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Optical properties of Diamond like Carbon films prepared by DC-PECVD

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ABSTRACT

Diamond-like carbon (DLC) thin films were deposited at different substrate temperatures using methane and hydrogen gas in DC-PECVD at $2x10^{-1}$Torr. From the light transmission using UV-VIS spectroscopy it was found that the optical transition had changed from allowed indirect transition to allowed direct transition as the substrate temperature increased. The Optical gap increased with temperature, highest of 3.034 eV was observed at 573 K, beyond which it dropped. Colour of the film changed from light brownish to a colourless transparent film in the higher temperature. The Urbach energy decreased from 1.25 eV to 0.75 eV with increasing substrate temperature till 573 K and a slight increase after it. This trend is attributed to change in sp^3/sp^2 ratio or change in structure. The cluster size decreases with temperature, resulting in larger band gap and the structure more ordered. Similar pattern is also witnessed in the emission spectrum of the photoluminescence.

| Diamond like carbon | Optical properties | DC-PECVD | Optical gap | Urbach Energy |

1. INTRODUCTION

Diamond like Carbon (DLC) usually designates a form of hydrogenated carbon (a-C:H) containing lesser than 50% of sp^3hybridisation[1] Commonly, amorphous carbon can have a mixture of sp^3,$sp^2$and even sp^1 with presence of hydrogen. A secondary determinant of quality of film was found to be the fractional content of hydrogen. As its presence is known to stabilize the sp^3bond[3, 4]

It has gained remarkable interest in films and 'Diamond like' coating due to desirable properties ranging from low dielectric constant, high band gap, chemical inertness and extreme hardness. In addition optical gap is found to have a significant dependence on deposition parameters which defines the sp^3 and sp^2ratio [2, 3] thus leaving more room to fabricate desired films. However the microstructural reason for the change is not clear yet and is subject of on-going research

The present paper will concentrate on the change in optical properties of films deposited at with different substrate temperature ranging from 373K to 673K while other parameters were fixed at certain value.

2. EXPERIMENTAL

Diamond-like carbon films were deposited using direct current plasma enhanced chemical vapour deposition (DC-PECVD).There are two power supplies used in this study. A DC power supply that provides voltage up to 1.5kV with a maximum current of 1.0 mA that helps the formation of plasma. The next power supply is used to heat the system. By supplying the power to the cathode, the substrate could be heated to a desired temperature this is connected to temperature sensor for measuring the substrate temperature during the deposition

The source gas CH4 (1%)+Ar(39%)+H(60%)and nitrogen were used whose flow rates was measured by a mass flow controller (MFC).The gas flowed downstream along the inter-electrode gap and was evacuated with vacuum pump(rotatory mechanical pump) and measured by pressure gauge (Piraniguage).Prior to each deposition, the chamber was evacuated to a base pressure of $8x10^{-2}$Torr as it minimises contamination of the samples. A pressure of $2x10^{-1}$Torr was maintained throughout the deposition time of 30 minutes. Corning glass substrates were ultrasonically cleaned in chromic acid in (Brason 3210) for 40 minutes followed by distilled water and blown dry.

Thickness measurement was carried out with Ellipsometer model L117 He-Ne laser by Gaertner Scientific Corporation with a fixed wavelength of 632.8 nm. Transmittance scanning was performed with UV-VIS spectrophotometer model UV-3101PC within the wavelength range of 200 to 800 nm as in the Figure 1. The absorption coefficient was calculated from the transmittance (T) according to

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right)$$

where d is the thickness.

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Using Photoluminescence spectrometer (Perkin Elmer) DLC samples were exited with different wavelength from 200 to 800nm.the excitation was done at a fixed excitation slit 11.0 nm and emission slit 15.0nm.The photoluminescence spectra was thus acquired.

3. RESULTS & DISCUSSION

3.1 optical gaps (E$_{opt}$)

