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A COMPARISON OF THREE TECHNIQUES FOR DEPOSITING DLC FILMS AT TEMPERATURES BETWEEN 25 AND 100° C

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Astract Diamond-Like Carbon (DLC) films have been deposited on silicon, glass and plastic surfaces by three different techniques: (a) Pulsed Laser Ablative Deposition, (b) Remote Microwave or DC Plasma Deposition, and (c) Moving Acetylene Flame Deposition. All three techniques were found to be capable of depositing hard films on these surfaces without raising the substrate temperatures above 100°C.The films produced were analyzed by X-ray, electron, Raman, IR, and visible spectroscopy, for hardness and adhesion, and by SEM for surface morphology. An extensive search for the optimum conditions for the formation of hard, adhering and transparent films has shown that it is essential that during the deposition process the surface is bombarded by high energy positive ions. The optimum conditions were found to be most easily achieved with a glow discharge.

Keywords: Diamond like carbon, Thin films, Pulsed laser ablation, Microwave plasma, Acetylene flame

INTRODUCTION

Diamond like carbon (DLC) films, which appear to have been first deposited by Aisenburg and Chabot[1] in 1971, are metastable amorphous materials. They have now been prepared by a number of different techniques, including hot filament chemical vapor deposition (CVD), direct current (DC), radio frequency (RF) and microwave plasma CVD, sputtering, ion beam and laser ablation from the carbon containing gases, vapours and polymers[2,3], and from combustion flames. Recently several reports and reviews have appeared[4] which discuss the preparation and characterization of DLC films deposited on a variety of substrates. Most of the reported work which can be found in the literature describes techniques which form crystalline hard films at high substrate temperatures (800 - 1200° C).

DLC films grown under most growth conditions have been found to have a hydrogen content in the range 10 - 50% [5,6,7]. Many properties of DLC films, including structural, mechanical, optical and electronic, depend upon the hydrogen content in the films. It has been found that although hydrogen improves the optical properties, it degrades the mechanical properties[8,9]. Although high thermal conductivity and electrical resistivity makes them an excellent coating for heat dissipation in microelectronics, the high deposition temperature remains a liability because of the accompanying device degradation.

Most work being reported on diamond/DLC films[4,10] is on polycrystalline films deposited by high temperature CVD, which not only suffers from the defect discussed above, but results in surface roughness ranging from a fraction of a micron to more than ten microns. If those hard coatings are used for tribological coatings on moving parts in contact with one another, abrasion becomes a major problem. The work described in this paper is an attempt to find the optimum conditions for the deposition of hard transparent films at substrate temperatures no higher than 100°C so that deposition is possible on almost any material which could benefit from such a coating. In the present paper we report an investigation of DLC films prepared near room temperature using three different techniques: (a) pulsed laser ablation of carbon containing soids ("Ablative Deposition"), (b) downstream growth from an electrical discharge in a mixture of hydrogen and acetylene or methane ("Plasma Deposition"), and (c) deposition with a rapidly moving flame from an oxy-acetylene torch ("Torch Deposition").

EXPERIMENTAL

(a) Plasma Deposition (PD)

The apparatus used for depositing DLC films by microwave or DC plasmas consists of a small deposition chamber in the shape of a bell jar on a stainless steel flange fitted with a copper block which holds the substrate. The copper block contained a water circulating system, an electrical heater and a thermocouple which allowed the substrate temperature to be fixed anywhere between 5 and 400°C. A metal grid made of a fine tungsten wire could be positioned above the substrate so

that a potential anywhere between ±2000 volts could be applied to a wire mesh immediately above the substrate. The feed gases flowed over the sample from a 1 cm diameter tube in which a microwave plasma could be established by directing up to 200 watts of 2450 MHz radiation. A tantalum electrode was positioned at the upstream end of the plasma. The plasma extended to within 2 cm of the substrate, but only the accelerated positive ions reached beyond the grid to the substrate surface.

