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Diamond-like carbon films with extremely low stress

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Abstract

We in this paper report different ways to realise thick diamond-like carbon (DLC) films with stress values lower than 0.5 GPa. Thick DLC films grown by conventional r.f. self bias technique often delaminate from the substrates due to the presence of high compressive stresses of the order of 4–7 GPa. We have made an in-depth study of the delamination problem of DLC films at NPL and found that only for substrates kept away from the plasma (plume) it is possible to grow thick DLC films. This goes to show the heating of the substrates, when in contact with the plasma, appears to be one of the most important factors giving rise to the high stress values. Techniques that have produced consistently low stress values (0.2–0.5 GPa) in this laboratory are pulse plasma PECVD and the one using dc saddle field fast atom beam source. Electronic properties of the materials so produced have been estimated by evaluating Urbach energy using photothermal deflection spectroscopy (PDS) measurements. A correlation between the unbound hydrogen in these films, as measured by a nuclear technique (ERDA), and the stress levels has been found. Deposition rate, room temperature conductivity, optical bandgap and refractive index have also been measured for these films.

Keywords: Carbon; Coatings; Plasma processing and deposition

1. Introduction

Compressive stresses in DLC films grown by the more conventional r.f. self bias technique is often significantly high (4–7 GPa). This creates a serious technological problem when one desires to obtain these films in thickness exceeding about a micron for applications like AR coating on Ge optics in 8–12 μm. High stress lead to peeling, blistering and delamination.

It has been considered that somehow high intrinsic stresses are perhaps unavoidable as high stresses seem to stabilize the carbon network in a fashion that high hardness for such films become possible. Fully constrained network model of growth as proposed by Phillips and Thorpe[1,2] is invoked to explain the existence of a critical C—C co-ordination over which the network remains overconstrained, i.e. rigid and hard and below which this becomes so called floppy. An optimum co-ordination number of 2.45 is required to obtain a degree of overconstraint [2,3]. However, one does not really know how much built-up stress should be expected in such a situation, i.e. what is the expected range of values of stresses in a film at optimum network co-ordination. Such high stresses do not normally allow one to grow DLC films more than a micron [4,5], since thicker films delaminate from the substrate easily. Initial experiments lead one to believe that perhaps more than 2-μm thick films may not be grown. Therefore, recent report of 10–25μm thick DLC films by the SAMCO group deservedly requires a close examination [6].

At NPL we conducted a very systematic study to understand stress behaviour of DLC films using following approaches:

1. dilution of the feedstock with N_2;
2. deposition at high frequencies (VHF), 100 MHz;
3. pulse plasma decomposition;
4. DC saddle field fast atom beam (FAB) source.

In all these techniques best results are obtained when the substrate temperature remains well controlled. Our investigations reveal that the stress values can be systematically reduced from about 4–6 GPa for the r.f. self bias grown films to less than 1 GPa for films produced by the pulse plasma and dc saddle field fast atom beam (FAB) techniques.

A close study of the large number of methods that have been used to grow DLC films, as reported in the literature reveals the following:

r.f. self bias technique, though widely practised may not, perhaps, be capable of yielding low stress films because of the following reasons, (a) for achieving sufficiently high self

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bias values to get hard enough films, we need to apply high r.f. power and thus a higher degree of dissociation of hydrocarbon molecules. In this way more unbound hydrogen gets incorporated in the films, which has been identified to lead to enhanced compressive stresses [4]. In an assessment of the limitation of the r.f. self bias technique for growing DLC films, Catherine [7] and subsequently Grill et al. [4] pointed out that to generate large enough self bias (to impart the impinging film forming precursors with sufficient energy to form hard DLC films through the process of subplantation) one intuitively applies high power. At such high power levels various reactions in the bulk plasma are changed in a fashion that lead to an increase of the unbound hydrogen which, in turn, leads to a higher stress level in these materials; (b) Positive ions from the plasma bombard the substrate surface due to the negative dc self bias potential on the cathode. As a result of the ion impact the substrate temperature increases, which also causes an increase of stress in the DLC films [8]. In recent work Huai et al. [9] have shown that a degradation of diamond-like character to takes place with increasing substrate temperature above 25°C.