In agreement to what the physical observation of the colour of the film suggest, the films become more transmitting with increase in the substrate temperature within the visible range. The lowest transmittance of 81 % is recorded for the film prepared at 373 K and the highest of 97 % for 673 K. the absorption coefficient is derived from Figure 1.
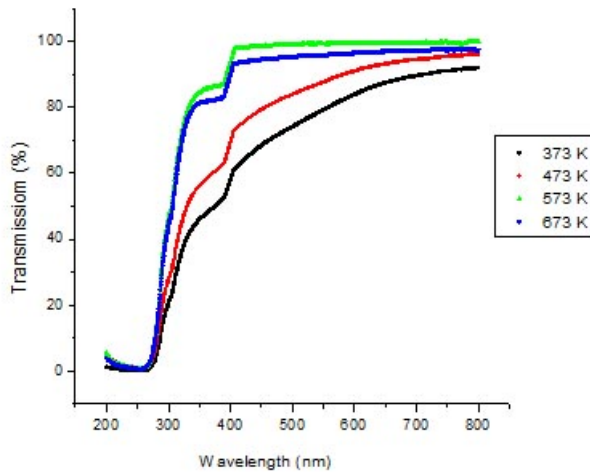
In order to determine the type of transition involved the graph of $ln\alpha$ vs $lnh\nu$ is plotted as shown in the Figure 2the gradient of the graph m indicates the type of transition

$$\alpha h\nu = A\left(h\nu - E_{opt}\right)^{m}$$

where α is the absorption coefficient, E_{opt} is the optical gap A is a constant, $h\nu$ is photon energy. The value of m categorizes the transition into the four types as listed. Allowed direct transition ($m=1/2$), forbidden direct transition ($m=3/2$), allowed indirect transition ($m=2$) and forbidden indirect transition ($m=3$)[5]

The gradient is observed decreasing with increase in substrate temperature in the range 2.24 to 0.46s, which is between allowed indirect and allowed direct.as the inset in the figure shows, films prepared at 373 K undergo allowed indirect transition, however the transition changes to allowed direct as temperature increases to 673K.

Projecting the vertical linear till it crosses the x axis in the graph of $(\alpha.h\nu)^2$ versus photon energy $(h\nu)$ gives the point which indicates the optical gap (E_{opt}) of the film as in Figure 3(a) and (b)
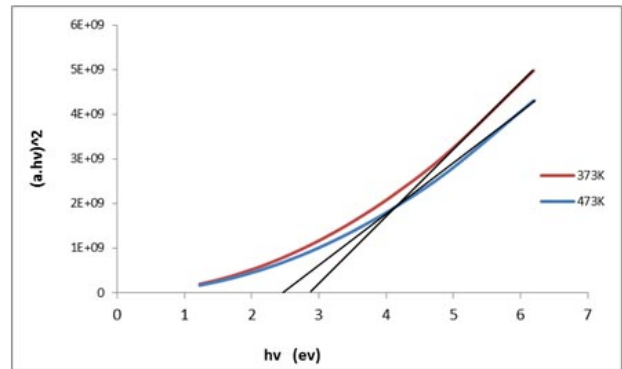

Fig. 1 Transmittance spectra for different Substrate Temperature

Figure 3(a) Graph of $(\alpha.h\nu)^2$ versus $h\nu$ for 373K and 473 K

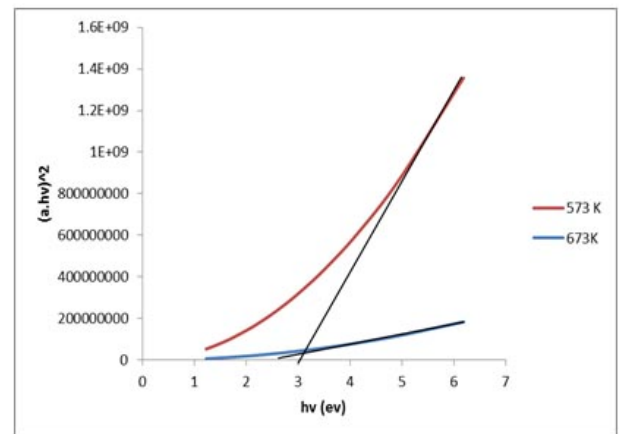Fig. 2 The graph of $ln\alpha$ versus $lnh\nu$

Figure 3(b) Graph of $(\alpha.h\nu)^2$ versus $h\nu$ for 573k and 673K

The optical band gap increases with the substrate temperature and slight decreases afterwards. The Gap is observed to be 2.769 eV at 373 K. it increases up to 3.034 eV at 573 K and again decreases to 2.887 eV at 673K Consistent with the result obtained by [4].

