

On the determination of the sp^3 to sp^2 ratio in diamond-like carbon thin films

Somna S. Mahajan, H.C. Barshilia, B.R. Mehta, V.D. Vankar

Thin Film Laboratory, Department of Physics, Indian Institute of Technology, Delhi 1100 16, India

Received 15 July 1996; accepted 7 November 1996

Abstract

The carbon bonding ratio in diamond-like carbon (DLC) thin films has been estimated from the e_2 spectra obtained by spectroscopic ellipsometry. A method has been developed to find out the atomic fractions of sp^3 - and sp^2 -bonded carbon atoms by combining the various features of the existing methods. The atomic fraction of sp^2 -bonded carbon atoms has been determined by fitting the gaussian curves in the experimentally observed e_2 spectra in the low energy range (< 4 eV). The atomic fraction of sp^3 -bonded carbon atoms has been determined by calculating the total electron density in the DLC matrix. The amount of hydrogen present in DLC films has also been taken into account.

Keywords: Carbon: Chemical vapour deposition: Ellipsometry: Optical properties

1. Introduction

Diamond-like carbon (DLC) thin films, both amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H), have attracted considerable interest in recent years. The unique combination of properties of DLC thin films such as extreme hardness, chemical inertness, optical transparency, etc., reflect unusual bonding characteristics [1-5]. It is known that carbon atoms can form bonds with three different types of hybridization: sp^3 , sp^2 and sp^1 leading to diamond-like (sp^3), graphitic (sp^2) and linear (sp^1) networks. In the presence of hydrogen, disordered polymeric regions may also be present in the matrix. In addition, recent investigations of a-C:H films suggest the presence of segregated TT bonded carbon clusters and voids in DLC matrix [6-8]. The structure of DLC films is thus extremely complex. It has been shown that the optical and electrical properties of DLC thin films are largely determined by the relative proportion of sp^3 and sp^2 sites in the matrix [9-12]. The amount of sp^1 sites in most of these films is negligibly small and is generally ignored.

Several different techniques have been employed for the estimation of sp^3/sp^2 ratio in the DLC films. These techniques include infrared (IR) spectroscopy, electron energy loss spectroscopy (EELS), nuclear magnetic resonance (NMR) and Raman spectroscopy [5,13-18]. IR spectroscopy provides information mainly where carbon is

bonded to hydrogen. Raman spectroscopy, on the other hand, is highly sensitive to the amount of graphitisation. Thus these techniques individually cannot give information about the bonding ratio if both C-C and C-H bonds are present. EELS is a highly sensitive technique for the surface microstructure and gives information on very small region near the surface. NMR, although it is a bulk sensitive method, provides information only if a large amount of material is available. Because of these limitations, estimates of the sp^3/sp^2 ratio obtained by various authors differ over a wide range.

In addition to the above-mentioned techniques, the dielectric constant of the DLC films has also been used for determining the sp^3/sp^2 ratio. Savvides [19,20] has calculated the sp^3/sp^2 ratio in a-C and a-C:H films using the energy dependence of the imaginary part of the dielectric constant of these films. The ϵ_2 and ϵ_1 data of these films have been determined from the reflectance and transmittance data in the energy range 0.5-7.3 eV and using the Kramer-Kronig relations. The IT electron fraction is evaluated by comparing the ϵ_1 first moment for the a-C film to that of pure graphite which directly gives the fractional concentration of sp^3 -bonded carbon atoms. This technique, although very useful, has some limitations. For example, the range of the data between 0 to 9 eV must be obtained to get all of the 77 electron contribution to ϵ_2 . There is considerable overlap between a and TT electron contribu-

tions between 5 and 9 eV. If the TT electron contribution from this overlap region is not separated and taken into consideration, considerable error is expected to be introduced in the calculations. It has also been pointed out that the energy dependence of e_2 for a-C and graphite near 7 eV is quite different and, thus, a comparison between the f_2 first moment of graphite and a-C will be justified only at higher energies (> 8 eV) [21]. In addition, for a-C:H films containing a considerable amount of hydrogen, the fractional concentration of sp^3 - and sp^2 -bonded carbon atoms cannot be determined directly because of the presence of hydrogen which also contributes to a transitions.