In the pulse plasma technique substrates cool down during the OFF period of the pulse whereas in a conventional r.f. discharge substrates get heated continuously during the growth processes and after long enough time growth rate is found to decrease. It is this observation which we made a few years ago, while optically monitoring a DLC growth for AR coating for 10 μm application, through a semiconductor laser based OTM traces, made us think in terms of pulse plasma growth. During this time we also experimented extensively with a modified pulse technique to grow a-Si:H films and found interesting results [10–12]. However, it is Yamada et al. [8]. who undertook the pulse plasma growth of DLC films for the first time. These authors also confirmed that since positive ions from the plasma bombard the substrate surface due to the negative dc self bias potential on the cathode, as a result of the this ion impact the substrate temperature increases. The dc glow discharge technique where substrates are kept on the cathode has been carefully examined by Grill and Patel [4]. The reason for lower stresses in the films grown by this technique has been attributed to the comparatively lower power densities used to obtain the required self bias values (in the r.f. system, relatively high r.f. power densities are used to achieve high enough substrate bias).

Saddle field fast atom beam source, extensively investigated by the present authors, has all the attributes of a dc and a r.f. discharge [13–15]. It may be noted here again that substrates are not required to be placed in close contact with the discharge and, thus, do not easily heat due to bombardment of ions as in the case of r.f. self bias technique.

Thus, it becomes abundantly clear that it is, perhaps, the substrate heating during growth that somehow is implicated in the occurrence of the phenomena of high compressive stress in DLC films.

2. Experimental details

The pulsed plasma grown films used in the present study were prepared in a capacitatively coupled asymmetric PECVD reactor. The details of the deposition system have been described elsewhere [16]. In these experiments we have used three different hydrocarbon sources, two gases (methane, CH_4 and acetylene, C_2H_2) and a vapour (benzene, C_6H_6) to grow DLC films. For the pulse plasma decomposition of the hydrocarbon gases and a vapour, pulsed power was applied to the cathode using a r.f. generator (RF5S, RF Plasma Products, Inc., USA), which has a provision to generate both continuous wave (cw) and amplitude modulated r.f. pulses.

The deposition conditions for the pulse plasma grown films were as follows: applied ON power density: 0.42–2.0 W/cm^2; dwell time: 150 ms; duty cycle: 30%, pressure: 25 mTorr; flow rate: 3.2 sccm.

The dc saddle field fast atom beam grown DLC films that were investigated in the present study were prepared at a distance of ~6 cm by aspirating hydrocarbon gases (CH_4 and C_2H_2) and C_6H_6 vapours into a saddle field fast atom beam source (Ion Tech. Ltd., presently Atom Tech. Ltd., FAB 110–2) mounted in a 30 cm diameter vacuum system. The source operates at 0.5–2.0 kV in the pressure range 10^{-4}–10^{-3} Torr and is of modular design to cover increasingly larger areas. The operation of the source is dependent only on the regulated current output from the power supply and the discharge voltage which is decided by the gas flow (pressure and consequently by setting of the needle valve etc.). Other details of the experimental set-up and the saddle field FAB source have already been described elsewhere [13–15].

A number of measurements on DLC films grown by these two techniques were carried out. The values of intrinsic stress of these films were evaluated from curvature induced in the substrate due to the deposited film. The curvature was measured by using a laser scanning technique [17]. Knoop hardness of these films were measured at a 50 g load. Optical transmission measurements were carried out on these films using a Shimadzu (model 3101PC) spectrophotometer and the values of optical band gap (E_g) evaluated from the intercept of Tauc's plot of $(\alpha h\nu)^{1/2}$ vs. hν (where α is the absorption coefficient and $h\nu$ is the photon energy). A Rudolph manual photoelectric ellipsometer system (type 4360-300E) with an angle of incidence 70° at the 546.1 nm wavelength was used to estimate the refractive index values. The values of Urbach energy (E_0) were evaluated by the photothermal deflection spectroscopy (PDS) technique. The measurement of the room temperature conductivity was carried out on planar samples. The planar samples were made by evaporating aluminium on these films in a vacuum of 10^{-6} Torr. The total hydrogen content of the DLC films has been estimated using elastic recoil detection analysis (ERDA) and the IR spectroscopy technique has been used to determine the bonded hydrogen content.

