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Particle Deposition of Diamond-Like-Carbon on Silicon Wafers using Inductively Coupled PECVD

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Abstract: Coating a surface with an appropriate particle layer changes the surface material properties and is an important tool for friction and wear reduction. Diamond-Like carbon (DLC) coatings are highly in use for various applications owing to their characteristic properties such as low friction and low wear resistance, and high hardness value. In the present work, DLC particle films on p-type Si substrates by inductively coupled plasma enhanced chemical vapour deposition(IC-PECVD) were deposited. Fourier transform infrared spectroscopy revealed that DLC films were composed of sp^3 and sp^2 C-H bonds. Raman Spectroscopy was used for investigations into sp^3/sp^2 ratio of the deposited carbon particles bonding. hardness and Young's modulus were evaluated by indentation method using nano-hardness tester. The results showed that the deposited IC-PECVD DLC particle film had excellent chemical and mechanical properties. The developed films showed high value of hardness of 18 GPa, Young's modulus 190 GPa and a minimum I_D/I_G ratio of 0.18.

Keywords: Thin film, diamond like carbon, Raman spectroscopy, hardness, Young's modulus.

1 Introduction

Thin films are deposited onto bulk materials (substrates) to achieve wear resistant properties that are unattainable in the substrates alone. Thin films involve deposition of individual particles, like titanium nitride coatings on cutting tools and chromium coatings on plastic parts for automobiles. Different materials in solid, liquid, vapour or gas are used for film forming. Methods of deposition are physical vapour deposition (PVD) and chemical vapour deposition (CVD). All thin-film deposition processes consist of the following steps. Firstly, a source of film material is selected. Next, the material is transferred on to a substrate for the deposition. In few cases the annealing of the deposited film is also required. The synthesized film is then analysed to evaluate its properties. In both PVD and CVD, the major issues concerning to the source materials are contamination of the film and supply rate. During the transport of the source material and deposition over substrate there is a possibility of contamination which needs to be avoided. As the properties of the film depend upon the process parameters, deposition rate and the ratio of elements supplied to compound films should be maintained uniform throughout the film deposition process [1].

Diamond-Like Carbon films are amorphous coatings which basically consist of carbon particles. A DLC film consists of sp^3 and sp^2 carbon structures. In the DLC films, sp^2 bonded graphite-like structures are embedded in a sp^3 bonded carbon matrix. DLC films exhibit excellent properties such as high hardness, low coefficient of friction and low wear rates, suitable for tribological applications [2- 4]. DLC are deposited on a variety of substrates by PVD and CVD techniques. Physical vapour deposition and chemical vapour deposition techniques. Jatti et al. [5] reported that that the properties of DLC films change considerably depend on the process parameters and method of deposition.

The DLC films contain 0% to 40% of hydrogen, which is either chemically associated with carbon or can be in free state [6] as per the method of deposition used. Jatti et al. [7] applied Taguchi method for experimental design and to predict the optimal values of process parameters in the film deposition process.

Hydrogenated DLC films deposition by RF plasma CVD technique is a well-established method. Properties of the films can be customised as per the requirements by varying the process parameters such as Bias frequency, bias voltage, gas composition, pressure etc. The bias voltage most significantly affects the properties of DLC films among all these variables [8, 9]. Any change in bias voltage during the

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deposition process results in the change in the DLC film structure. The high ion density in inductively coupled plasma improves the reactivity of the precursor gases significantly in the CVD chamber, resulting in the reduction of deposition temperature without affecting the film quality [9].

In the proposed work, p-type silicon substrate was used for depositing DLC films by IC-PECVD technique and the films are studied for their microstructure, hardness and Young's modulus. As the p-type of silicon material has smaller dark current, hence it is selected as substrate for current study. IC-PECVD is widely accepted technique in industry particularly for thin film production. The primary reason for acceptance of IC-PECVD is that deposit thin films at lower temperature than thermally driven CVD.