The bang gap is determined by the π states which are near the Fermi level. The filled π states form the valence band and the empty π * states form the conduction band in all amorphous carbons, and so they control the size of the optical gap [6]. [7] States that the size of the gap depends on the configuration of the sp^2 sites. Therefore increases in the gap are attributed to reduction in the sp^2/sp^3 ratio and also reduction in the average size of the sp^2 cluster. Smaller cluster size have larger gap which are also in agreement to Robertson model [9]. Figure 4. Shows the optical band gap *(Eopt)* as a function of substrate temperature

A peak value of 3.034 eV at 573 K is achieved, past which it decreases reaching to an agreement with [8]. Beyond 573 K the thin film tends to stabilize the sp^3 bonding and introduce larger disorder energy. This disorder energy is akin to stabilisation energy and forming larger clusters results in smaller band gap.at 673 K the degree of crosslinking C-C network is increased leading to larger cluster thus decreased optical band gap.
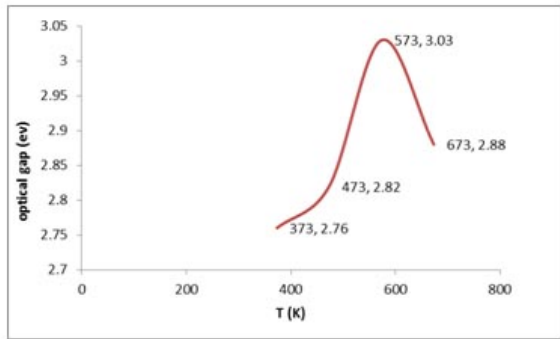
Figure 4. Optical band gap *(Eopt)* as a function of substrate temperature

3.2   Urbach Energy (Eₒ)

Urbach energy correlates on the one hand with the amount of topological disorder and on the other hand, with the photoconductive properties, the photoconductivity being higher and the trap density lower for lower values of E_o In amorphous carbons, E_o indicates the total change in $sp2$ content [10]

It can be deduced from a plot of lnα versus photon energy as in Figure 5. The straight line slope in this region is proportional to $1/E_o$ [11] and the E_o calculated for each sample is shown in table 1.

The decrease in the Eo is due to decrease in the band tail as sp^2 localized state decrease, hence a similar pattern to optical band gap.It was found that the urbachenergy,E_o decreases with the increasing substrate temperature and

later a slight increase. E_o decreases from 1.25 eV at 373 K to 0.75 eV at 573 K, however a slight increase of 0,83eV beyond 573 K.
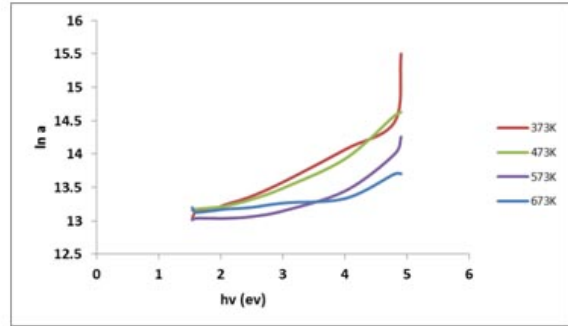
Figure 5. Graph for Urbach plot comparison.

Table 1 Urbach energy for films deposited at different substrate temperature

Substrate temperature(K)	Urbach energy (Eₒ) (eV)
373	1.25
473	1
573	0.75
673	0.83

Whereby it can be said that the average coordination number decreases at increasing optical gaps [10] thus the slight increase at 573 K can be explained in terms of optical bang gap.

Of the two disorder in DLC films,Urbach energy measures the inhomogeneous disorder related with the statistical distribution of sp^2 clusters and chains of different shape and size[10]However, it is not understood why the 'inhomogeneous disorder' should increase in polymer-like a-C:H samples with increasing optical gaps and decreasing cluster size.

3.3   Photoluminescence

Optical excitation creates an electron hole pair. These carriers can recombine non-radiatively, a relaxation that doesn't involve the emission of a photon, but involves the emission of vibrational energy (phonons) and emission of photons with lower energy or radiatively with the release of light (luminescence) Luminescence has been found in a-C:H as its high defect densities favour Non-radiative luminescence because it causes intermediate relaxation. The luminescence spectra depend mainly on the optical band gap, the defect density, the excitation energy and the temperature. it has been reported that the peak of the luminescence spectra of lower gap occurs above its Tauc. The luminescence peak is seen to increase only slowly with gap. The luminescence efficiency is high in a-C:H, particularly in samples with a wide gap [6]. However [10] argues that there is no clear relationship between the

photoluminescence peak energy and the optical gap to which this paper also agrees.