Demichelis et al. [21,22] have employed a different method for calculating the sp^3/sp^2 ratio for DLC films using e_2 and e_1 data obtained from R and T measurements in the photon energy range 0.49-6.52 eV. A gaussian-like distribution of TT electronic density of states is assumed which is then fitted in the e_2 data in the low energy range (< 4 eV). The contribution of a transitions is then deduced using Kramer-Kronig relations and the measured values of e_2 data. The Wemple-Didomenico (W-D) model [23] is employed to obtain the dispersion energy and average excitation energy. Knowing the plasmon energies, the f -sum rule is used to estimate the sp^3/sp^2 ratio. The reliability of this method is very much dependent on the justification in employing the W-D model where the ϵ_n spectrum in the higher energy range (> 9 eV) is assumed to be a 5-shaped function, replacing the true e_2 spectrum. It has also been mentioned that this will lead to only the general information about the intensity and the interband energy spacings of the transitions involved. The second assumption in this method is the gaussian approximation to the entire TT bands. In a-C and a-C:H films, the gaussian approximation is correlated to the distribution of regions containing sp^3 bonds [24]. This is valid to a first approximation as long as these regions are small. The third assumption in this model is on having an energy separation between the TT bonding and TT^* antibonding orbitals and those between the a and σ^* orbitals. For the films containing purely graphitic regions, as in the case of evaporated carbon thin films, this assumption works well because of the clear separation between TT and a absorption regions. However, for a-C:H films having complex structures, one may expect gap states in the spectral density function and obvious problem arises because of the overlap of the absorption regions.

It is clear that each of the methods described above has certain limitations specially when applied to a-C:H films. Thus, the accurate determination of the sp^3/sp^2 ratio in DLC films is still a matter of debate. The values of the sp^3/sp^2 ratio obtained by Demichelis et al. and Savvides for the same data for the DLC samples have been reported and the values differ by a factor of 3 to 4 [20,21]. We have used the methods of Savvides [19] and Demichelis et al. [21] to calculate the sp^3/sp^2 ratio in our films and have found the numbers to differ significantly. In order to obtain

a realistic value of the sp^3/sp^2 ratio, we suggest a modified method. The modified method is essentially based on calculation of w_{dl} over the entire region of absorption (0-9 eV) by fitting a gaussian curve in the experimentally observed e_2 data. The contribution of σ electrons from the hydrogen present in the DLC matrix has also been taken into account. The method is described in the following section.

2. Modified method for the determination of sp^3/sp^2 ratio

The contribution of TT transitions to e_2 spectrum (ϵ_{2n}) is obtained from the experimentally observed e_2 spectrum by fitting a gaussian curve in the low energy range < 4 eV using the following expression [21]:

$$\epsilon_{2n} = (B/E^2) \exp\left\{E/(2\sigma_n)\right\} \times \exp\left[-((E - E_p)/2\sigma_n)^2\right] \quad (1)$$

where B is the scaling factor, E_p is the peak energy and $2\sigma_n$ is the peak width. The ϵ_{2n} curve thus generated is extended up to 9 eV, so that it contains all the possible TT transitions. The effective number of TT electrons per carbon atom (n_n) taking part in the optical transitions is evaluated by substituting the value of ϵ_{2n} in place of e_2 in the well-known sum rule, relating the effective number of valance electrons per atom to the imaginary part of dielectric constant [19,25]. Thus, n_n is given by the following equation:

$$n_n = 0.766 \left(\frac{M(d)}{E} \int \epsilon_{2n}(E) dE \right) \quad (2)$$

where M is the atomic mass, d is the density of the film in kg m^{-3} and E is the photon energy in eV which varies from 0 to 9 eV. The typical density of our films was 1350 kg m^{-3} . If A is the atomic density (number of atoms per unit volume), the number of TT electrons per unit volume is given by:

$$K = An_n \quad (3)$$

To find out the effective number of a electrons per atom, it is necessary to integrate Eq. (2) in the energy range 9-25 eV, as a electrons are responsible for the transitions in this energy range. In the absence of the experimentally measured e_2 data in the above energy range, we have calculated a electron density (N_a) from the total number of electrons per unit volume ($N_w + N_{ir}$) in the films as described below.

