Deposition of diamond like carbon (DLC) and C–N films using ion beam assisted deposition (IBAD) technique and evaluation of their properties

J PRABHJYOT PAL, S C PATIL, S B OGALE*, S M KANETKAR, L GANPATHY[†] and P RAMA RAO[†]

Department of Physics, University of Poona, Pune 411 007, India
[†]Excel Superconductor Inc., 140-29 Keyland Court, Bohemia, New York 11710, USA

Abstract. Diamond like carbon films and C–N films were prepared using ion beam assisted deposition technique (IBAD). Tribological properties were studied by subjecting DLC coated films to the accelerated wear tests. These tests indicated a significant improvement in the mechanical surface properties of glass by DLC coating. Better wear features were obtained for thinner DLC coating as compared to the thicker ones. We also studied the optical properties and obtained a band gap of 1·4 eV for these films. An attempt was made to prepare C_3N_4 films by using IBAD. We observed variation in the nitrogen incorporation in the film with the substrate temperature.

Keywords. Ion beam assisted deposition; DLC films; C–N films; tribological properties; RBS analysis.

1. Introduction

Diamond like carbon (DLC) films and C–N films are subject of considerable interest due to their very special mechanical and optical properties. The DLC films are known to exhibit high value of hardness (Pethica *et al* 1985; Jiang *et al* 1990), chemical inertness (Dischler *et al* 1983; Mori and Namba 1984), and low sliding coefficient of friction (Enke *et al* 1980; Memming *et al* 1986). The C–N films are also expected to show similar or even superior properties as compared to the DLC films depending on the nature of the C–N bonding and the possibility of realizing a fraction of the dispersed (β–C_3N_4) phase, which is predicted to have a hardness greater than that of diamond (Liu and Cohen 1989, 1990).

The DLC films have been deposited by several methods such as dual ion-beam sputtering (Banks and Rutledge 1982; Nabot and Paidassi 1990; Deutchman *et al* 1991), hydrocarbon decomposition with pulsed, rf and dc plasma (Whitemell and Williamson 1976; Sokolowski *et al* 1979; Enke 1981), low energy ion bombardment (Khan and Woollam 1984) and Ar ion bombardment of evaporated carbon films (Spencer *et al* 1976; Fujimoro and Nagai 1984). The C–N films have been prepared mostly by dc magnetron sputtering (Chen *et al* 1993), rf sputtering (Kin Man *et al* 1994), shock compression of nitrogen containing organic materials (Wixom 1990), and pyrolysis of organic compounds having high nitrogen content (Leon Maya *et al* 1991) etc.

In the present paper we report ion beam assisted deposition (IBAD) of DLC

*For correspondence.

films on glass/quartz and C–N films on single crystal silicon (100). IBAD involves the bombardment of thermally evaporated thin films by low energy ions (N_2^+, Ar^+ etc.) during film growth. In our case we evaporate pyrolytic graphite with the simultaneous bombardment of Ar^+ and N_2^+ in order to have films of DLC and C–N, respectively.

Usually, crystal growth is promoted by elevating substrate temperature which enhances mobility of the deposited surface atoms. Higher temperature also leads to improvement in film-substrate adhesion by promoting a minimal required interface reaction. In the case of ion assisted deposition the energy deposited by the impinging ions provides the extra mobility without the need to raise the global temperature. The ion energy also produces atomic motion in the bulk by the so called atomic mixing phenomenon over a length scale of a few nanometres (Muller 1986a,b). This leads to higher film density and enhanced adhesion with the substrate.