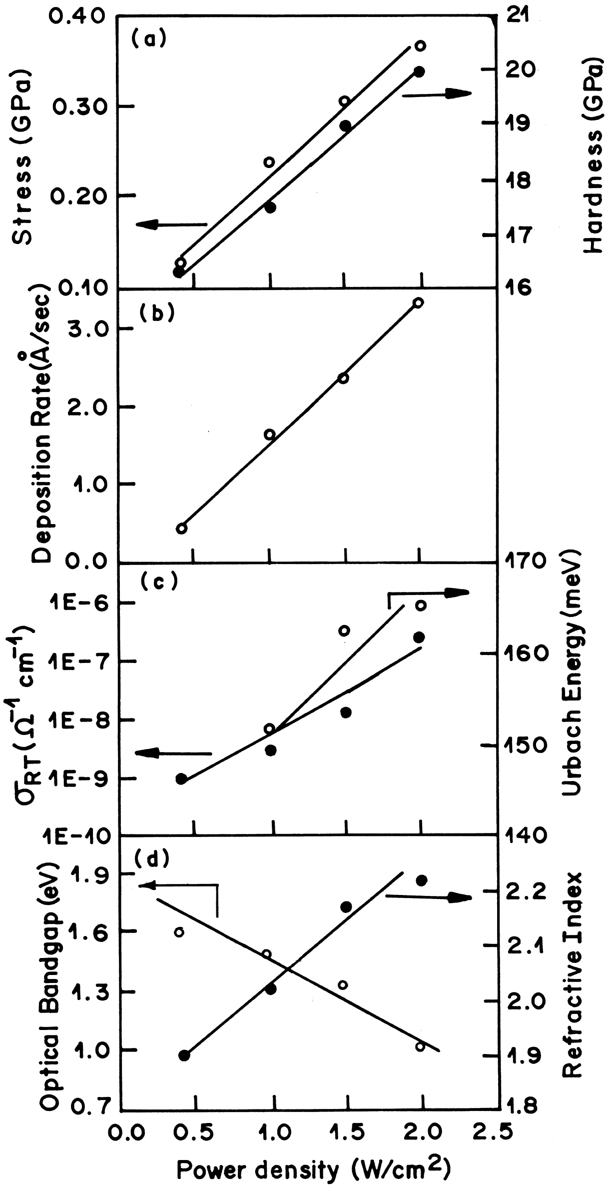

Fig. 1. Effect of power density on (a) stress and hardness (b) deposition rate (c) Urbach energy and room temperature conductivity (d) optical bandgap and refractive index of DLC films grown at constant dwell time (150 ms) and duty cycle (30%).

3. Estimation of film properties and discussion of results

3.1. Pulse plasma grown DLC films

The pulse ON power level was systematically varied to grow hard DLC films and to study their other properties.

Fig. 1a shows the variation of stress and hardness as a function of ON power density. The stress and hardness values of these films increase with the increase in power density. From these results it appears that hardness and stress values are interrelated, similar to cw discharge produced DLC films [18–20]. For the pulse discharge grown films the stress values varied from 0.13 to 0.37 GPa with the increase of ON power density from 0.4 to 2.0 W/cm^2, these values are significantly lower when compared to the stresses in cw discharge grown films.

Table 1 compares the properties of pulse and cw discharge grown films. For this comparison data related to two representative films are shown in Table 1. Other films also behave in a similar fashion. CP-1 and DCRF-1 are pulse and cw discharge produce films grown at power density of 0.42 W/cm^2 (in the case of pulse discharge, power means ON power level of the pulse). One observes, at a specific power density of 0.42 W/cm^2, as shown in Table 1, that the stress values can be reduced from 4.6 GPa to 0.13 GPa by using the pulsed discharge technique alone. During the cw operation, films grown at high power density ($>$ 0.45 W/cm^2, corresponding to a self bias voltage more than 350 V), delaminate from the substrates as soon as they were taken out from the process chamber. This was due to the high level of stresses present in these films.

Fig. 2 shows the rise in temperature of the substrates kept at the cathode with the change of self bias voltage for discharge sustained in C_2H_2. It is evident from Fig. 2 that with the increase in applied power, the energy of the bombarding ions on the substrate increases, which in turn causes enhancement of the substrate temperature.