As each carbon atom contributes four electrons and each hydrogen atom contributes one electron to the DLC matrix, the total number of electrons per unit volume is given by the following expression:

$$N_w + N_a = A(4f_c + f_H) \quad (4)$$

where ($N_w + N_{ir}$) is the total number of TT and a electrons

per unit volume and f_c and f_H are the atomic fractions of carbon and hydrogen respectively. Also,

$$f_C + f_H = 1 \tag{5}$$

and

$$f_C = 3f_2 + f_3 \tag{6}$$

where f_2 and f_3 are the atomic fractions of sp^2 - and sp^3 -bonded carbon atoms respectively. Now knowing the atomic fraction of hydrogen (f_H) in the films, the atomic fraction of carbon atoms (f_c) can be calculated by using Eq. (5). Substituting the values of f_c and f_H in Eq. (4) gives the total number of electrons (N_{TT+CT}) per unit volume. The number of a electrons per unit volume is then calculated by subtracting the total number of IT electrons per unit volume A^{\wedge} (Eq. (3)) from the total number of electrons ($TT + cr$) per unit volume (Eq. (4)) as follows:

$$N_a = A(4f_c + f_H) - A n_{IT} \tag{7}$$

As each sp^2 -bonded carbon atom contributes one IT electron and three cr electrons, each sp^3 -bonded carbon atom contributes four a electrons and each hydrogen contributes one cr electron to the DLC matrix, the number of IT and cr electrons per unit volume (A^{\wedge} and A^{\wedge}) can be expressed in terms of the atomic fractions of sp^3 - and sp^2 -bonded carbon atoms. Therefore,

$$K = A f_3 \tag{8}$$

$$N_{cr} = A(3f_2 + 4f_3 + f_H) \tag{9}$$

The ratio N_a/N_{cr} is given by the following equation:

$$N_a/N_{cr} = (A f_3) / A(3f_2 + 4f_3 + f_H) \tag{10}$$

and also

$$f_2 + f_3 + f_H = 1 \tag{11}$$

Thus, by knowing the values of N_a , N_{cr} and f_H , the atomic fractions of sp^3 -bonded carbon atoms (f_3) and sp^2 -bonded carbon atoms (f_2) can be calculated using Eqs. (10) and (11).

3. Experimental

The DLC films were obtained by two different techniques. The unhydrogenated DLC film labelled as UH was obtained by the ion beam assisted deposition (IBAD)

technique. In this technique, the pyrolytic graphite was evaporated by an electron beam onto the substrate with the simultaneous impingement of the film by energetic Ar^+ ions generated from a 8 cm. Kaufmann ion source. The thickness of the film UH determined by Talystep (Taylor Hobson, UK) was about 0.3 μ m. The hydrogenated DLC films, labelled M1-M4, were deposited by microwave plasma chemical vapour deposition (MWPCVD). The system consisted of a microwave power supply (model GMP12KE, Sairem, France), a quartz tube used as a deposition chamber, rectangular wave guide, a three-stub tuner and a power meter. The lower part of the quartz tube was connected to a diffusion pump and a rotary pump. The DLC films were deposited on p-type silicon substrates polished with diamond paste with an average particle size of 1-2 μ m. The substrates were ultrasonically cleaned with organic solvents, dried up and subsequently placed into the deposition chamber. Prior to the deposition, the chamber was evacuated to a pressure of 10^{-6} Torr and the working pressure of a few Torr was maintained during the period of deposition. The typical deposition parameters of these films are illustrated in Table I. The thickness of these films was of the order of 0.35 μ m.

The imaginary part of the dielectric constant ϵ'' of these films was obtained by a rotating polarizer spectroscopic ellipsometer (model ES2G, SOPRA, France) in the photon energy range 1.5-4.5 eV. In this technique, a beam of polarized light is incident on the sample and as a result the polarization state of the light gets modified after getting reflected from the sample. This change in the polarization state is recorded in terms of the ellipsometric angles $\tan \psi$ and $\cos \Delta$, where $\tan \psi = \frac{r_p}{r_s}$, the ratio of the reflection coefficients of the parallel and perpendicular components of the electric field E respectively and $\cos \Delta = \frac{A_{Tp} - A_{Ts}}{A_{Tp} + A_{Ts}}$, phase shift between the reflected parallel and perpendicular components of the electric field E respectively. The complex dielectric constant ($\epsilon = \epsilon' + i\epsilon''$) of these films is obtained using the following relation [26]:

$$\epsilon'' = \sin^2 \theta \left[\frac{1 + \tan^2 \phi}{(1 + p f)} \right]$$

where θ is the angle of incidence and p is the complex reflectance ratio given by $(\tan \psi / i)^{1/\Delta}$. X-ray diffraction studies were carried out using the X-ray diffractometer (model DMAX RB300, Rigaku, Japan) in a glancing angle mode. Elastic recoil detection analysis (ERDA) was carried out using a 15 UD Pelletron accelerator to estimate

