

## RF magnetron sputtered deposited metal-doped diamond like carbon thin films: structural, morphological, mechanical, and optical properties

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The present study investigates the surface, structural, mechanical and optical properties of (0, 1%, 2%, 3%, 4%, 5%) palladium doped diamond like carbon (Pd;DLC) thin films prepared by using r. f. magnetron sputtering technique. The structural, mechanical, surface, and optical properties were measured by Energy Dispersive X-rays (EDX), Raman spectroscopy, Vickers Hardness Measurement (VHM), atomic force microscopy (AFM), and Spectroscopy Ellipsometry, respectively. EDX results clearly indicated the presence of palladium metal into DLC matrix. Raman spectroscopy results reveal that all Raman spectra consist of two main peaks as D-band (1355.7 to 1359.3) and G-band (1558.9 to 1577.9). Additionally,  $I_D/I_G$  ratio increases monotonically from 0.391 to 0.504 with increasing palladium concentration. With increasing doping concentration, AFM shows a modest increase in roughness of Pd-DLC thin films. The decline in the hardness of Pd-DLC films from 9.38 Gpa for 1% to 8.90 Gpa for 5% were observed by using Vickers Hardness Measurement (VHM). Spectroscopy ellipsometry showed that  $E_g$  reduced from 2.11 to 1.68 eV by adding the palladium concentration in Pd-DLC film. The decrease in the optical bandgap energy over the wide range is due to enrichment of  $sp^2$  contents than undoped film. The results reveal that incorporation of palladium produced prominent change in different properties of DLC film by increasing  $sp^2$  content. At 5% doping 1.68 eV band gap is achieved which is very ideal for solar cells fabrication. Therefore, this film is very good for solar cells and LEDs fabrications.

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*Keywords:* Thin film, Graphite, Sputtering, Dopant, Pd-DLC, Optical bandgap

### 1. Introduction

More than two decade, researchers are taking interest in the study of diamond like carbon (DLC) thin films due to its attracting properties like chemical inertness, optical transparency, wide range of tuneable optical bandgap, protective coating, higher hardness, low coefficient of friction,

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mechanical, tribological properties, higher wear resistance and thermal conductivity [1-6]. In DLC film,  $sp^2$  ( $\pi$ ) and  $sp^3$  ( $\sigma$ ) bonding are two main features, and the change in  $sp^2/sp^3$  ratio can cause the variation in different properties [7]. Beside all these advantages, the industrial applications of DLC are limited due to compressive stresses and adhesion to the substrate during the synthesis of DLC thin films [8]. Many research groups are working to overcome these drawbacks of DLC thin films by using different methods like doping, irradiation etc [9]. In these methods, doping in DLC with metals or non-metals is very suitable to achieve the specific  $sp^2/sp^3$  ratio, tune the band gap and enhance the sticking with substrate [10-21]. Metal doping in DLC improves the compressive stresses and adhesion to substrate, which is hot demand of industry in these days [22, 23]. Usually, non-carbide and carbide types of metals are added in DLC film. The metals like (Ti, W, and Cr etc.) create reaction with carbon and generate carbides belong to the carbide family. The other type of metal dopants (Au, Pt, Cu and Pd etc.) does not react with carbon and referred as non-carbide family [24, 25]. These components generate clusters in DLC, enhancing the graphitic character of the material, which improves the film's optical qualities. Pd has been doped in DLC, in this work. It has superior qualities like low resistivity, high conductivity, high catalytic activity, tunable optical modes, high resistance to corrosion and improves the adhesion of DLC to the substrate. If Pd has been doped in DLC film, no carbide is formed. It serves as a host matrix and is encircled by carbon atoms, resulting in conductive pattern in the structures of DLC, such as Au doped DLC [26]. This conductive pattern enhances the electrical qualities of film as we have reported earlier [27]. In this project, we have improved the sticking of DLC film with substrate and reduce its band gap energy with Pd doping. With these properties this DLC film will helpful for improving the life time and efficiency of optoelectronics devices like solar cells and LEDs. In dye sensitized solar cells, the life time of cell is disturbed due to corrosion of platinum (Pt) against electrolyte. As DLC is more stable therefore, if a thin layer of DLC is coated on Pt then it will improve the life time and efficiency of cell.