Figure 6.Shows the Photoluminescence peaks for different samples at different substrate temperature and Table 2 indicates the excitation energy required. A pattern similar to the Optical gap was observed in terms of excitation energy as well, assuming there are no traps in the structure and considering the peak wavelength it becomes Evident from the figure that the energy requirement for different samples vary across the different temperatures. The energy required increases with temperature till 573 K and then decreases. The PL bands indicate a change in shape beyond the substrate temperature of 573 K although the peak centres around 3.26 eV. The band becomes broader and the intensity also increases with temperature. This feature is attributed to the recombination centre associated with the thin films.
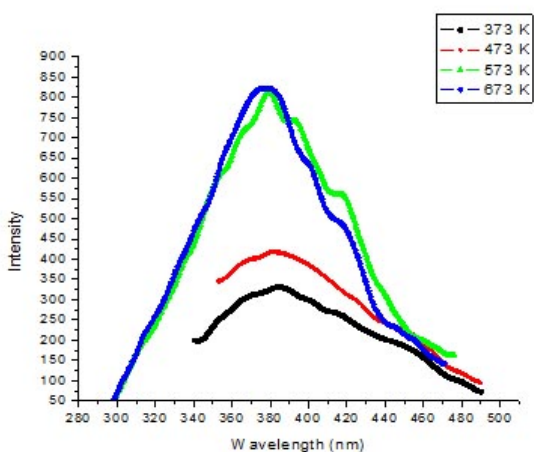

Figure 6 variation of peak wavelength with substrate temperature

Table 2 Photon energy required to maintain the intensity at different substrate temperature

Substrate temperature(K)	Excitation wavelength (nm)
373	320
473	320
573	265
673	260

All the deposition parameters were fixed except for substrate temperature. The highest photoluminescence peak intensity is observed at 673 K and the lowest at 373 K substrate temperature. At high temperature of 573 K the C-H bonding begins to break leading to more disorder in the samples thus increasing the photoluminescence intensity as the temperature increases however the decline beyond 573 K similar to Urbach energy and Optical gap is observed.

4. Conclusion

UV-VISspectrophotometric measurement of light transmission indicated that optical transition changed from allowed indirect to allowed direct as the substrate temperature increased in DLC films. Optical band gap increased with temperature with a maximum observed at 573K of 3.034 eV and a decrease beyond that temperature. This is due to stabilisation of the sp^3 bonding which introduces larger disorder energy leading to greater degree of crosslinking C-C network thus decreased optical band gap.

Urbach energy decreased with increase in temperature down until 0.75 eV at 573 K and increase at 673K, a pattern that is witnessed in photoluminescence where the highest intensity is observed at 573 K and a slight decrease beyond and lowest at 373 K. The decrease in the Urbach energy is because of decrease in the band tail as sp^2 localized state decreases while this pattern in photoluminescence is because of disorder in the film that increases with temperature.

Hence we can conclude that substrate temperature has an obvious effect on the optical properties of DLC thin films .As substrate temperature reached 573K the optical gap achieved was maximum

REFERENCES

[1] A. Grill. Diamond and Related Materials, 8 (1998), 428–434.
[2] Rusli, Amaratunga, A.J. and Silva, S.R.P. Diamond and Related Materials, 3 (1994)817-820.
[3] K.B.K.Teo,A.C.Ferrari,G.Fanchini,S.E.Rodil,J.Yuan,J.T.H.Tsai,E.la urenti,A.Tagliaferro,J.Robertson,W.I.Milne. Diamond and Related a Materials,11 (2002)1086-1090.
[4] F.A.Mahmoud,SH.SH.Saresmbinov,O.Yu.Prikhodko,andA.P.Ryagu zova. Journal of Ovonic research, 6(2010)253-257
[5] A. Abdelghany, S N Elsayed, A H Abou El Ela and N H Mousa,Pergamon. 0041-207X(1995)00210-3
[6] J. Robertson, National Power Laboratory, Leatherhead Surrey, 22 (1991) 7.
[7] C.W. Chen, J. Robertson, Journal of Non-Crystalline Solids ,227–230 (1998) 602–606.
[8] R.Gago, N.Huangc, M.P Kulish, U. Kreissig, Y.X. Leng, M.F. Maitz, H.Sunc, and Vinnichenko, Thin Solid Films. 455 –456 (2004) 530–534
[9] J. Robertson, Diamond and Related Materials, 12(2003)79-84.
[10] G. Tagliaferro., Fanchini., Diamond and Related Materials ,13 (2004) 1402–1407
[11] A. Ates, B. Gurbuluk., M. Yildirim, S. Dogan, T. Yildirim. and S. Tuzemen..Turk J ph, 26 (2002)127-129