It has been observed in this laboratory during the deposition of DLC films on Ge substrate for antireflection application in the 8–12 μm range, where the growing films was monitored using a semiconductor laser based optical thickness monitor (OTM) working at 670 nm, that growth rate of DLC films does not remain constant. It was found that as the deposition of the film proceeds, the OTM signal goes through a series of maxima and minima. A representative OTM trace is shown in Fig. 3. It can be easily seen from Fig. 3 that the maxima and minima are not equally spaced in time. As the deposition of the film proceeds, the spacing of the maxima/minima increases, which means the deposition rate decreases. For thickness of DLC films corresponding to a few $\lambda/4$ points, this change of deposition rate does not become readily discernible. In some published literature this observation is reported differently as the onset of a compaction phase of film density etc. In fact, Yamada et al. [8] did indeed find a change in the film density with the increase of

Table 1
Comparative study of the cw and the pulse plasma grown DLC films

Sample no.	Power density (W/cm^2)	Stress (GPa)	Hardness (GPa)	Deposition rate (Å/s)	Refractive index	Optical band gap (eV)
CP-1	42 (pulse)	0.13	17.29	0.42	1.62	1.60
DCRF-1	42 (cw)	4.60	15.00	6.70	2.13	1.15

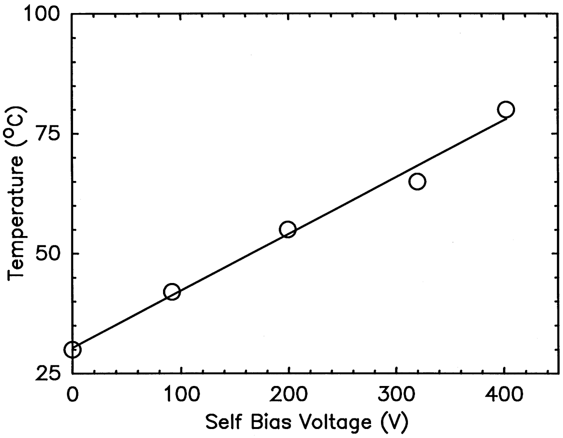

Fig. 2. Change in the temperature of substrate with the variation of self bias voltage in C_2H_2 plasma.

substrate temperature due to the continuous impact of ions ranging in energy up to 100 eV, as is normally encountered during the growth of hard DLC films [21].

By adopting the pulsed discharge technique, it became possible to deposit low stress DLC films even at higher power densities as shown in Fig. 1a. This is because using the periodic deposition mode the deposition temperature has been controlled, as during the off period of pulse, substrates get sufficient time to cool such that the substrate temperature does not increases as in case of continuous discharges. Specifically, the substrates were found to remain close to the ambient temperature even after more than an hour of discharge. Under similar conditions, substrate temperature reached close to 100°C in the cw mode deposition as a result of ion bombardment. It is known for a given deposition pressure, the maximum ion energy is proportional to the electric field and this correlated reasonably well with the self bias voltage. Since the self bias voltage was found to increase with the applied r.f. power density, the increase in substrate temperature seen with the increase of self bias voltage (as shown in Fig. 2) is consistent with increased ion energy caused by enhanced ion bombardment. Thus, the substrate temperature increases and consequently the compressive stress in these films grown by cw discharge. A similar observation was also made by Yamada et al. [8]. In addition, pulsing helps in relaxation of adions and allowing them more time to settle, which may also be the reason for low stresses in these films. It is believed that the most probable growth mechanism of DLC films, involves the subplantation of incident ions [22–25]. Incident ions of sufficient energy penetrate the solid, enter an interstitial position below the surface layer and increase the local density. However, the energetic carbon ions cause atoms to be incorporated into spaces in the growing film which are smaller than the usual atomic volume [26] and this leads to an expansion of the film outwards from the substrate. In the plane of the film, however, the film is not free to expand and the entrapped atoms cause macroscopic compressive stress [22]. Generally, this happens in the DLC films grown by the more conventional continuous mode r.f. asymmetric PECVD deposition.

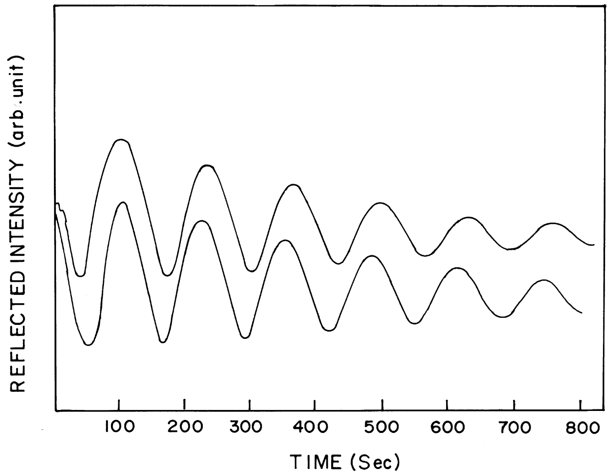

Fig. 3. In situ measurement of light reflection vs. time while growing DLC films using a OTM (wavelength used 670 nm).