Table I
Deposition parameters of DLC films

Film	Microwave power (W)	Operating pressure (Torr)	Substrate temp. (°C)	CH ₄ flow rate (seem)	H ₂ flow rate (seem)	Deposition time (h)
M1	600	1	600	18	200	4
M2	600	1	600	16	200	4
M3	600	1	600	12	200	4
M4	600	1	600	8	200	4

the atomic fraction of hydrogen atoms in the hydrogenated DLC films. A detailed method has been described elsewhere [27].

4. Results and discussion

A typical X-ray diffraction pattern of the DLC film, M1, shown in the Fig. 1 confirms that the films used in the present study are amorphous in nature. Fig. 2 shows the variation of the imaginary part of dielectric constant ϵ_2 with photon energy in the range 1.5-4.5 eV for the film UH. The ϵ_2 spectrum shows a broad hump with a maximum at about 3.2 eV. The behaviour is in accordance with the results reported by Savvides [19,20]. The maximum value of ϵ_2 is 4.35 at 3.2 eV and matches reasonably well with the data for amorphous carbon films reported by Savvides. A gaussian fit (ϵ_{2IT}) to the ϵ_2 spectrum, represented by a dashed line is also shown in the figure. The ϵ_{2IT} curve fits well to the ϵ_2 spectrum for lower energies (1.5-3.2 eV) but deviates substantially in the higher energy (>3.2 eV) range. Similar fittings have also been carried out for the films M1 to M4 to find out the corresponding ϵ_2 spectra.

Fig. 3 shows the ϵ_2 spectra for the films M1-M4. The amount of hydrogen in these films estimated by ERDA was found to be about 25 at.%. In general, the variation of ϵ_2 with energy is similar for all the films. The ϵ_2 spectra of all the films show a hump at about 2.1 eV. The shape of the spectra are close to gaussian on the lower side of the hump. The maximum value of ϵ_2 is 1.65 for the film M1 and decreases to as low as 0.75 for the film M4. These values are very low as compared to those for unhydrogenated film UH (as shown in Fig. 2). This is a typical observation and is consistent with the reported literature [28]. It should, however, be noted that the peak values and position of the ϵ_2 are very sensitive to the microstructure of the films and vary over a wide range. The only maximum in ϵ_2 spectrum in the experimental energy range is due to the $\pi-\pi^*$ transitions caused by the sp^2 co-ordination in the DLC matrix. The $cr-a^*$ transitions cannot be seen in the limited energy range of observation for the experimental technique employed here. The value of ϵ_2 maximum depends upon the amount of sp^2 -bonded sites in

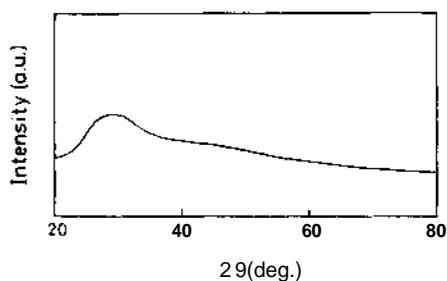


Fig. 1. A typical X-ray diffraction pattern of the DLC film.

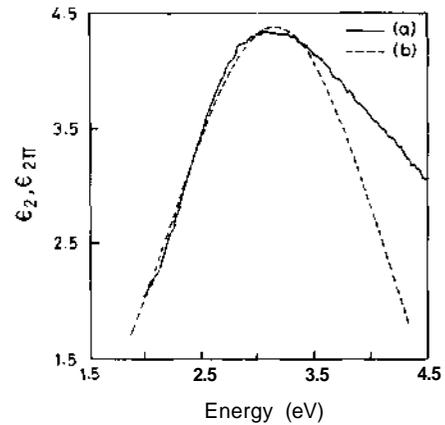


Fig. 2. Variations of (a) experimentally observed ϵ_2 and (b) gaussian fit with energy for the film UH.

the film. The spectra indicate that the film M1 has maximum number of sp^2 sites, film M4 has the minimum number of sp^2 sites and other films have in between values.