2. Experimental

In our experiments, the DLC films were deposited on float glass, mineral glass and quartz whereas the C–N films were deposited on (100) oriented silicon. The deposition involved electron beam evaporation of pyrolytic graphite (Union Carbide Ltd.) using a 2 kW e-beam evaporator (Varian, model VT 922-0020) onto the substrates with simultaneous impingement of the growth front by energetic ions. The ions were derived from an 8 cm Kaufmann source (model ID 3501). The ion energy was varied from 100 eV to 1000 eV in different depositions. Use of an energy of 300–400 eV led to optimum film quality in the case of both the DLC and C–N films. The optimum ion flux for DLC deposition was about 0·35 mA/cm^2 (Ar^+) and that for the C–N films was 0·5 mA/cm^2 (N_2^+). The thickness was monitored with quartz crystal and the ion flux was measured with a Faraday cup. The thicknesses of DLC films were between 30 Å and 300 Å whereas those of C–N films were around 1000 Å. The substrates were held at ambient temperature during the deposition of DLC films whereas the C–N films were deposited at different substrate temperatures from 100–500°C. Deposition rates for DLC and C–N films were typically between 0·5 and 1 Å/sec, respectively. Optical properties of DLC films were studied using UV-VIS spectroscopy. Ball-on-disc type wear tester was used to assess the wear performance of DLC coated float glass samples *vis-a-vis* uncoated float glass sample. The C–N films were characterized using Raman and Rutherford backscattering spectroscopies.

3. Results and discussion

3.1 *DLC films*

To assess the wear performance of DLC coated samples, we assembled a ball-on-disc type wear tester in our laboratory. In this system a hard steel ball (diameter, 10 mm) was slided onto the sample for different periods of time at a speed of 300 revolutions per minute with a load of 50 g. Loss of the material due to the ball sliding over the sample was measured with the help of a microbalance with an

accuracy of 1 μg. Weight loss of the material as a function of time for constant rotational speed and load was studied. These values are given in table 1.

Figure 1 shows the weight loss of materials as a function of time for the uncoated glass and DLC coated glass. From these curves it can be noted that the loss of material with time is significantly lower for the DLC coated glass. In the same figure, additional lines have been shown indicating what could have been the wear loss if wear were linear in time. It is clear that the weight loss of the material in both the cases increases with time sublinearly. This type of sublinearity can be explained with the help of figure 2 as follows. As shown in figure 2a at time $t = 0$, the ball is in touch with the sample surface with the force of $F = 50 \text{ g} \times 980$ cm/sec^2 acting over the contact area A_0. The local pressure applied on the sample surface then becomes $P = F/A_0$. Now at time $t = t_1$, the ball penetrates vertically through some distance and the effective contact area under the ball becomes more as shown in figure 2b. Since the load is constant throughout the experiment, as the contact area increases the effective local pressure due to sliding ball decreases, causing low weight loss of material at any local point with a time interval. Of

Table 1. Weight loss of DLC coated and uncoated glass samples as a function of time.

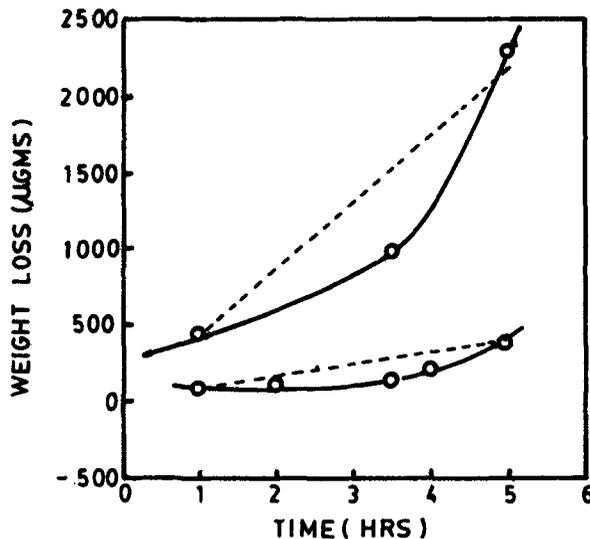| Thickness (Å)	30 Å	100 Å	300 Å	Uncoated
time (h)	Weight loss in μg			
1	20	30	80	400
2	50	62	98	–
3	90	120	132	972
4	116	–	200	–
5	–	–	378	2290