## 2. Experimental details

Good morphology of DLC films is major requirement for industrial applications. For this purpose different deposition techniques are used to synthesise DLC thin films, such that plasma enhanced chemical vapour deposition (PECVD) [28-31], filtered cathode vacuum arc [32-34], pulsed laser deposition (PLD) [35, 36] and magnetron sputtering [37-42]. Generally, at larger scale for industrial applications, the magnetron sputtering is good technique which is used for the fabrication of DLC thin films.

In this experiment six DLC thin films (one pure and five Pd;DLC thin films) were prepared by using PFG 600 RF magnetron sputtered system. In all thin films, silicon (1 0 0) having  $1\text{ cm} \times 1\text{ cm} \times 0.4\text{ mm}$  dimensions was used as substrate. The substrates were washed with isopropyl alcohol (IPA) and dilute acetic acid and for 15 minutes each, respectively to remove oxides on the surface of the substrates. A graphite target (99.99%) in the shape of disc with 3-inches and 1 cm of diameter and thickness was fixed in the holder of target for sputtering keeping a constant distance (10 cm) from the substrate. For the preparation of Pd; DLC films, five strips of Pd (99.99%) with different sizes were placed one by one at the centre of target for control co-sputtering of palladium and graphite to get the doping percentage. The size of the strips was determined by the graphite disc's % area. For example, if 1% of a graphitic disc is covered with Pd strip, the resulting film is known as 1% Pd-DLC film, and so on.

Before starting the deposition, the chamber of the sputtering machine was evacuated up to  $1.33 \times 10^{-5}$  mbar of base pressure and then gas of Argon was used for the co-sputtering of the graphite and palladium at the base pressure of  $1.6 \times 10^{-1}$  mbar. The substrate was fixed at the negative DC- biasing of 650 V, reflected power (REFP) was zero, forward direct power (FWDP) was 100 W and 100 Sccm of flow rate for the Argon gas in the chamber. The synthesis of films was carried out at 13.56 MHz radio frequency for 30 minutes at the room temperature of  $25\text{ }^\circ\text{C}$  for all thin films. (0, 1, 2, 3, 4, and 5%) Pd;DLC thin films were prepared.

### 2.1. Characterization

The EDX was used to find the palladium concentration in the Pd-DLC films. EDX results are shown in Fig. 1; the results confirm the presence of palladium in the films.