Since the number of sp^2 and sp^3 sites are different in these films, the corresponding values of n_{eff} are also expected to differ significantly. The values of n_{eff} provide an idea of the sp^3 to sp^2 ratio in the films. The calculated values of n_{eff} for the film UH and for the films M1-M4 are shown in Figs. 4 and 5 respectively. As expected, the values of n_{eff} are largest for the film UH and lowest for the film M4. The n_{eff} value increases with photon energy and is expected to reach a value of 1 at about 9.0 eV. Beyond 9.0 eV, the contribution due to $a-a^*$ transitions to n_{cn} rapidly increases and reaches a value of 4 at about 25 eV. In the films M1-M4 as shown in the Fig. 5, the values of n_{eff} are quite small (0.037-0.02 at 4.0 eV). This is because of the small amount of sp^2 -bonded carbon atoms in the films. The variation of the effective number of π electrons per atom (n_n) with energy for the film UH is also shown in Fig. 4. As the ϵ_2 curve fits very well to the ϵ_{2IT} curve in the low energy range (< 4 eV), n_{eff} and n_n have the same values at these energies. The low values of ϵ_2 in the high energy range as compared to ϵ_2 , results

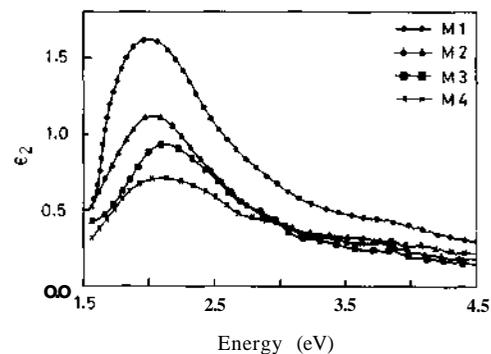


Fig. 3. Variation of ϵ_2 with energy for the films M1-M4.

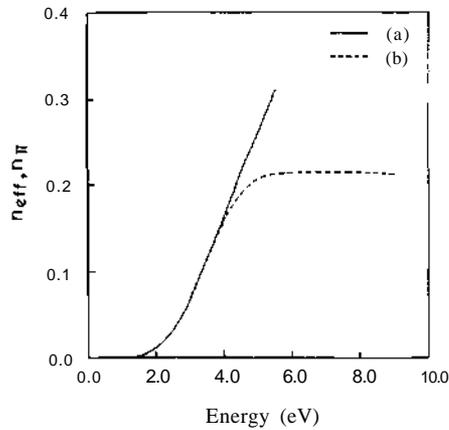


Fig. 4. Variations of (a) n_{eff} and (b) $n^$ with energy for the film UH.

in the saturation of n_n at about 6 eV. A similar trend of n_w for the films M1-M4 has also been observed. A quantitative estimation of the sp^3/sp^2 ratio is discussed below.

Table 2 shows n_n and the corresponding values of sp^3/sp^2 ratio (f_2/f_1) for the film UH and the films M1 to M4, determined by the modified method. The values of n_{eff} and the sp^3/sp^2 ratio for these films obtained by the Savvides method are also given in the table for comparison. The modified method gives the value of sp^3/sp^2 for the film UH as 3.7. In contrast, the sp^3/sp^2 ratio is large for the films M1 to M4 and varies between 38.5 and 73.9. Although the sp^3/sp^2 ratio obtained by both the methods show a similar variation in going from the film UH to the film M4, the modified method seems to give higher values of sp^3/sp^2 . The observed increase in the sp^3/sp^2 ratio for the films M1 to M4 with the decrease in the CH_4/H_2 gas flow ratio is consistent with the reported results [29]. As already discussed, both the methods are based on the determination of f_2 from the e_2 data by calculating the effective number of electrons per atom contributing to the TT transitions. In the present study, in order to reduce the effect of the overlapping of IT and a transitions in the higher energy range (> 5 eV), the effective number of TT

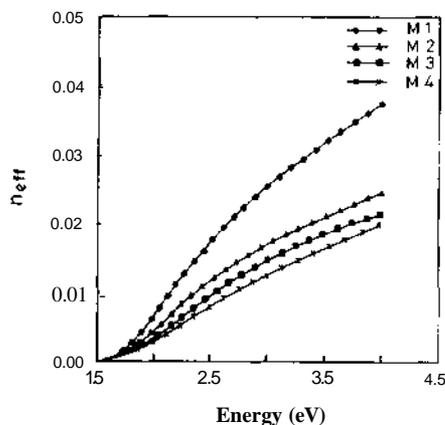


Fig. 5. Variation of n_{eff} with energy for the films M1-M4.