Figure 1. Weight loss of material as a function of time.
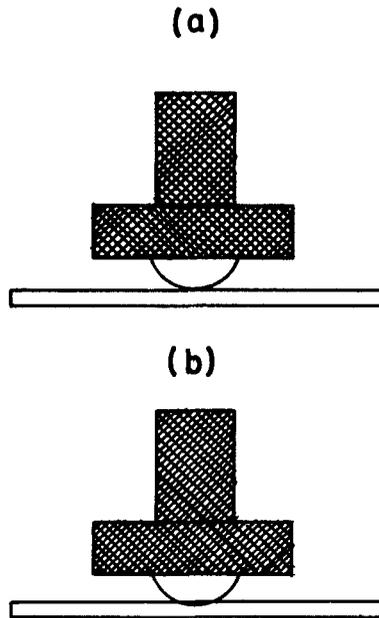
(a)

(b)

Figure 2. Geometry of sliding ball with respect to (a) at time $t = 0$, ball is in contact with sample surface of area A_0 and (b) at time $t = t_1$, ball is in contact with sample surface with wear area A_1 $(A_1 > A_0)$.

course, the total area over which the loss occurs increases and hence we have a product of a decreasing function and an increasing one. The sublinearity shows that the decreasing function operates more efficiently.

The amount of wear was also determined by microscopic examination of the wear scar using an optical microscope. Figures 3a and b show optical micrographs of the uncoated glass and 300 Å DLC coated glass, respectively. No specific differences in the surface features can be observed. Figure 4a shows the optical micrograph of the uncoated glass for a wear time (viz. the time for which the sample is rotated at a speed of 300 rpm with a load of 50 g) of 1 h and figure 4b shows the optical micrograph of the DLC coated glass for the same wear time. These two photographs together indicate that the wear scar in the case of the uncoated sample is significantly prominent than the DLC coated sample. In the case of DLC coated sample there is only slight appearance of a line with very low contrast with respect to the coated surface. Figure 5a shows the optical micrograph for the uncoated glass for a wear time of 3 h and figure 5b shows the optical micrograph of DLC coated glass sample for the same wear time. In these photographs also we observe major wear scar in the case of uncoated sample whereas there are only tiny scratches on the DLC coated surface. These observations and comparison of the wear scars in case of uncoated and coated samples clearly indicate major improvement in the mechanical surface properties of glass due to DLC coating.

To study the optical properties, different glass/quartz samples were coated with DLC of varying thicknesses in the range 30 Å to 300 Å. Transmission and reflection
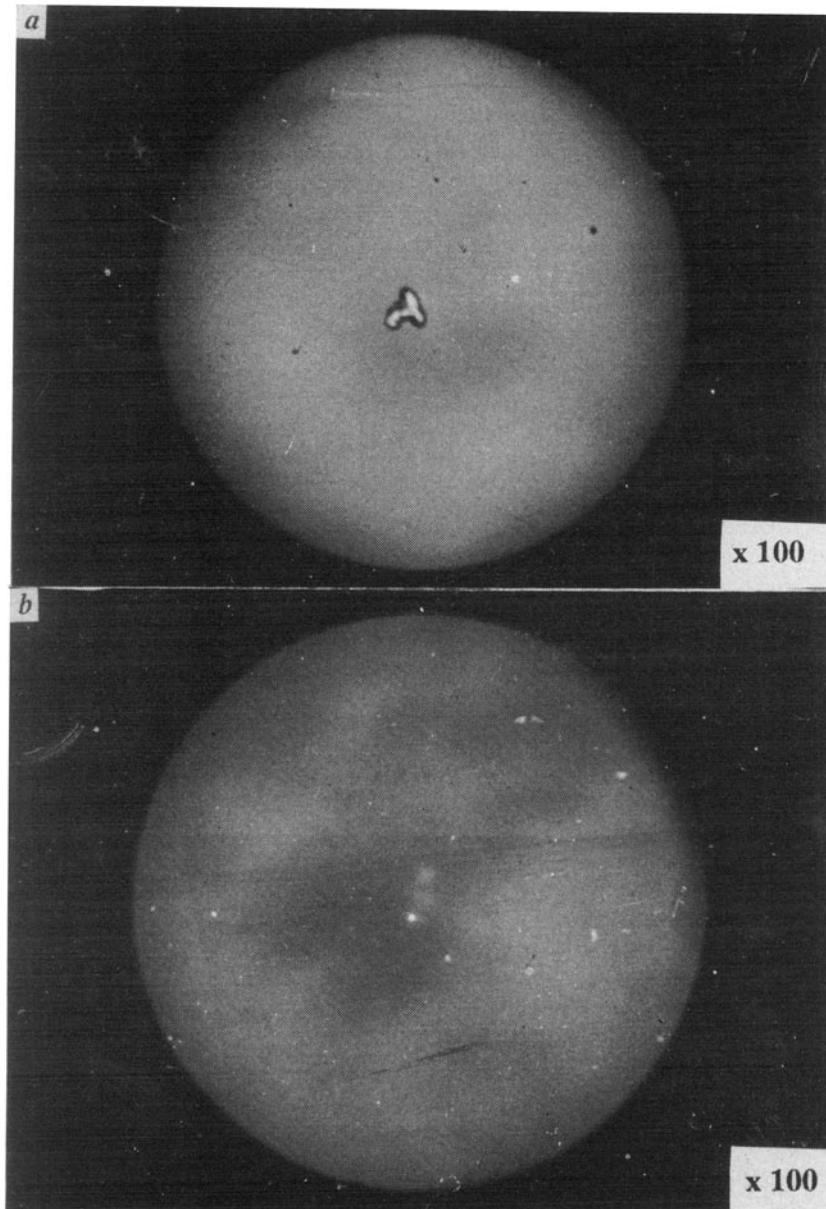
Figure 3. Optical micrograph of (a) uncoated glass and (b) 300 Å DLC coated glass.