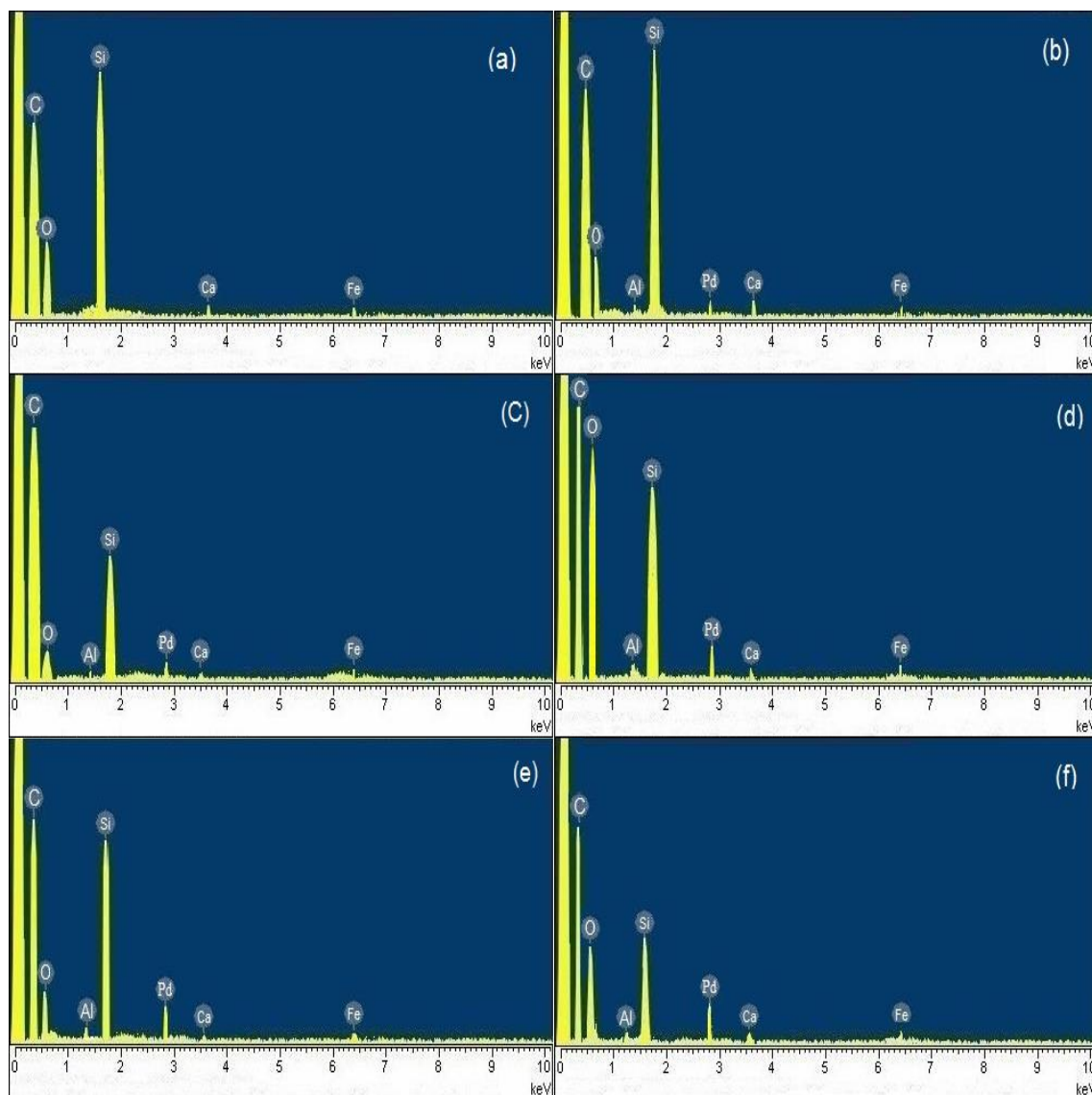


Fig. 1 (a-f) EDX of undoped and Pd;DLC films

The palladium percentage (1, 2, 3, 4 & 5) in the films is 1.09% ( $\pm 0.27\%$ ), 2.13% ( $\pm 0.31\%$ ), 3.08% ( $\pm 0.43\%$ ), 4.57% ( $\pm 0.62\%$ ), 5.17% ( $\pm 0.48\%$ ), respectively. Moving forward, these films are characterised by Raman spectrometer for structural analysis, Atomic Force Microscope for the surface roughness and to observe the topography, Vickers Hardness Measurement for the hardness measurement and optical properties was explored with spectroscopic ellipsometer. The film's thickness was measured using ellipsometry and was found to be between 288 and 319 nm.

## 3. Results and discussion

### 3.1. Raman Spectroscopy

Raman spectroscopy is a useful and non-destructive technique to find out the carbonaceous arrangement in carbon film. In this work, the transitional carbon bonding states were

confirmed by using Raman spectroscopy. The spectra of raman of undoped and Pd-DLC films deposited under the different concentrations of Palladium from 1 to 5% at room temperature in the range of 1100 to 1800  $\text{cm}^{-1}$  are shown in Fig. 2.