2 Particle Depositions and Characterisation

2.1 DLC Processing

Inductively coupled plasma enhanced chemical vapour deposition technique was used for the DLC film deposition. A standard reaction chamber powered by a 13.56 MHz RF power source was used for this purpose. The substrate used was a P-type silicon wafer (100) of 1.5 cmx1.5 cm square area and 500 µm thickness. The substrate was first cleaned by ultrasonification in tri-chloro-ethylene for 10 minutes followed by cleaning using acetone for ten minutes. Methane (CH_4) was used as carbon source gas with hydrogen (H_2) as diluent. The substrate was kept in the PECVD chamber, and the vacuum of $4x10^{-6}$ mbar was created in the chamber. Methane and hydrogen were used for purging the chamber to rule out the possibility of contamination of the film. The substrate was cleaned for 10 minutes with hydrogen plasma. The methane and hydrogen gases in the chosen ratios were passed in the chamber and RF power of 50 Watts was used to create the plasma. The inside pressure of the chamber was controlled by using a throttle valve and the rate of gas flow was kept constant at 10 sccm throughout the deposition process.

2.2 Fourier Transform Infrared Spectroscopy

The chemical structure of the developed films was characterised using FTIR spectroscopy to understand the IR bond characteristics. FTIR is a well-recognised tool to identify the chemical bonds in a molecule by analysing the infra-red absorption spectrum, which is more of a molecular fingerprint. The wavelength of the absorbed light characterises the chemical bond. The IR spectra of synthesized DLC films were obtained using Vector 22 FTIR spectrometer, Brucker Make. The radiation absorption bands were observed ranging from of 2600 cm^{-1} to 3300 cm^{-1} matching with the sp^3 and sp^2 bonded carbons in the C-H group.

2.3 Raman Spectroscopy

Raman spectrometer, Labram 010 Model of DILOR-JOBIN-SPEX make was used to study the Raman spectra of the DLC films. He-Ne laser of wavelength 632 nm and 3 mW power was used as the source. After Gaussian curve fitting of the obtained Raman spectra, the ratios I_D/I_G were computed from the D-peaks and G-peaks areas.

2.4 hardness and Young's modulus of DLC film

The integrated optical (Nikon) / atomic force microscope (Surface Imaging Systems) equipped with a Berkovich diamond indenter of triangular-pyramid shape was used as nano hardness tester. It was fitted with an indenter which was progressively forced into the film and the force-displacement curve was plotted which formed the mechanical print of the material. The hardness and Young's modulus were calculated by the Oliver-Pharr method [10].

3 Results and Discussions

The process parameters bias voltage, Bias frequency, deposition pressure and gas composition were varied and experiments were carried out. Table1 summarizes the process parameters, obtained values, I_D/I_G ratio, hardness and Young's modulus values. It can be seen from table 1 that process parameters such as Bias Voltage set at -50 V, -100 V, -150 V, Bias Frequency set at 6 kHz, 0.25 kHz, 20 kHz based on experimental requirements. Deposition pressure set at 1.95 µbar, 2.95 µbar, 4.46 µbar, 2 µbar, 6 µbar based on experimental requirements. Gas composition set at 90:10 and 60:40 based on experimental requirements. All the experimental trials are finalized based on the initial trials, literature review and machine capability.

3.1 Fourier Transform Infrared Spectroscopy

Figure 1 illustrates The FTIR spectra of DLC films deposited by changing bias voltages, bias frequencies, deposition pressures and gas compositions are shown in Figure 1. Fourier transform infrared spectroscopy (FTIR) is a useful tool that provides valuable information as to the chemical bonds, molecular structures, and miscibility of components. The infrared spectral scan is generated and done in the mid-infrared region, 400–4000 cm^{-1}. The stretching modes of FTIR spectra lie in the range 3100 cm^{-1} to 2800 cm^{-1} whereas the bending modes lie in the range 1700 cm^{-1} to 1300 cm^{-1}. The C-H absorption band in the range 3100 cm^{-1} to 2800 cm^{-1} typically corresponds to sp^3 and sp^2 bonded carbons [11]. Three peaks are clearly observed in figure 1 at 2969 cm^{-1}, 2924 cm^{-1} and 2854 cm^{-1}.
These peaks correspond to C-H, sp^2 and sp^3.