spectra were acquired with a Perkin-Elmer Lambda spectrophotometer. This instrument was used in double-beam transmission and reflection mode. Figures 6 and 7 are the plots of transmission (T) and reflection (R) (in%) vs thickness for different wavelengths in the visible range. For lower thicknesses we observe that T and R do not vary much with wavelength. Also, transmittivity of DLC decreases whereas
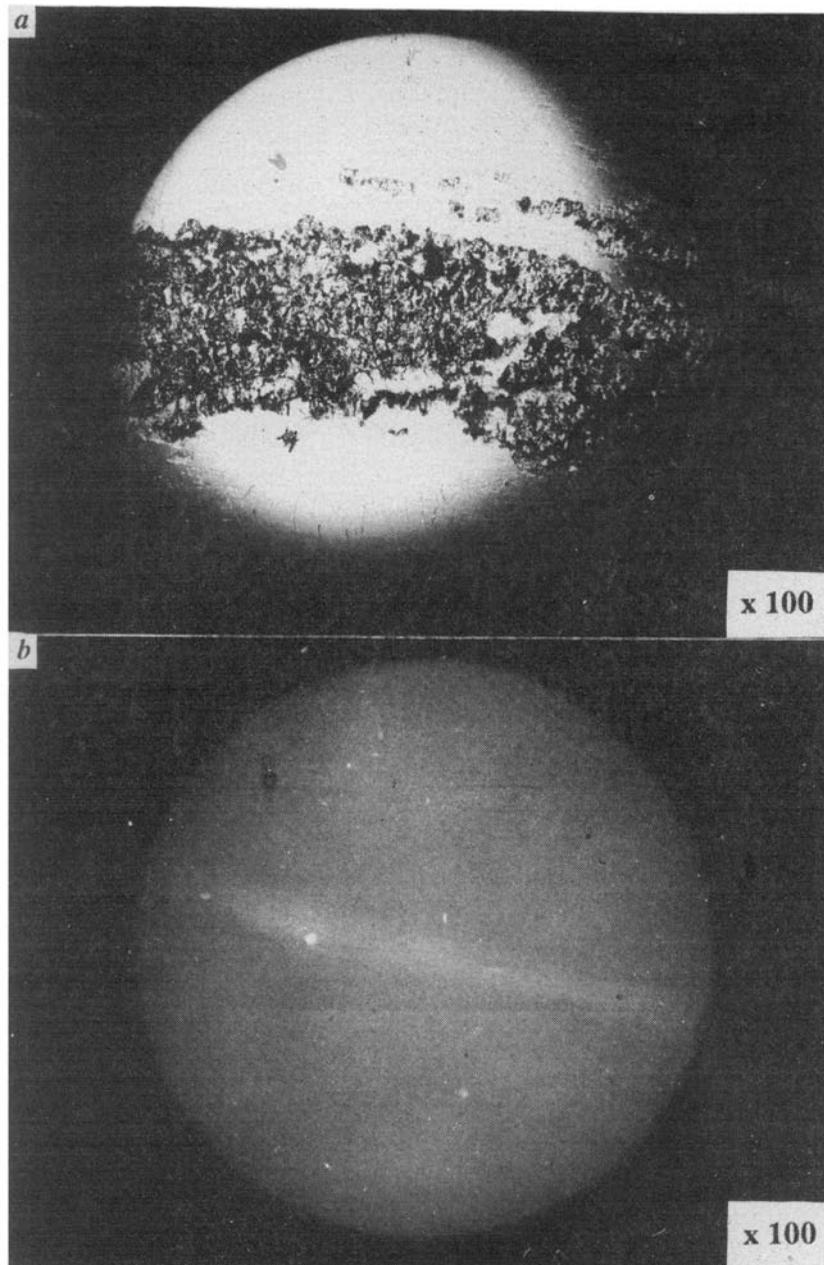
Figure 4. Optical micrograph of 1 h wear tested sample of (a) uncoated float glass and (b) 300 Å DLC coated float glass.