The compressive stress caused by the implanted atoms is associated with an increase in the strain energy of the films. Therefore, a reduction in the stress by the movement of the implanted atoms to the film surface is energetically favored [22]. The implanted atoms, however, are prevented from moving by the repulsive force exerted by the surrounding atoms and also subsequent bombardment of ions. The implanted atoms, thus, are in metastable locations within a few nm of the film surface [22]. It is, therefore, likely that atoms which acquire more than a certain excitation energy will escape from their metastable positions on the surface of the film. A significant fraction of the energy of a bombarding ion is transferred to a violent motion of the atoms in the area of impact. This intense local heating, or thermal spike [27], can provide the energy required to release the implanted atoms from their metastable positions within the film. But even then it is generally found that hard a-C:H films are under high compressive stresses, of the order of several GPa. This may be because in continuous discharges, subsequent bombardment of ions does not allow implanted atoms of the film surface to relax and settle.

Thus, in a pulse plasma discharge during the OFF period of the pulse, implanted atoms may get sufficient time to move to the film surface, relax and settle there. Another possible argument could be that as deposition rates are quite low in the case of the pulse mode of deposition, compared to continuous mode deposition, this mode of deposition allows the atoms to relax far more conveniently.

Since the temperature of the substrate increases during the course of the deposition due to the ion bombardment of the surface, this could modify the properties of the resulting films to an extent, though this increase of the temperature is only about 100°C. In this context, it may be mentioned that the carbon phase is sensitive to the temperature of the

Table 2
Properties of DLC films grown by the pulsed plasma discharge using different hydrocarbon sources

Sample no	Hydrocarbon used	Stress (GPa)	Hardness (GPa)	Deposition rate (Å/s)	E_g. (eV)	Refractive index	Density (g/cm^2)	Co-ordination no.
CP-27	CH_4	0.43	18.71	0.07	1.60	2.31	1.59	2.52
CP-2	C_2H_2	0.23	17.48	1.66	1.47	2.18	1.55	2.51
CP-21	C_6H_6	0.16	15.55	1.00	1.40	2.05	1.48	2.49

substrate upon which the carbon species impinge [28]. In another report, it is mentioned that films with significant sp^3 content evolved at 70°C, or even at lower temperature on a Ni substrate, whereas sp^2 rich films evolved at 100°C and higher temperatures [23]. This indeed is surprising since the energy associated with such temperature is negligible $<$(0.1 eV) compared to the energy of the film forming carbon species ($\approx$ 10–100 eV). During cw deposition it has been mentioned that with the increase of ion energy (self bias voltage) the substrate temperature increases up to $\approx$100°C, and along with this stress values also increase. Thus, taking everything that has been said so far into account it is found that there exists convincing evidence that even a 100°C temperature rise can have a profound effect on the stress levels in DLC films.

No specific reason could be assigned to this significant increase of stress and not so significant increase in the substrate temperature on ion bombardment during cw discharge conditions. The only possible explanation may be that during the early phase of deposition of these films, films are found to be less dense and as deposition proceeds they became more and more dense. This way one is trying to build a DLC network of a less dense structure followed by increasing compact and dense phase. Intuitively, one feels such a network will be more stressed.

Thus, pulsing have two effects (i) relaxation of adions (or adatoms) and (ii) control of the substrate temperature. Both these favor a reduction of residual stress in DLC films.

It is found that the deposition rate is lower in the case of pulsed discharge compared to cw discharge as shown in Table 1, which is only to be expected. For 0.42 W/cm^2 of power density, the deposition rate was found to be only 0.42 Å/s in the case of pulsed discharges as compared to 6.7 Å/s in cw discharges. This is partly due to the fact that these power levels are maintained only for a short duration. Even then one would intuitively expect an arithmetic sum of the individual deposition rates for ON power duration; but surprisingly this is not the case. A similar observation was also made for a-Si:H pulse plasma growth by Anandan et al. [10]. As shown in Fig. 1b, the deposition rate increases from 0.43 to 3.33 Å/s with the increase of power density from 0.42 to 2.0 W/cm^2 for pulsed discharge grown films. This result is quite expected, since increasing the power density is known to enhance the deposition rate whether it is cw discharge [18–20] or pulsed discharge [8].