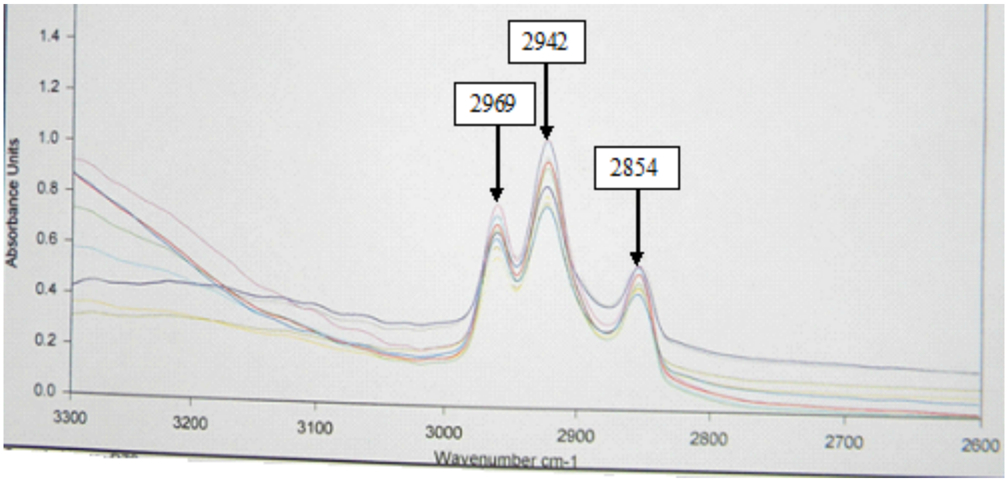

Fig. 1: FTIR Spectra of DLC films.

Table 1: Experimental parameters and observed values.

Run No.	Bias Voltage (volts)	Bias frequency (kHz)	Deposition Pressure (µbar)	Gas composition %	I_D/I_G Ratio	hardness (GPa)	Young's modulus (GPa)
1	-100	6	1.95	90:10	--	17.01	196.95
2	-100	6	2.95	90:10	0.89	16.52	189.74
3	-100	6	4.46	90:10	0.75	17.32	186.56
4	-150	6	6	60:40	0.44	15.23	166.84
5	-100	6	6	60:40	0.32	17.96	191.22
6	-50	6	6	60:40	0.18	15.73	177.52
7	-150	0.25	2	90:10	0.30	18.43	185.16
8	-150	6	2	90:10	0.77	16.88	175
9	-100	6	2	90:10	--	18.44	165.41
10	-100	20	2	90:10	0.33	16.65	172.81
11	-50	6	2	90:10	0.22	16	196
12	-150	6	2	90:10	0.29	16.2	180

3.2 Raman Spectroscopy

The Raman spectrum was observed to be basically dependent on the sp^2 bonding in the carbon and also on the sp^3 carbon bonding. With higher sp^3/sp^2 ratio the sp^2-clusters which are graphite like were found to decrease in size and number and the I_D/I_G ratio was also observed to decrease [12]. Figure 2 shows the Raman spectrum obtained for DLC films. The two peaks were observed at 1329 cm^{-1} and 1507 cm^{-1} inconsistent with sp^3 and to sp^2 carbon bond respectively. The I_D/I_G ratios were determined from the areas under D-peaks and G-peaks. Figure 3 and 4 show the variation of I_D/I_G ratio versus bias voltage. The I_D/I_G ratio was observed to increase with increase in bias voltage for 6 kHz Bias frequency, 6 µbar deposition pressure & 60:40 (CH_4:H_2) gas composition. This can be attributed to the presence of higher sp^2 carbon content.