reflectivity increases with increasing film thickness. The optical band gap of DLC film was obtained from the Tauc relation,
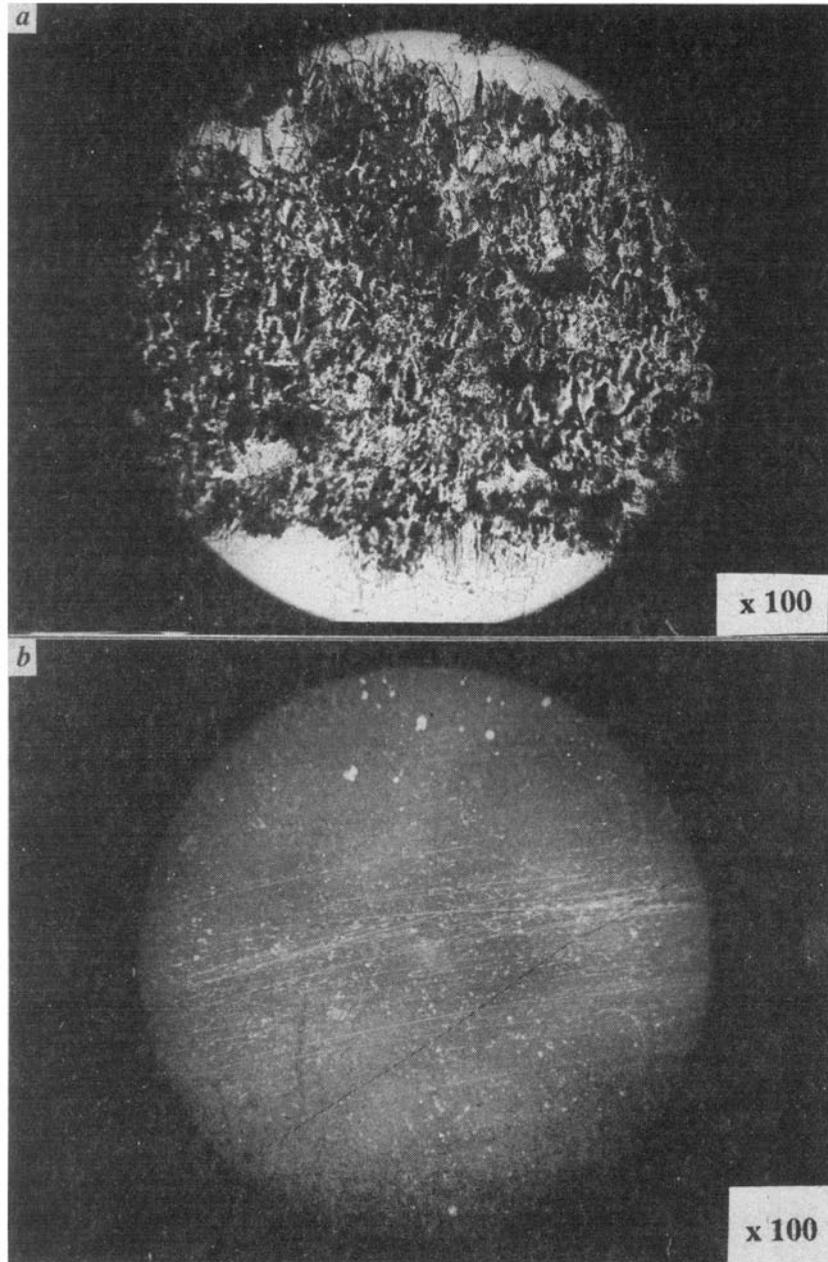
$$(\alpha E)^{1/2} = B \, (E - E_g) \, ,$$