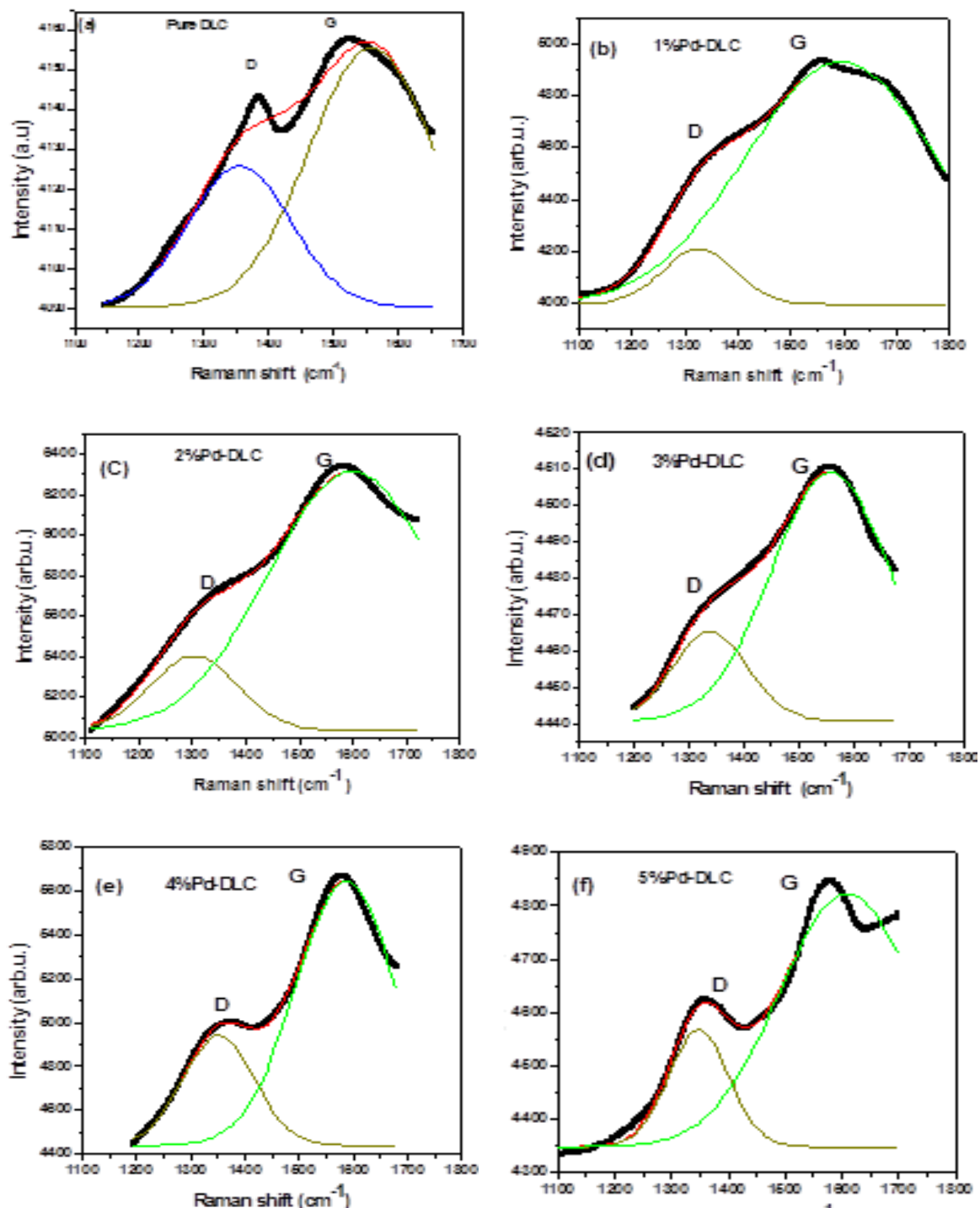


Fig. 2 Raman spectra of undoped and Pd; DLC.

All spectra consist of G-band and broad shoulder D-band. These two main bands are the individuality of DLC films because of  $\text{sp}^2$  sites only in the visible excitation. The breathing form of  $\text{sp}^2$  elements in ring forms is ascribed to the D-band at about 1350  $\text{cm}^{-1}$ , while the stretching

form of all sets of  $sp^2$  carbon atoms, whether in rings and chain, is attributed to the G-band at about  $1560\text{ cm}^{-1}$ . The phase structure of DLC thin films is confirmed by these bands [43]. To find the centre positions, FWHM, and  $I_D/I_G$  ratio of D-band and G-band were deconvolute by Gaussian two peak fitting in the range of visible Raman spectra. These values are shown in the Table. 1.

Table 1. Structural parameter of undoped and Pd-DLC films.

Thin Films	G peak's position ( $\nu_G$ )	D peak's position ( $\nu_D$ )	G peak's FWHM ( $\Delta\nu_G$ )	D peak's FWHM ( $\Delta\nu_D$ )	$I_D/I_G$
Pure DLC	1558.9	1355.7	195.53	157.60	0.391
1% Pd-DLC	1559.2	1358.4	362.04	136.92	0.401
2% Pd-DLC	1568.6	1355.9	316.13	162.28	0.436
3% Pd-DLC	1560.2	1345.2	216.41	137.15	0.451
4% Pd-DLC	1577.9	1359.3	198.72	131.66	0.504
5% Pd-DLC	1576.4	1356.8	241.26	106.81	0.462