The values of Urbach energy (E_0) of such pulse plasma grown films were evaluated from photothermal deflection spectroscopy (PDS) and have been plotted in Fig. 1c, as a function of ON power density of the pulse discharge. It is evident from Fig. 1c, that with the increase of ON power density E_0 values also increase, which is consistent with the change in the stress values, i.e. with the increase of E_0 values the stress values also increase. Similar trend of E_0 variation with stress is observed for the cw discharge grown films and the E_0 values varied from 252 to 311 meV corresponding to films grown at applied power density varying from 0.1 to 0.42 W/cm^2. It is known that E_0 is a measure of the disorder in the material. One can infer from this that stress and disorder of the material may be interrelated. It is noted that continuous wave discharge grown films shows higher E_o values than pulsed discharge grown films. This is also consistent with the observed stress behavior of these films, i.e. pulse discharge grown films have lower stress values than cw discharge grown films. To the best of our knowledge such a direct observation of the correlation of the reduction in stresses and increase in the order of the film network, obtained by pulsing the power source, has not been reported earlier. Furthermore, the change in the observed values of E_0 are found to be consistent with the change in the electrical and optical properties of DLC films of varying stress, i.e. with the increase of E_0 values, the optical bandgap decreases and the electrical conductivity increases.

Fig. 1c shows the variation of room temperature conductivity as a function of ON power density. It is evident that with the increase of power density electrical conductivity of the films increases. There are about two orders of magnitude higher conductivity obtained for films grown at 2.0 W/cm^2 than those grown at 0.42 W/cm^2 power density.

Fig. 1d shows the variation of the optical bandgap and the refractive index as a function of ON power density of the pulsed discharge. It is evident from Fig. 1d that the optical bandgap decreases and the refractive index increases with the increase of ON power density. Now the increase of power means an increase in the energy of bombarding species during growth of DLC films, which helps to remove the weakly bonded hydrogen from the film. This leads to a reduced E_g and enhanced refractive index. A similar behavior has been observed in cw discharge grown films [28].

Table 2 shows the properties of DLC films grown using similar pulse parameters but varying hydrocarbons gas composition, from methane (CH_4) to acetylene (C_2H_2) and then to a vapor, benzene (C_6H_6). A close study of Table 2 reveals that the properties of the films grown by the pulsed plasma discharge using three different source material, i.e. CH_4, C_2H_2 and C_6H_6 show a trend similar to the films grown by the cw discharge. However, if one compares these values

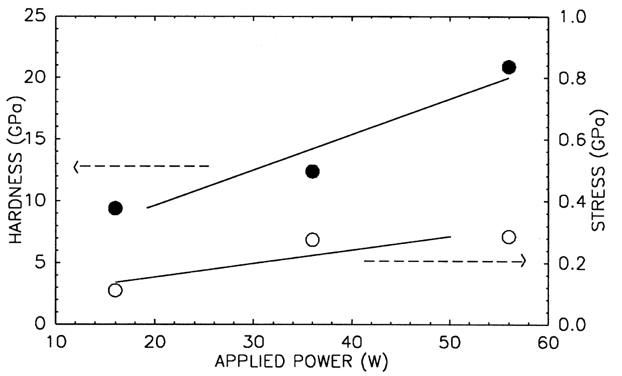

Fig. 4. Variation of hardness and stress with applied power for DLC films grown using C_2H_2 gas in a saddle field fast atom beam source.

with cw discharge grown films, significant differences will be noticed in the absolute values of the various properties. Thus the pulsed form of applied power appears to have a more significant effect on the properties of these films than the type of source material used to form these DLC films. It may be noted that stress values being reported in this paper are perhaps as low as claimed by ART group [29] for their Diamond-like Nanocomposite (DLN) films. Now if success of DLN coatings rest solely as attainment of such low stress (not taking into account their atomic scale composition), we may, perhaps for the moment, argue that existing DLC reactors can be upgraded by pulsing their r.f. supplies in a desired fashion.