Figure 5. Optical micrograph of 3 h wear tested sample of (a) uncoated float glass and (b) 300 Å DLC coated float glass.

where α is the absorption coefficient, E the energy, B a constant and E_g the optical gap. The Tauc plot for the case of 100 Å DLC coated on quartz is shown in figure 8 and the optical band gap turns out to be 1·4 eV.
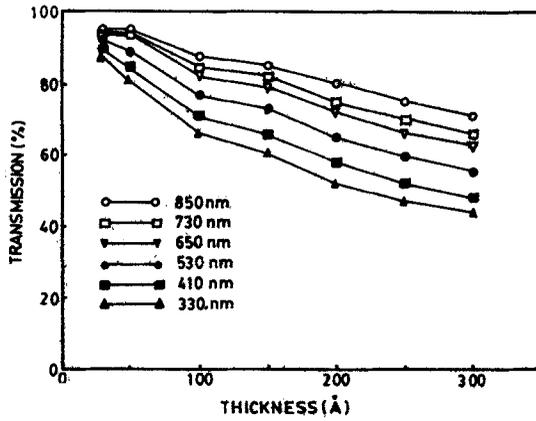
Figure 6. Plot of transmission (*T*) in % vs thickness of DLC for different wavelengths of light in the visible region.
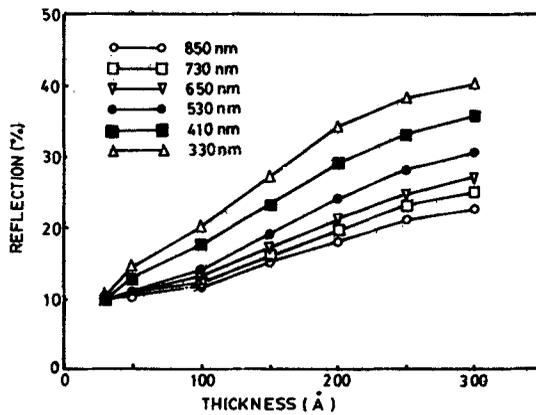

Figure 7. Plot of reflection (*R*) in % vs thickness of DLC for different wavelengths of light in the visible region.
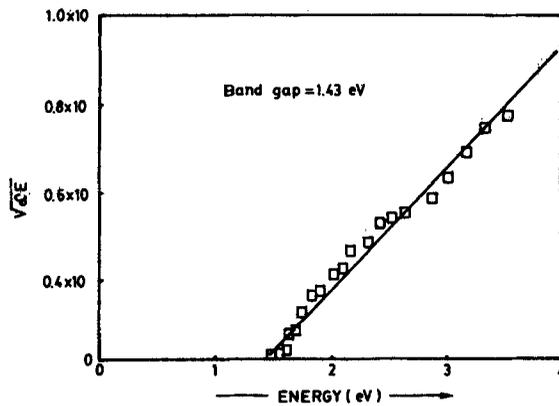