The centre positions, integrated intensity ratio and FWHM for the D-band and G-band are useful to determine the arrangement of carbon bonds in DLC film. The D-band range from  $1345.2$  to  $1359.3\text{ cm}^{-1}$  and G-band range from  $1558.9$  to  $1577.9\text{ cm}^{-1}$ . The doping of palladium into the DLC matrix slightly shifts the D-band and G-band toward higher wave number. This behaviour of DLC with addition of Pd metal indicates the improvement in size and  $sp^2$  cluster in the film. Shifting of G-band toward higher wave number also the evidence that  $sp^2$  contents are increased by doping concentration. FWHM of D-band is primarily responsive to the structural disorder which is mainly due to the bond length and angle deformation in films [44]. The values of FWHM of G-band are larger for Pd-DLC films than undoped but on the other hand the values FWHM of D-band decrease by the doping of palladium as compared to pure DLC films. Intensities for both D-band and G-band are increased by the addition of Palladium in DLC matrix. The broadening of G-band and increased intensity are connected to the progress in  $sp^2$  sites [7]. The improvement of intensity in D-band also reflect the higher concentration of  $sp^2$  contents because it assigned C/C  $sp^2$  bonded carbon which seems to be aromatic in structure [12].

The ratio of  $I_D/I_G$  is the essential parameter to relate the  $sp^3$  and  $sp^2$  contents in DLC.  $I_D/I_G$  ratio has non-linear relationship with  $sp^3$  sites. If  $I_D/I_G$  ratio increases  $sp^3$  contents decrease and films are more in graphitic nature [45]. The incorporation of palladium into the DLC shows that  $I_D/I_G$  ratio linearly increase, which is related to enhancement in the graphitization of DLC film [7]. Increase in the  $sp^2$  sites also related to other properties of DLC thin films like improvement of conductivity, reduction in internal stresses and hardness of thin films [8]. In brief the Raman spectra show that by the addition of palladium in DLC film, the graphitic nature of films is enhanced.

### 3.2. Atomic Force Microscopy (AFM)

Topographical features and surface roughness for pure DLC and Pd-DLC films are observed by using AFM with area of scan  $2 \times 2\ \mu\text{m}$  for all films, as shown in Fig. 3.