3.2. dc saddle field fast atom beam grown films

It was also found that DLC films produced using a saddle field source adhere well to glass, and silicon substrates. The values of internal stress of these DLC films were found to be in the range of 0.1–0.5 GPa. This also seemed to improve the ageing behaviour of the DLC films. It may be noted that the stress values reported here are very much less than the stress values obtained in films that are deposited using the r.f. self bias technique and comparable to pulse plasma grown films. Fig. 4 shows the variation of stress values with the power applied to the FAB source for the DLC films grown using C_2H_2 as the source gas. From Fig. 4 it is clear that the values of stress increases with the applied power.

The Knoop hardness values (HK) at 50 gm load for DLC films grown using CH_4, C_2H_2 gases and C_6H_6 vapours aspirated in the saddle field source, lie in the range 9–21 GPa. Fig. 4 shows the variation of hardness values with the power applied to the FAB source for the DLC films grown using C_2H_2 as the source gas. The hardness values are found to increase with the increase of power, higher applied power leading to an enhancement of the energy of the radicals participating in the formation of the DLC films. At such high energies a process of compaction (density increase) of the DLC films takes place with the consequent increase of hardness values. Some other properties of these films grown using different hydrocarbons in a saddle field fast atom beam source are presented in Table 3.

The values of the Urbach energy (E_0) were found to be ~280 meV, 260 meV and 180 meV for DLC films grown using CH_4 and C_2H_2 gases and C_6H_6 vapours, respectively. These values of E_0 reported here for the DLC films indicate that the properties are found to be precursor dependent whereas the results reported in the literature for the films grown using the r.f. self bias technique [30] are found to be relatively precursor independent. Broad band tails are usually found in a-C:H and the values of E_0 is frequently over 500 meV [31] but somewhat narrower tails ($E_0 \approx 300$ meV) have been seen in a-C:H by Dischler et al. [32]. The values of E_0 in highly tetrahedral hydrogenated amorphous carbon (ta-C:H) are found to be ~350 meV [33]. Thus, the values of E_0 evaluated for the DLC films grown using CH_4, C_2H_2 gases and C_6H_6 vapours by a saddle field FAB source, in the present study, are found to be significantly lower than the values of E_0 (300–500 meV) for the DLC films reported in the literature [31–33], and are comparable to pulse plasma grown films, and far more than the values of E_0 (~50 meV) for the hydrogenated amorphous silicon (a-Si:H) films usually mentioned [34].

Incorporation of hydrogen in the DLC films decides a number of properties of these films. In the present investigation hydrogen content in these films has been estimated using the FT-IR and ERDA techniques. FT-IR provides the information about the bound hydrogen in these films and ERDA the total hydrogen. From these measurements unbound hydrogen in these films has been estimated and a correlation has been found to exist in the stress behaviour of the films and amount of unbound hydrogen. For these studies, a set of DLC films were grown at different power applied to the FAB source, using C_2H_2 as the feed gas. The total hydrogen concentration in these films was found to be very low and a maximum of ~ 8 at.% has been observed. In the published literature [35,36] FAB deposited DLC films

Table 3
Properties of DLC films grown using different hydrocarbons in a saddle field source

Serial no.	Properties	CH_4	C_2H_2	C_6H_6
1.	Deposition rate at 6 cm distance at specific power (Å/min)	11.7 (7.2 W)	37.7 (4.5 W)	21.7 (4.5 W)
2.	Room temperature conductivity at 35°C (Ω^{-1} cm^{-1})	10^{-9}–10^{-8}	10^{-8}–10^{-7}	10^{-9}–10^{-8}
3.	Optical bandgap (eV)	1.0–1.30	1.0–1.30	1.20–1.30
4.	Refractive index at 546.1 nm.	2.10–2.29	1.80–2.57	2.50–2.52

Table 4
Hydrogen concentration of the DLC films grown using saddle source

Gas used (at.%)	Pressure (mbar)	Power (W)	Stress (GPa)	Total H_2	Bound H_2 (at.%)	Unbound H_2 (at.%)
C_2H_2	5×10^{-3}	16	0.11	5.62	3.11	2.51
C_2H_2	5×10^{-3}	36	0.28	5.31	2.65	2.66
C_2H_2	5×10^{-3}	56	0.29	3.40	0.48	2.90
CH_4	5×10^{-3}	30	—	7.86	6.24	1.62

using C_2H_2 as the feed gas, a minimum 22 at.% of hydrogen has been reported when a beam energy corresponding of ~ 0.8 kV was used to form these films. However, during the present investigations beam energies used to deposit DLC films were in the range corresponding of 1.0 to 2.0 kV, which may be the reason for the low hydrogen incorporation in these films. Similar results were also reported by Walters et al. [36] in the DLC films grown by FAB and PECVD techniques.