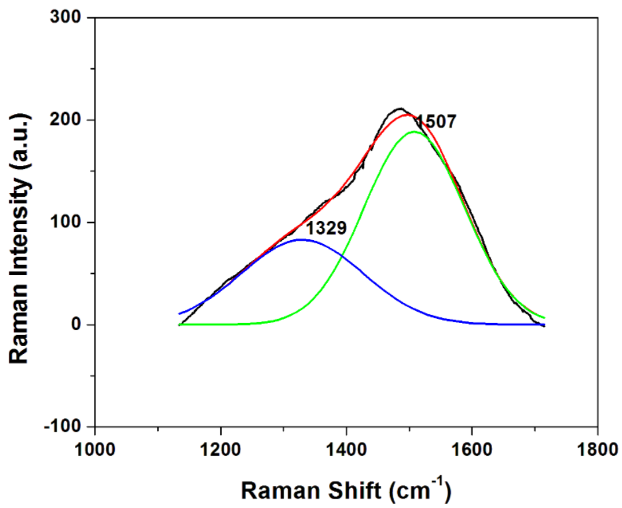

Fig. 2: Raman spectrum for DLC film.

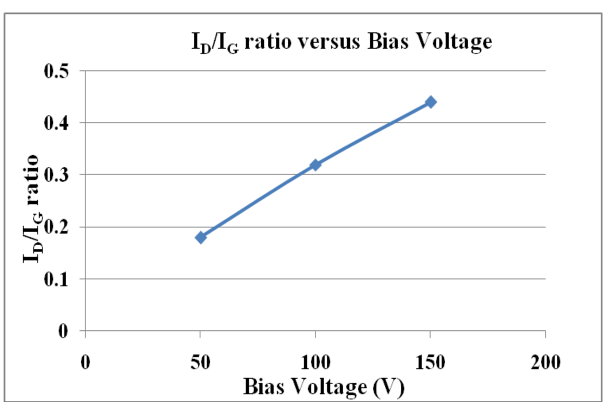

Fig. 3: ID/IG ratio versus Bias Voltage at 60:40, 6 kHz, 6 µbar.

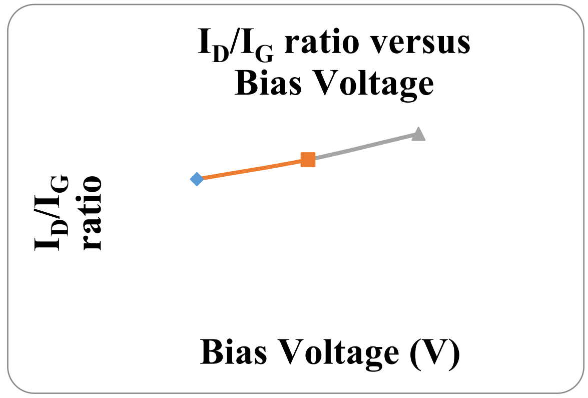

Fig. 4: I_D/I_G ratio versus Bias Voltage at 90:10, 6 kHz, 2 µbar.

3.3 Hardness and Young's modulus of DLC film

The hardness and Young's modulus of the DLC films were calculated from the indentation load versus displacement data. Figure 5 shows the variation between the load and the displacement of DLC film. The reported values of hardness and Young's modulus were obtained after taking the average of 4 indentations (a, b, c and d) taken on each sample. The rates of loading and unloading were maintained constant at 10 mN/min. The maximum load applied and maximum depth of indentation are 5 mN and 125 nm, respectively for 60 seconds. It can be appropriately concluded that the full deformation was limited within the film which confirms that the hardness and Young's modulus were obtained from the films only, and do not include any substrate effect [13]. The residual displacement was observed 50 nm for a total displacement of 125 nm. It can be concluded that the film had undergone 60% elastic deformation and remaining 40% plastic deformation. hardness and Young's modulus values for DLC film are shown in table1 and the values show that the films have high hardness and Young's modulus. Figure 6 & 7 are the curves plotted between the hardness and bias voltage while figure 8 and 9 show the plot between Young's modulus versus bias voltage. From figure 6 and 7 it is observed that the hardness was less at low bias voltage and then it attains a maximum similar to diamond like character. With the increase in bias voltage, the DLC film exhibits more graphite like structure. Thus, the highest value of hardness is observed at a bias voltage of -100 volts. From figure 8 and 9 it is observed that the Young's Modulus is less at low bias voltage and then it attains a maximum similar to diamond like character. With the increase in bias voltage, the DLC film exhibits more graphite like structure. Thus, the highest values of Young's modulus were observed at a bias voltage of -100 volts.