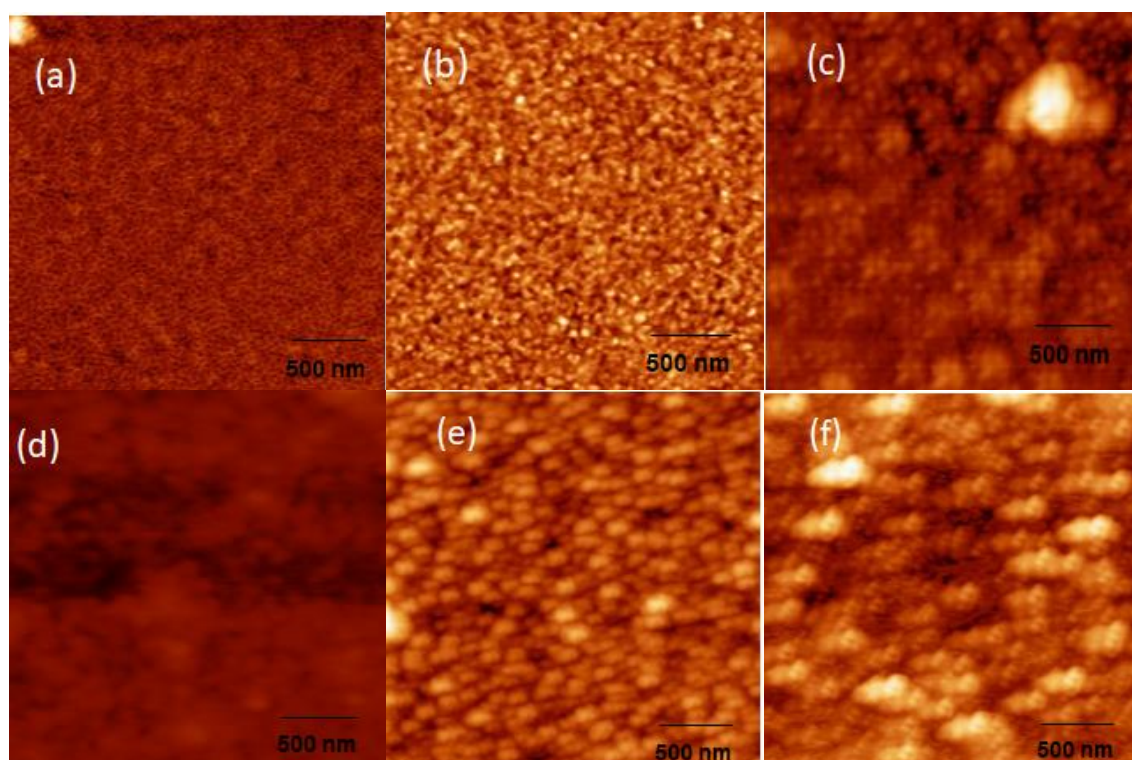


Fig. 3. AFM of undoped and Pd;DLC

With a root mean square (RMS) surface roughness ( $R_{rms}$ ) of 1.72 nm, the undoped DLC (Fig. 3(a)) has a smooth surface. Pure DLC film has nano-pores on its surface that contain carbon chains. Figures 3(b-f) is showed 2D morphology graphs of Pd;DLC films with concentrations of 1, 2, 3, 4, and 5% of Pd, respectively. The morphology of 1% Pd-DLC film is rougher than pure DLC film; also, the cyclic network is broken in this film, which is observed in the undoped DLC. Further doping of palladium (2% to 5%) results into increase in  $R_{rms}$  values as well as small spherical particles are appeared on the surface and the size of these particles increase with the doping concentration. The  $R_{rms}$  values of 1, 2, 3, 4, and 5% Pd;DLC films are 2.07, 3.99, 4.25, 3.41, and 5.67 nm, respectively. When sputtered atoms from the palladium target hit on the substrate with higher velocities, they form localize heat zone to host the carbon atoms. The carbon atoms sputtered from the graphite target stack around the palladium [46]. The stacking of carbon atoms increases the particle size and thickness of the thin films.

### 3.3. Vickers Hardness Measurement (VHM)

The hardness of DLC and Pd;DLC films is estimated with a Shimadzu HMV-2 micro-Vickers Hardness tester with 490.3 mN load for 5 seconds. To avoid the substrate indentation very low power was used to measure the hardness of Pd;DLC films. Hardness of the DLC film is also an important parameter which can indirectly relate to  $sp^2$  or  $sp^3$  contents. The hardness of the films shows non-linear behaviour with the  $sp^2$  sites. If hardness increases  $sp^2$  sites decrease, on the other hand if hardness decreases  $sp^2$  contents increase.

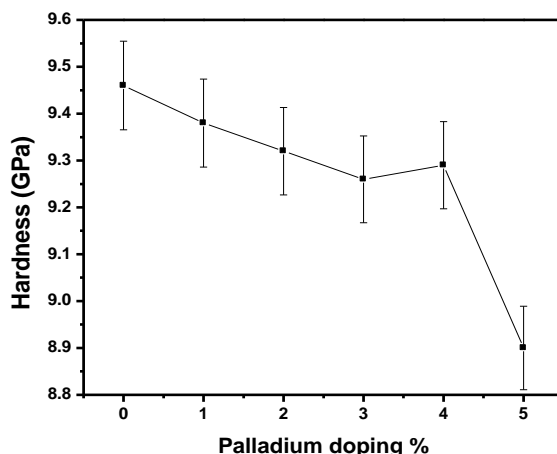


Fig. 4. Hardening of DLC film with palladium doping.

Fig. 4 (with 1% error bars) shows the fluctuation in hardening of DLC films with changing palladium concentration. Hardening of DLC film was 9.46 Gpa. Hardness gradually decreased with doping. Hardening of Pd;DLC thin films ranges from 9.38 Gpa for 1% Pd;DLC film to the 8.90 Gpa for the 5% Pd;DLC film.

The gradual reduction the hardness of the films is because of increasing graphitic behaviour. Other possible reasons for the reducing the hardening of films are  $sp^2$  clusters' interlinks, progress in graphitic nature, development of nanocluster, splitting the continuity of carbon networks, reduction in the internal stresses and lattice order improvement generated by varying the angle and length of C-C bonds. Despite this, the hardening of these films is considered sufficient for coating purposes on various instruments [47].