(b) Ablative Deposition (AD)

A Lumonics excimer laser employing ArF and KrF lines was used to ablate graphite, C_{60} and solid organic polymers. The polymer targets were mounted for ablation on a holder that incorporated a heater and a thermocouple. The substrate on which the deposition occurred was mounted on a holder facing the target and a few cm away. It was also equipped with a heater and thermocouple. A grid was placed in front of the substrate so that an electric field could be applied between the target and the substrate. A quartz crystal microbalance was mounted beside the substrate holder to monitor the ablation rate. The excimer laser beam was focused on the target through a sapphire window behind which all the above assembly was mounted in a vacuum chamber hooked to a vacuum pump. Pressures in the range from 10 to 250 mTorr were used in the deposition experiments.

(c) Torch Deposition (TD)

A small oxy-ethylene torch was used for depositing DLC films on single crystal silicon and glass substrates. To assist in keeping the substrate cool and to facilitate the more uniform coating of large areas, a motor was used to drive the stage on which the torch was mounted. This stage could be moved horizontally in an oscillatory fashion along one direction while it was slowly advanced in a perpendicular horizontal direction. The height of the torch relative to the substrate could also be continuously varied in order to select different regions of flame for contact with the substrate. The oxygen to acetylene ratio was kept at 0.85 throughout the experiment.

The films made by all three techniques were examined under SEM

for surface topology, TEM and XRD for structure analysis, IR and Raman spectrometry, ASTM scratch tester for adhesion and hardness. Some of the films were annealed under vacuum. The structures of films grown by all three techniques were analyzed using SEM, TEM and XRD. FTIR spectrometry was used to assess the hydrogen content of the films.

RESULTS

Initially a graphite target was used to produce films. It was found that hard films could indeed be produced with this technique, however, the target surface became pitted as the ablation proceeded, and the ablation rate dropped to very low levels. We consequently investigated the possibility of using other materials as targets. Materials that were tried included buckminsterfullerene (C_{60}), polyethylene, teflon, polystyrene, polycarbonate, and PMMA (lucite). PMMA targets were found to produce films of comparable quality to those obtained from graphite targets.

The structures of the amorphous hydrogenated DLC films were analyzed by X-ray diffraction using copper K_α radiation to obtain the diffraction pattern. Three typical X-ray diffractograms of DLC films on silicon are shown in Fig. 1. They were prepared by three different techniques all at a substrate temperature of 50°C. In the case of the films

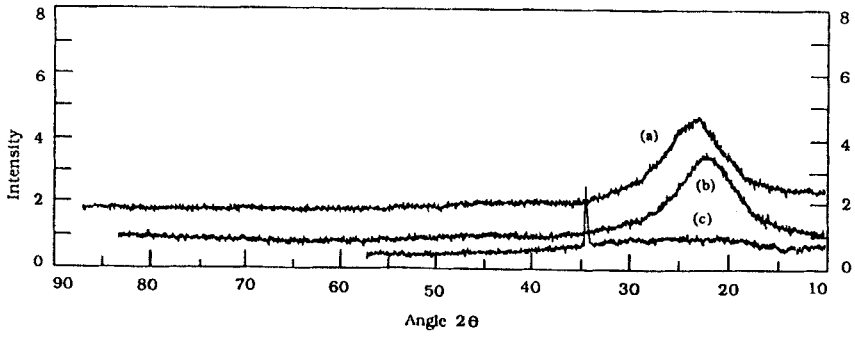

Fig. 1. X-Ray diffractogram of DLC films grown by (a) PD of acetylene and hydrogen on single crystal silicon substrate with 50°C substrate temperature, (b) Pulsed Laser Ablation of PMMA in air at 20 millitorr pressure onto single crystal silicon surface at 50°C, (c) MAF technique onto silicon at 50°C sink temperature.

made by TD, the surface temperature of the substrate (when the flame is in contact) is probably considerably higher. The recorded temperature is the substrate bulk temperature, which is in thermal contact with the heat sink maintained at constant temperature by a heater and the circulating water at 5°C. It is clear that the films are amorphous having no crystalline order. All the films were found to have X-ray diffractograms like those in Fig. 1, except the very thin ones which were sufficiently transparent for the X-rays to show the silicon diffraction peaks seen in Fig. 1c.