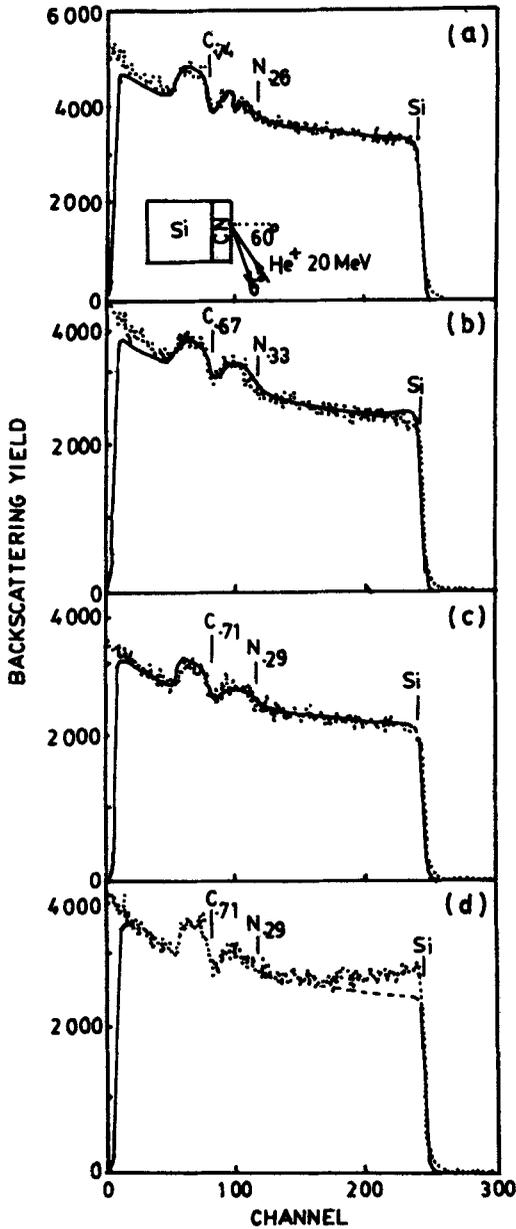**Figure 8.** Tauc plot of energy *E* in eV vs $(\alpha E)^{1/2}$ for 100 Å DLC on quartz.

Figure 9. Rutherford backscattering spectra of C–N films deposited at substrate temperature of (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C.

From table 1 (or figure 1) the weight loss for uncoated glass for 1 h sliding is 400 μg whereas the weight loss for DLC coated glass samples having DLC thicknesses of 30 Å, 100 Å and 300 Å is 20, 30 and 80 μg, respectively. This clearly indicates a significant improvement in the mechanical surface properties of
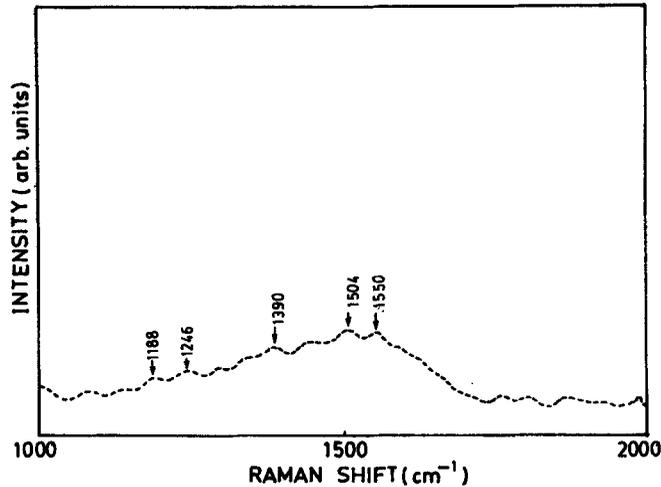
Figure 10. Laser Raman spectrum of C–N film on Si (100) substrate with 33% nitrogen.

glass by DLC coating. Interestingly, the 30 Å film shows superior wear features as compared to the 100 Å and 300 Å films. This should reflect a higher diamond like character of a thinner film as compared to the thicker one. In the initial phase of growth, the mechanism would involve growth of DLC on glass while in the latter phase, DLC on DLC. It appears that growth of DLC on DLC progressively degrades its quality. Detailed Raman and IR reflectance studies are in progress to understand these aspects of growth.