### 3.4. Optical analysis

Spectroscopy ellipsometry is used to characterize the optical characteristics of pure and Pd-DLC films. For the measurement,  $65^\circ$  was the incident angle. Data obtained from machine was in the format of delta and psi which represent the amplitude and phase differentials, respectively. Due to the technique's indirect nature, ellipsometry data is frequently adjusted to models, which are usually selected according to the system under investigation. In the present work, 2-layer model was used; in which base layer is the Si with constant thickness and the layer to be examined is amorphous carbon a-c with and without Pd inclusion.

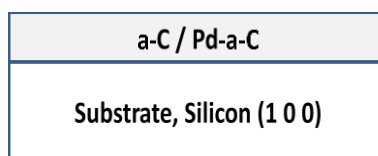


Fig. 5. The layer of carbon over the substrate of Si.

Figure 5 shows a block diagram for transparent material. The data is fitted by treating the upper layer as a Cauchy layer, which is a valid assumption in this case. Furthermore, because Pd is thought to be dispersed in the layer of carbon, such a model is suitable. For the films deposition the substrate surface was chemo-mechanically polished, so he model does not include any roughness of surface. As demonstrated in Equ. 1, the coefficient of absorption ( $\alpha$ ) of thin films is associated to the coefficient of extinction ( $k$ ).

$$\alpha = 4\pi k/\lambda \quad (1)$$

Equation 2 of the Tauc relation was used to compute the optical band gap energy ( $E_g$ ) for all thin films [48].

$$(\alpha h\nu)^{1/n} = A (h\nu - E_g) \quad (2)$$

In Equ. 2,  $h\nu$ , and  $A$  are energy of photon, and constant, respectively. The type of transition is represented by the exponent  $n$ . The value of ' $n$ ' is 2, and  $\frac{1}{2}$  for direct, and indirect band gaps, respectively.  $(\alpha h\nu)^2$  plots vs  $h\nu$  in direct transition, and the linear component of the curve is extended to = 0 to obtain the value of the associated  $E_g$ .