Table 2
 sp^3/sp^2 ratio of the: DLC films

Film	Modified method					Savvides method			
	f_2	n_n	A	f_1	f_2/f_1	n_n	f_1	A	f_2/f_1
UH	0	0.214	0.786	0.214	3.7	0.262	0.625	0.375	1.7
M1	0.25	0.019	0.731	0.019	38.5	0.037	0.928	0.072	12.9
M2	0.25	0.015	0.733	0.015	48.9	0.024	0.953	0.047	20.3
M3	0.25	0.014	0.736	0.014	52.6	0.022	0.958	0.042	22.8
M4	0.25	0.010	0.739	0.010	73.9	0.020	0.962	0.038	25.3

electrons per atom has been obtained from the e_{2n} data instead of e_2 data. Also, the contribution of a electrons due to hydrogen present in the DLC films has been taken into account. Thus, the sp^3/sp^2 ratio obtained by the modified method are different from that by Savvides in which this contribution has been neglected.

Our approach of estimating the sp^3/sp^2 ratio is simple and is basically a modification over the methods described earlier. As the $< r$ electron contribution has been taken into account by estimating the total electron density in the DLC matrix, the approximations of the W-D model used in the Demichelis method are largely overcome and thus, the modified method can successfully be applied to determine the sp^3/sp^2 ratio even if e_2 data is available in a very limited energy range. This is normally the case when optical instruments, such as a spectrophotometer or spectroscopic ellipsometer, are used. As the contribution of the a electrons due to hydrogen present in the DLC films has also been considered, the method is applicable to both hydrogenated as well as unhydrogenated DLC films. In addition, the e_2 data is obtained from the experimentally measured e_2 spectra in the low energy range in which the overlap due to a and IT electron transitions is minimum, e_{2w} is expected to give a more realistic values of the effective number of TT electrons per atom as compared to that using e_3 . Also, as the e_{2T} spectra in the complete energy range (0-9 eV) is obtainable from the extension of the gaussian fit, the normalization of the first moment of e_2 with respect to graphite is not required in the present calculations.

As already described, the atomic fraction of sp^3 -bonded carbon atoms, i.e. f_2 , has been determined from the e_2 spectrum. In DLC films having small fraction of sp^2 -bonded atoms, small errors in the E_2 data will result into a large variation in the sp^3/sp^2 ratio. A precise determination of the e_2 data is required to make a good estimate of the sp^3/sp^2 ratio. Spectroscopic ellipsometry is known to provide accurate measurements of the optical constants as compared to the other techniques where one has to use the approximate Kramer-Kronig relations in order to calculate e_2 and e_2 data [26].

The applicability of the modified method depends only upon the validity of the gaussian approximation for the v electron density of states. Gaussian shapes for the TT - TT^*

bands have been proposed and used for the calculations of the sp^3/sp^2 ratio in the amorphous carbon matrix [21]. In addition, the film density and the amount of hydrogen present in the DLC matrix are the only other parameters required for the determination of carbon bonding ratio in the modified method. Both these parameters can be experimentally determined as has been done in the present study.

5. Conclusion

A modified method for the determination of the carbon bonding ratio in DLC films has been developed. The IT electron density is estimated by fitting a gaussian curve in the experimentally observed e_2 spectrum in the low energy range and then extending it to cover the required energy range. The a electron density is evaluated by subtracting 77 electron density from the total electron density in the DLC matrix. The ratio of cr/v electron densities is then used to determine the atomic fractions of sp^3 - and sp^2 -bonded carbon atoms. The contribution of a electrons due to the hydrogen present in the DLC matrix is also taken into account. The modified method is simple to apply, requires an experimentally measured e_2 spectrum in a limited energy range and can also be applied to DLC films containing a large amount of hydrogen.