3.2 C–N films

For the deposition of C–N films on Si(100) using IBAD technique we chose the nitrogen ion energy and current to be 300 eV and 40 mA respectively and varied the substrate temperature from 200–500°C. Carbon evaporation rate was maintained at 1 Å/sec. These parameters were so chosen that the number of ions arriving at the substrate/cm^2/sec was 1·33 times the number of evaporating carbon atoms/cm^2/sec for achieving C_3N_4 stoichiometry. These films were characterized using RBS in order to determine chemical composition of the C–N films. Figures 9a–d show the RBS data for the films deposited at the substrate temperatures of 200°C, 300°C, 400°C and 500°C. The atomic percentage of nitrogen in these cases is 26%, 33%, 29% and 29%, respectively. For C_3N_4, there should be 57% nitrogen ideally whereas we get maximum nitrogen incorporation of 33% only. Further investigations are in progress for increasing the nitrogen content in C–N films using this technique. The representative Raman spectrum of C–N film with 33% nitrogen is shown in figure 10. This spectrum shows a broad hump between 1100 and 1700 cm^{-1} with features near 1390 cm^{-1} (D peak) and 1550 cm^{-1} (G peak) similar to those of DLC. The features near 1200 cm^{-1} and 1500 cm^{-1} correspond to vibrational modes of linear C–N bonds. All the spectral features are in general agreement with the C–N Raman spectra reported in literature for films obtained by other techniques (Chen *et al* 1993).

4. Conclusions

Tribological properties studied by subjecting DLC coated films to the accelerated wear tests confirmed a significant improvement in the mechanical surface properties of glass by DLC coating. We obtained better wear features for thinner DLC coatings as compared to the thicker ones. From the study of optical properties we obtained a band gap of 1·4 eV of DLC films. C–N films prepared using IBAD technique indicated a maximum of 33% nitrogen only. Variation in the nitrogen content in the C–N film with substrate temperature was observed.

Acknowledgements

References

Banks B A and Rutledge S 1982 *J. Vac. Sc. Tech.* **21** 807
Chen M Y, Li D, Lin X, Dravid V P, Chung Y W, Wong M S and Sproul W D 1993 *J. Vac. Sc. Tech.* **A11** 521
Deutchman A H and Partyka R J 1991 United States Patent[19] 4,992,298
Dischler B, Bubenzer A and Koidl P 1983 *Appl. Phys. Lett.* **42** 636
Enke K 1981 *Thin Solid Films* **80** 227
Enke K, Dimigen H and Hubsch H 1980 *Appl. Phys. Lett.* **36** 281
Fujimoro S and Nagai K 1984 *Jpn. J. Appl. Phys.* **20** L194
Jiang X, Reichett K and Stritzker B 1990 *J. Appl. Phys.* **68** 1018
Khan A A and Woollam J A 1984 *J. Appl. Phys.* **55** 4299
Kin Man Yu, Cohen M L, Haller E E, Hansen W L, Liu A Y and Wu I C 1994 *Phys. Rev.* **B49** 5034
Leon Maya, Cole D R and Hagaman E W 1991 *J. Am. Ceram. Soc.* **74** 1986
Liu A Y and Cohen M L 1989 *Science* **245** 841
Liu A Y and Cohen M L 1990 *Phys. Rev.* **B41** 10727
Memming R, Jolle H J and Wirenga P E 1986 *Thin Solid Films* **143** 31
Mori T and Namba Y 1984 *J. Appl. Phys.* **55** 3276
Muller K H 1986a *J. Vac. Sc. Tech.* **A4** 184
Muller K H 1986b *J. Appl. Phys.* **59** 2803
Nabot J P and Paidassi S 1990 *Surf. Coat. Tech.* **43–44** 71
Pethica J B, Koidl P, Gobrecht J and Schuler C 1985 *J. Vac. Sc. Technol.* **A3** 239
Sokolowski M, Sokolowska A, Gokieli B, Michaelski A, Rusek A and Ramanowski A 1979 *J. Cryst. Growth* **47** 421
Spencer E G, Schimt P N, Joy D J and Sansalon F J 1976 *Appl. Phys. Lett.* **29** 118
Whitemell D S and Williamson R 1976 *Thin Solid Films* **35** 225
Wixom M R 1990 *J. Am. Ceram. Soc.* **73** 1973