Electron diffraction was used to supplement the information acquired by X-ray diffraction. Fig. 2 shows the transmission electron micrographs in the diffraction mode and in the image mode for the

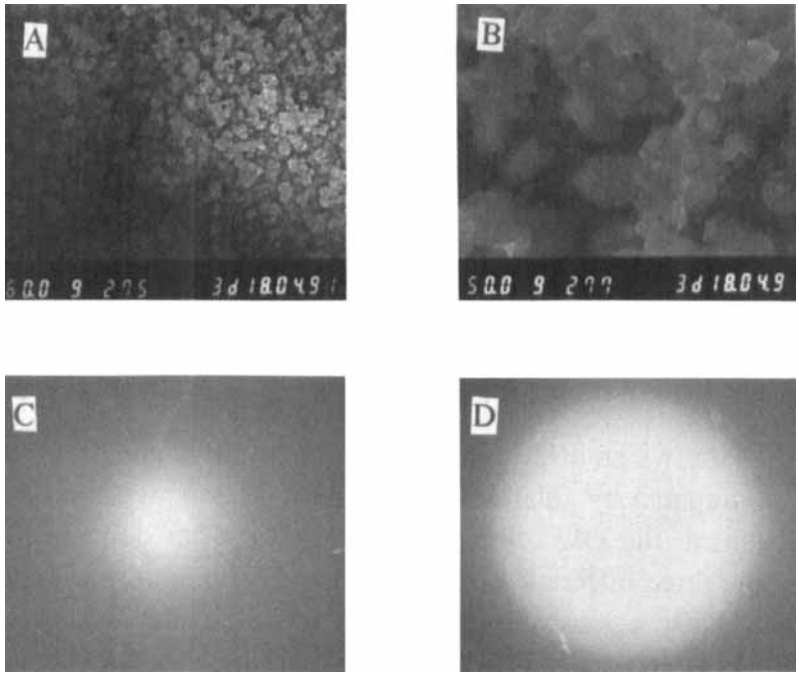

Fig. 2 Transmission electron micrographs of DLC films onto single crystal silicon (a) prepared by PLA of PMMA under environment freon-12 at 98°C, (b) Image of DLC film prepared by TD at 100°C temperature, (c) ED of DLC film prepared by PD 1% acetylene and 99% of hydrogen at 50°C, (d) Electron diffraction (ED) of DLC film prepared by PLA of buckminsterfullerene at 93°C.

DLC films deposited on silicon at substrate temperatures of 93° and 46° C and subsequently annealed for 4 hours at 150° C. The film in Fig. 2a was prepared by ablative deposition from buckminsterfullerene while that in 2b was prepared by remote plasma deposition. The transmission electron micrograph of the DLC film prepared by torch deposition at 100° C is shown in Fig. 2c. No crystallinity was observed by electron diffraction or X-ray diffraction in either case. It is interesting to note that the films prepared by ablative deposition close to 100° C in the residual environment of freon-12 were found to develop some microcrystallinity. The films prepared by all three techniques have been found to have very smooth surfaces,as shown in Fig. 3.

Fig. 3. Surface morphology and edge view of amorphous DLC film viewed under SEM at angle 15 degree from normal to surface.

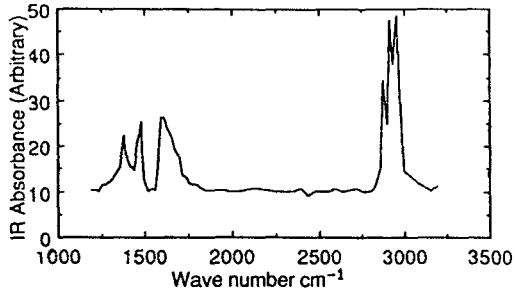

Fig. 4. FTIR spectra of DLC film prepared by PLA of PMMA at substrate temperature 72 degree.

Fig. 4 shows an FTIR absorbance spectrum of an "as deposited" DLC film prepared by ablative deposition on silicon at 72° C. Only the part relevant to the DLC film is shown. All the "as deposited" films made by the three different techniques have been found to have similar IR spectra. Only observable differences were the varying absorbance peak heights which could be attributed to varying film thicknesses, and hence could be normalized. However, after annealing the films, differences could be identified after such normalization. The Figs. 5-7 show the variation of major absorption peaks of the DLC films grown by the three techniques. All the films presented in Figs. 5-7 were annealed in a vacuum at 250° C after deposition. For the films grown by ablative deposition from PMMA

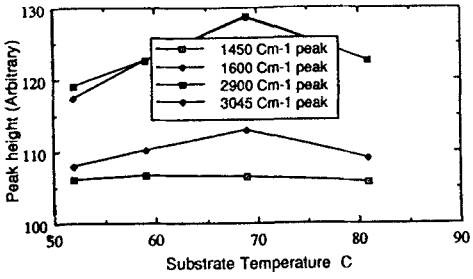

Fig. 5. Deposition temperature dependence of (major) peak height in the IR absorption spectra of DLC film prepared by PLA of PMMA in vacuum and subsequently annealed at 250° C.