Acknowledgements

Thanks are due to Professor K.L. Chopra and Professor S.B. Ogale for helpful discussions. One of the authors (SSM) is grateful to the Council of Scientific and Industrial Research (CSIR) for providing a research fellowship. The authors are also thankful to Department of Science and Technology, New Delhi, for financial support.

References

- [1] J.C. Angus, *Thin Solid Films*, 216 (1992) 126.
 [2] S. Aisenberg and R. Chabot, *J. Appl. Phys.*, 42 (7) (1971) 2953.

- [3] H.C. Tsai and D.B. Bogy, *J. Vac. Sci. Technol.*, A5 (6) (1987) 3287.
 [4] C.V. Deshpandey and R.F. Bunshah, *J. Vac. Sci. Technol.*, A7 (3) (1989) 2294.
 [5] B. Dischler, A. Bubenzer and P. Koidl, *Solid State Commun.*, 48 (2) (1983) 105.
 [6] M.A. Tamor and C.H. Wu, *J. Appl. Phys.*, 67 (2) (1990) 1007.
 [7] J. Robertson, *Adv. Phys.*, 15 (1986) 317.
 [8] F.W. Smith, *J. Appl. Phys.*, 55 (3) (1984) 764.
 [9] C.A. Davis, V.S. Veerasamy, G.A.J. Amartunga, W.L. Milne and D.R. McKenzie, *Philos. Mag. B*, 69 (6) (1994) 1121.
 [10] N. Savvides, *J. Appl. Phys.*, 5X (1) (1985) 518.
 [11] A. Rengan, J. Narayan, C. Jahnke, S. Bedge, J.L. Park and M. Li, *Mater. Sci. Eng.*, B15 (1992) 15.
 [12] J.J. Hauser, *J. Non Cryst. Solids*, 23 (1977) 21.
 [13] J. Fink, T.M. Heinzerling, J. Pfluger, B. Sheerer, B. Dishler, P. Koidl, A. Bubenzer and R.E. Sah, *Phys. Rev. B*, 30 (1984) 4713.
 [14] J. Fink, T.M. Heinzerling, J. Pfluger, A. Bubenzer, P. Koidl and G. Grecelnis, *Solid State Commun.*, 47 (1988) 687.
 [15] S. Kaplan, F. Jansen and J. Machonkin, *Appl. Phys. Lett.*, 47 (1985) 750.
 [16] A. Grill, B.S. Mcyerson, V.V. Patel, J.A. Reimer and M.A. Petrich, *J. Appl. Phys.*, 6/(1987) 2874.
 [17] J. Wagner, M. Ramsteiner, C. Wild and P. Koidl, *Phys. Rev. B*, 40 (3) (1989) 1817.
 [18] V. Palshin, E.I. Meletis, S. Ves and S. Logothetidis, *Thin Solid Films*, 270 (1995) 165.
 [19] N. Savvides, *J. Appl. Phys.*, 59 (12) (1986) 4133.
 [20] N. Savvides, *Mater. Sci. Forum.* 52&53 (1989) 407.
 [21] F. Demichelis, C.F. Pirri and A. Tagliaferro, *Phys. Rev. B*, 45 (24) (1992) 14364.
 [22] F. Demichelis, C.F. Pirri and A. Tagliaferro, *Diamond Relat. Mater.*, 1 (1992) 298.
 [23] S.H. Wemple and M. Didomenico, *Phys. Rev. B*, 3 (1971) 1338.
 [24] D. Dasgupta, F. Demichelis, C.F. Pirri and A. Tagliaferro, *Phys. Rev. B*, 43 (3) 2131.
 [25] F. Wooten, *Optical Properties of Solids*, Academic Press, New York, 1972, pp. 78.
 [26] J. Barth, R.L. Johnson and M. Cardona, in E.D. Palik (ed.), *Handbook of Optical Constants of Solids II*, Academic Press, New York, 1991, pp. 213.
 [27] D.K. Avasthi, Jaipal, G.K. Mehta, H.C. Barshilia, S. Sah, B.R. Mehta and V.D. Vankar, *Vacuum*, 46 (7) (1995) 623.
 [28] D.C. Green, D.R. McKenzie and P.B. Lukins, *Mater. Sci. Forum.* 52&53 (1989) 103.
 [29] G. Beamson, W. Brennan, N.J. Clayden and R.C.K. Jennings, *J. Polym. Sci.*, 1/ (1993) 1205.