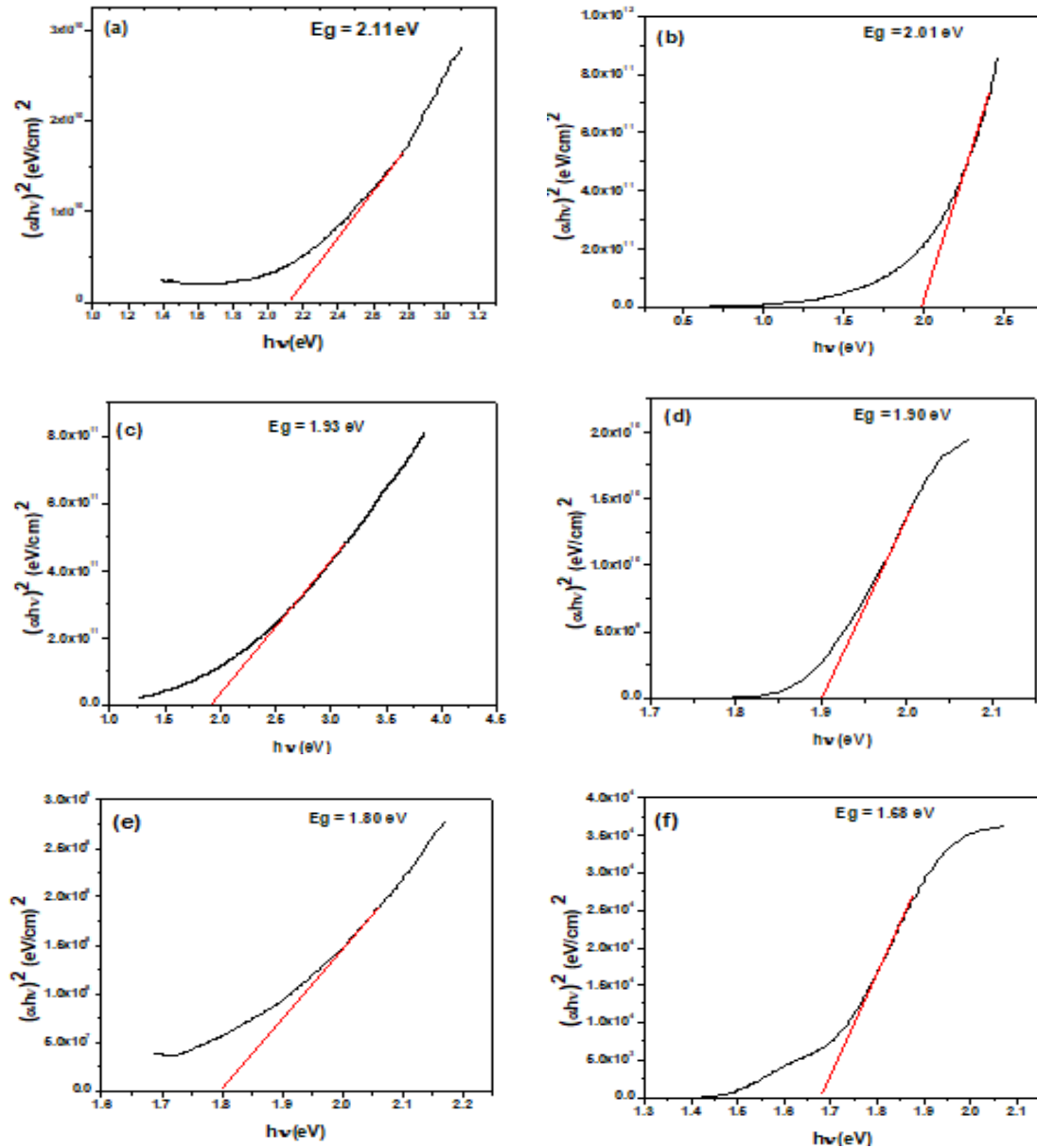


Fig. 6. Tauc plot of DLC and Pd;DLC films

Fig. 6 shows the tauc plots of undoped and Pd doped DLC films with increasing palladium content. The graphs show that the  $E_g$  of Pd-DLC films gradually decrease with the increasing doping percentage. The value of  $E_g$  is reduced from 2.11 eV (DLC) to 1.68 eV (%5 Pd;DLC). The values optical band gap energies obtained from the tauc plots are plotted as changing concentration



of palladium and data is well fitted as shown in **Fig. 6**. The optical bandgap energy mainly related to bond arrangement, microstructure and  $sp^2$  content. The  $E_g$  determined by the formation of band edge states formed by the  $\pi^*$  and  $\pi$  states. On the other hand, deep valance and conduction states are related to  $\sigma$  and  $\sigma^*$ . Since states of  $\pi$  are loosely bond and more closely to the Fermi level, play its main role to the  $E_g$  in DLC films. The other factor which can reduce the  $E_g$  is the increment in the  $sp^2$  cluster size by doping of metals [49]. Reduce in the values of  $E_g$  of Pd-DLC thin films, clearly the evidence that the palladium doping causes to enhance the cluster size and  $sp^2$  content in the DLC thin films.

#### 4. Conclusion

By RF magnetron sputtering technique DLC and Pd;DLC films were synthesized on silicon (100) substrate. Raman analysis showed that increasing palladium concentration also increases the  $I_D/I_G$  ratio from 0.391 to 0.504 which indicates the reduction in the defects and enhancement of the graphitic nature of films. The Raman peaks in all Raman spectra show a modest red shift due to the relaxing of internal tensions caused by palladium doping. Maximum shift both in D-band and G-band was detected for 4% doping. Furthermore, for pure DLC, the morphology displayed a smooth uniform nano-pore surface make an active cyclic chain. However, the morphology of 1% Pd-DLC became rougher as compared to pure DLC. Noteworthy, with further increase in doping, small spherical-like particles are fabricated, which enlarge their spherical size as doping concentration increases from 2% to %5 in Pd-DLC films. Furthermore, the roughness of Pd-DLC films also increases slightly by increasing the palladium concentration. The  $E_g$  of Pd-DLC films decreases from 2.11 eV to 1.68 eV which is the evidence of the enhancement the  $sp^2$  sites. Finally, the hardness of thin films also decreased from 9.39 Gpa to 8.90 Gpa with increasing palladium doping which further confirms that palladium doping increased the hybridization  $sp^2$ .

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