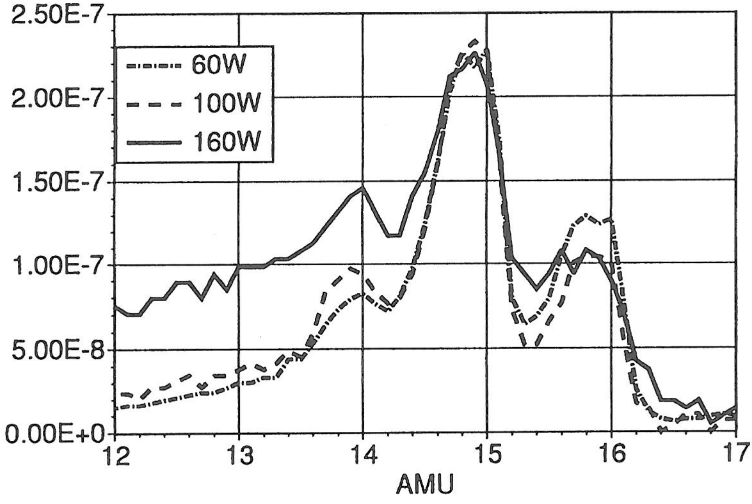

Fig. 2

Fig.2 Ion spectrum as a function of rf power

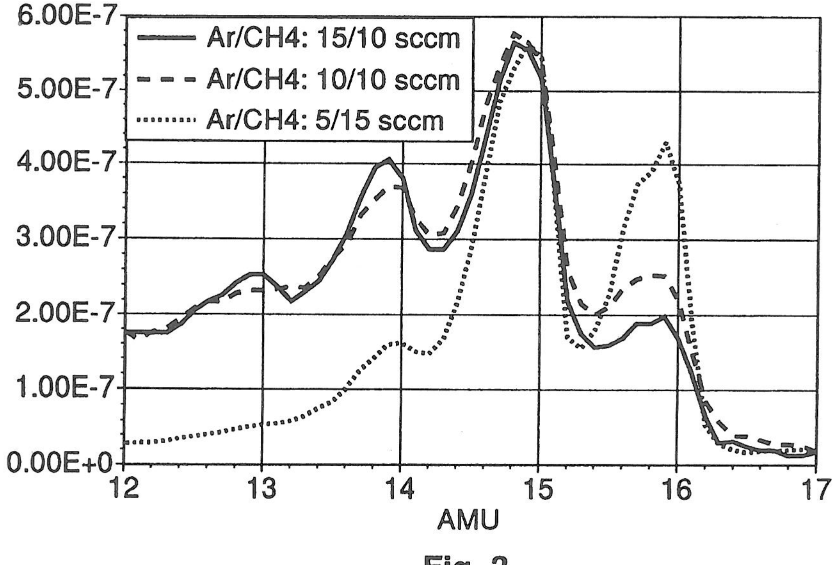

Fig. 3

Fig. 3 Ion spectrum as a function of Ar/CH_4 mixture ratios

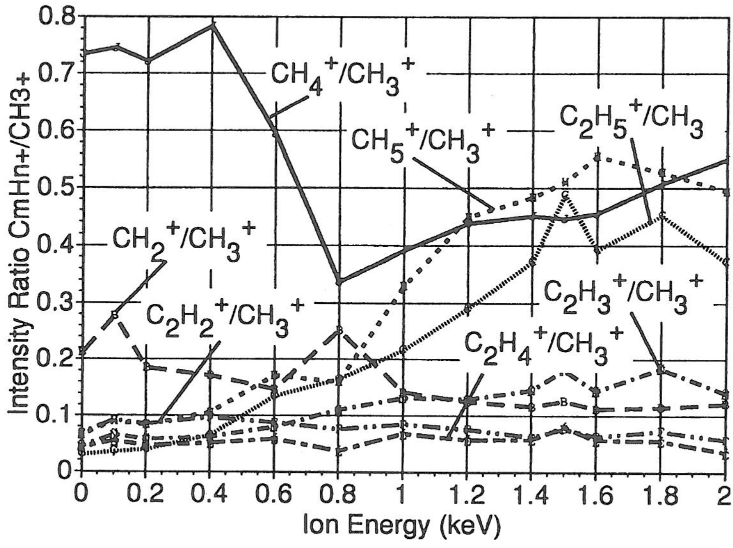

Fig. 4

Fig. 4 Ion abundance as a function of ion energy normalized to the CH_3^+ ion