From Table 4 it is evident that the hydrogen concentration decreases with the power applied to the FAB source. This is because an increasing bombardment of the films during growth, appears to remove the weakly bound hydrogen from the films. From Table 4 it is also evident that the hydrogen concentration increases in case of CH_4 deposited DLC films.

Grill et al. [4] were first to find a correlation between the amount of unbound hydrogen in DLC films and degree of residual stress in the films. System used for growing DLC films in their case had r.f. (13.56 MHz) power applied to the cathode and a varying negative DC voltage was also added through a r.f. choke. In the present study a saddle field fast atom beam source was used to grow such films and a similar correlation has been found, as evident from Table 4. We believe a similar relation exists also for the pulse plasma grown films, as measurements of these films are in progress. It thus appears that the relation between the unbound hydrogen and stress in DLC films is of a fundamental nature. It may be worth mentioning here that in a-Si:H system, particularly for films grown by hot filament technique, a similar correlation between the void density and stability of the a-Si:H films against Stabler–Wornski type degradation has been confirmed [37]. Without doubt confirmation of the existence of a correlation amongst the density of voids, unbound hydrogen, stress in a-Si:H films and their stability could indeed be a rewarding exercise.

4. Conclusions

It has become possible to deposit sufficiently thick and hard DLC films of significantly low stress values using pulse plasma enhanced chemical vapor deposition and also by dc saddle field fast atom beam technique. In the cw discharge (conventional r.f. asymmetric PECVD), at higher power density (>0.45 W/cm^2) the films delaminate from the substrate due to high stresses present in these films, but by the pulsing discharge, films were grown even at quite high power density (2.0 W/cm^2). It has been found that for the same amount of applied power density stress values can be reduced from 4.6 to 0.126 GPa by using pulsed discharges instead of continuous discharges.

During these investigations some very interesting results were obtained. For instance pulse, plasma discharge grown films showed lower Urbach energy than cw discharge grown films. This means pulsed discharge grown films are less disordered than cw discharge films. This is also consistent with observed low stress values for pulse plasma grown films.

It became possible to deposit more than 2.0 μm thick films of sufficient hardness on glass and c-Si substrates, using the pulse plasma technique, which otherwise appeared difficult in cw discharge conditions without extensive cooling (He).

The optical band gaps were found higher and refractive index values lower for the pulse discharge grown films than the cw discharge grown films, for the same amount of applied power density.

A possible growth mechanism of DLC films that is capable of yielding low stress values and high hardness may, perhaps, involve the following steps:

1. optimum ion energy to cause required densification of the growing DLC films;
2. relaxation of adions/adatoms impinging on the substrate surface;
3. control of the substrate temperature.

DLC films, were also formed by a saddle field fast atom beam source to which various hydrocarbon gases (CH_4, C_2H_2) and vapours (C_6H_6) were introduced with different C/H ratio. The following important observations were made:

1. the values of internal stress of these DLC films were found to be in the range of 0.1–0.5 GPa. These values are very much less than the stress values obtained in films that are deposited using the r.f. self bias technique and comparable to pulse plasma grown films;
2. in films formed by CH_4, C_2H_2 and C_6H_6 as source gases/vapours, scaling of the deposition rate as expected, i.e. 4–8 times, which is observed is the case of r.f. selfbias deposition technique, could not be observed;
3. the values of characteristics energy of band tails (Urbach energy, E_0) evaluated from PDS measurements for DLC

films grown using CH_4, C_2H_2 gases and C_6H_6 vapours are found to lie in the range 180–280 meV and this value decreases with the increase of carbon to hydrogen ratio in the hydrocarbon gases/vapours used [38];

4. the hydrogen concentration in these films determined from ERDA and IR analysis are found to be low and a correlation of the increase in the value of stress with unbound hydrogen is found to exist, as earlier predicted by Grill et al [4].

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