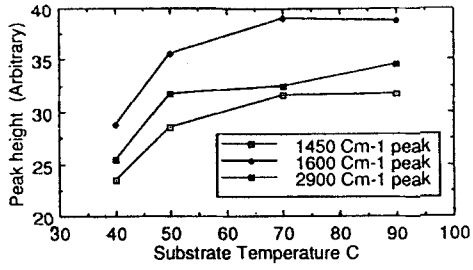

Fig.6. Deposition temperature dependence of peak height for major peaks in the IR absorption spectra of DLC film prepared by PD of acetylene and hydrogen in vacuum and annealed at 250° C.

(Fig. 5) the absorbance peak heights increase with deposition temperature up to a temperature of 70° C, after which they decrease. For the films grown by Plasma Deposition of acetylene and hydrogen the peak heights similarly increase up to 70° C, after which they plateau. With the acetylene torch deposition (Fig.7) the behavior is erratic, although there is similar trend with an initial increase in the deposition rate with temperature followed by decreasing deposition rates at in higher substrate temperatures. These variations in infrared absorption are also reflected in the hardness of the films as measured by a standard scratch test.

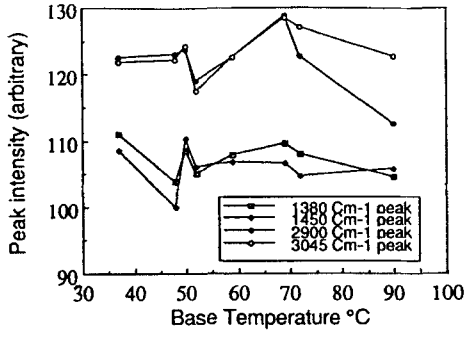

Fig. 7 Deposition temperature dependence of major peak height the IR absorbance spectra of DLC film prepared by MAF and subsequently annealed at 250° C.

The ASTM scratch test provides a measure of the combined hardness and adhesion of the films, and is useful if the material is to be

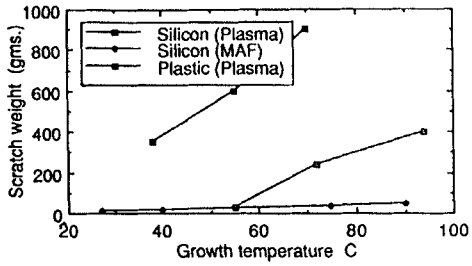

Fig. 8. Temperature dependence of weight required to put a scratch on the DLC film by ASTM scratch test for the films prepared by different techniques on silicon & plastic.

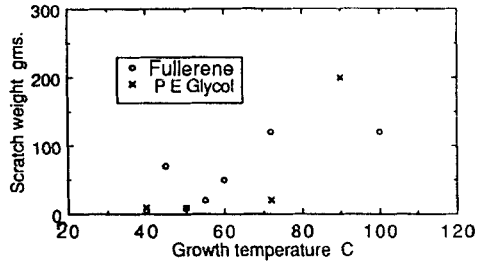

Fig. 9. Temperature dependence of weight required to put scratch on the DLC film by ASTM scratch test for the films prepared by PLA of buckminsterfullerene and polyethylene glycol on to silicon.

of value as a surface coating. Results on the scratch test are summarized in Figures 8 and 9. The DLC films deposited on silicon by ablative deposition are hard and firmly adherent to the substrate. Fig. 8 is a plot of weight on the scratch tester required to make a visible mark on the film versus growth temperature for DLC films from buckminsterfullrene and polyethylene glycol targets. A saturation in the hardness of films obtained from fullerene is observed around 68°C, while the films obtained by the same method from polyethylene glycol show a similar increasing trend, but no saturation point in the experimental temperature range. Fig. 9 shows a comparison of the scratch weight for films grown by the three techniques. The scratch weight increases with increasing growth temperature, but films grown by Plasma Deposition are harder and more adherent to the substrate.