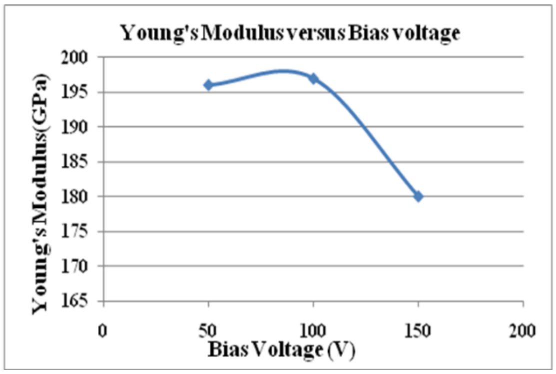

Fig. 5: Load-displacement curve of DLC film.

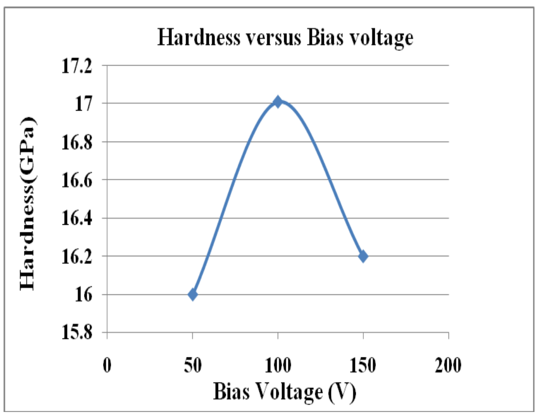

Fig. 6: hardness versus Bias Voltage at 60:40, 6 kHz, 6 µbar.

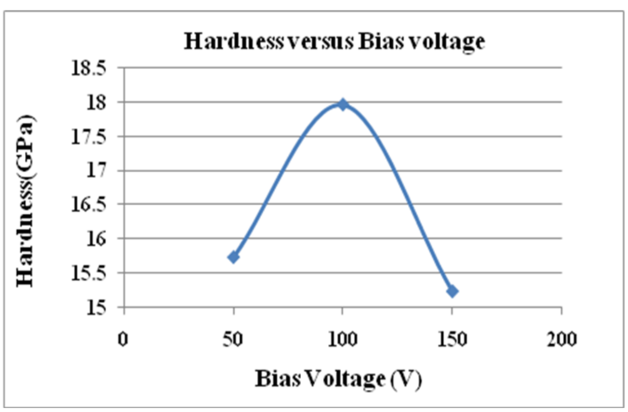

Fig.7: hardness versus Bias Voltage at 90:10, 6 kHz, 2 µbar.

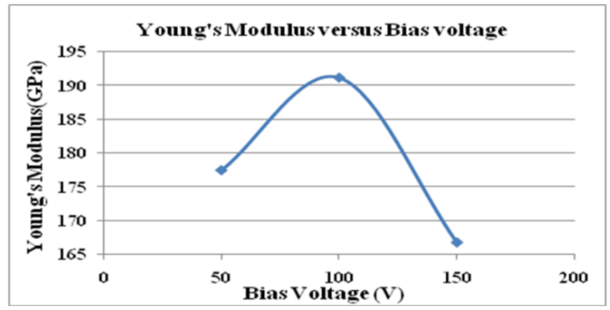

Fig. 8: Young's modulus versus Bias Voltage at 60:40, 6 kHz, 6 µbar.