Because no dramatic improvement in hardness and transparency could be had by changing the deposition conditions with any of the three techniques described above, hydrogen was eliminated from the PD process The decomposition was minimized by eliminating the microwave discharge (i.e. using only a mild DC glow discharge at a

pressure of 200 mTorr created by 1 kV, with the substrate grid biased at -1 kV). Unscratchable films could be produced by this technique. Conditions for the formation of transparent unscratchable films with this technique have yet to be explored.

DISCUSSION

The growth of diamond-like films at low temperatures is clearly very different than the growth of diamond crystals at high temperatures. At temperatures near 1000 K the gas phase precursors (C atoms and C containing radicals) are sufficiently mobile on the growing surface to move to the most stable lattice positions, and hence form a diamond lattice. This is not true at low temperatures where these precursors most probably stick to the first bonding site that they encounter. With very restricted surface mobility, the deposits that are formed are "soot-like" materials with a disordered carbon skeleton. In the presence of hydrogen the molecular fragments are simply smaller because the dangling bonds are saturated by hydrogen atoms before the carbon atoms can grow to become large polymers, and the material has the properties of a low molecular weight molecular crystal. In the absence of hydrogen, somewhat harder materials can form. However, without any way of increasing atom mobility on the surface, DLC films do not form.

To increase the mobility of the atoms as they are being deposited, without increasing the temperature of the substrate more than 100°C we have chosen to create conditions under which the surface is bombarded by positive ions. These ions are created in the ablation plume of the AD technique, in the plasma of the PD technique and in the flame of the TD technique. However the ratio of ions to neutrals and the velocities of the ions when they strike the surface appear to be crucial parameters.

In the AD technique we found it necessary to provide the ion energy directly by providing a high energy laser pulse. If the energy of that pulse was not high or concentrated enough, the addition of an accelerating potential was not sufficient to produce DLC films. Even so the films are hard only in the central portion of the ablation plume, while soot like deposits occur on the periphery.

Because the TD technique operates at atmospheric pressure, applying effective accelerating potential to the substrate was the greatest problem. We did not find that the film quality could be improved by the application of any bias to the substrate

In the PD technique softer films were produced when (a) hydrogen was added to the flow system, (b) the pressure was high, (c) the dissociation of the hydrocarbon was high, and (d) the applied potential was low. As pointed out above, the hydrogen atoms do not appear to serve a useful purpose in the deposition of DLC films as they apparently do in the case of diamond crystal growth. Conditions (b) to (d) all conspire to decrease the ratio of ions to neutrals, i.e. to increase the deposition rate or to decrease the ion bombardment rate. Consequently, the best films were prepared with a weak glow discharge in pure methane with a negative bias of about 1 kV on the screen immediately above the substrate.

REFERENCES

1. S. Aisenberg and R. Chabot: J. Appl. Phys., 42, 1971, 2953.
2. J. C. Angus, P. Koidl and S. Domitz, Plasma Deposited Thin Films, CRC Press Inc. Boca Raton, FL 1986, 89.
3. A. Grill, B. S. Mayerson and V. Patel, Diamond Optics, Proc. SPIE 1986, SPIE Ballingham WA V-969, 89.
4. e.g. See J. Mater. Res., 5 (11) 1990.
5. P.V.Koeppe, V.J. Kapoor, M. J. Mirtich, B. A. Bank and D. A. Gulino, J. Vac. Sci. Technol., A3, 1985, 2327.
6. M. J. Mirtich, D. M. Swee and J. C. Angus, Thin Solid Films, 146, 1987, 93.
7. J. C. Angus and F. Jansen, J. Vac. Sci. Technol., A6, 1988, 1778.
8. I. S. Athwal, B. R. Mehta and E. A. Ogryzlo, Unpublished.
9. A. Anttila, J. Koskinen, R. Lappalainen, J. P. Hirvonen, D. Stone and Paszkeit, Appl. Phys. Lett., 50, 1987, 132.
10. e.g. See Proc. 17th Int. Conf. on Metallurgical Coatings and 8th Int. Conf. on Thin Films, 1990.