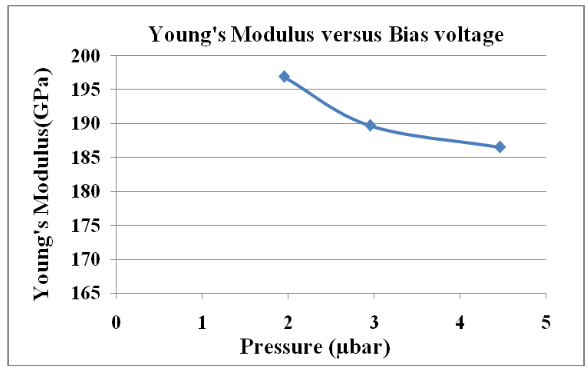

Fig. 9: Young's modulus versus Bias Voltage at 90:10, 6 kHz, 2 µbar.

Figure 10 depicts film hardness versus deposition pressure and figure 11 shows Young's modulus versus deposition pressure. The study concludes that the hardness and Young's modulus show higher values at lower deposition pressures. It can be attributed to the fact that at higher deposition pressures, the scattering of film forming species in plasma increases which results in the change in mean free path of impinging ions and the impact energy transferred to the substrate. The impact energy reduces with the increase in deposition pressure. This very well explains why at higher deposition pressure values there is decrease observed in hardness and Young's modulus of the DLC film.

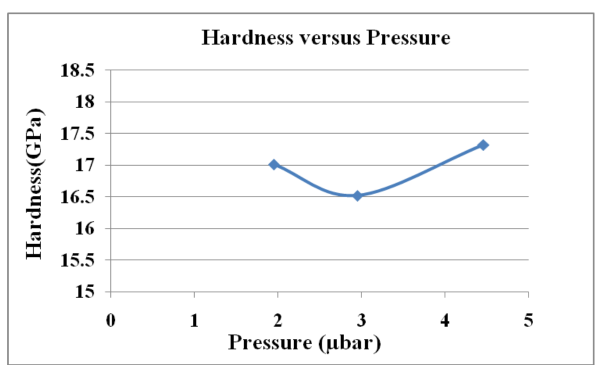

Fig.10 hardness versus Pressure at 90:10, 6 kHz, -100 V.

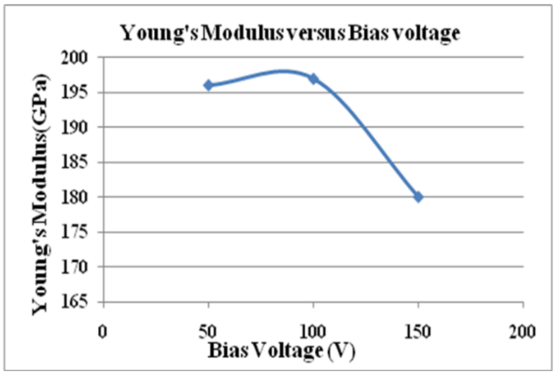

Fig. 11: Young's modulus versus Pressure at 90:10, 6 kHz, -100 V.

4 Conclusions

DLC particle films deposited on p-type silicon substrate by IC-PECVD technique under varying process parameters. During the deposition, the process parameters Bias frequency, bias voltage, gas composition and deposition pressure were varied. The deposited films were studied for their microstructure, hardness and Young's modulus. The experimental results show that the I_D/I_G ratio, hardness and Young's modulus depended directly on bias voltage. Also, hardness and Young's modulus were found to be inversely dependent on I_D/I_G ratio. The maximum values for hardness and Young's modulus were obtained at -100 volts of bias voltage. The experimental results conclude that the lower working pressures result in increased values of hardness and Young's modulus. This study reports the hardness 18 GPa, Young's modulus 190 GPa. Also the least I_D/I_G ratio of 0.18 was achieved in the synthesized DLC films.

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