

Bias enhanced nucleation and growth for improving the opto-mechanical properties of diamond-like carbon films

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Abstract. Diamond-like carbon (DLC) thin film is an amorphous carbon with high amount of sp^3 bonds and it is extensively investigated due to its excellent potential for application as an antireflection coating. Besides it has tunable opto-electronic and mechanical properties that depend on the sp^3/sp^2 fraction. This work seeks to investigate the enhancement of the opto - mechanical properties of DLC thin films by *in situ* control of the nucleation and growth of DLC thin films. Thus DLC thin films have been deposited on SiO_2 substrates using unbalanced RF magnetron sputtering at a constant power density of 4.4 W/cm^2 and various substrate bias voltages in the range -25 to -100 V . Raman spectroscopy has been used to determine the sp^3 fractions from the area ratios of the D-peak and G-peak (I_D/I_G). The results show that ratio vary between (0.55-0.63) corresponding to sp^3/sp^2 ratio in the range (1.07-1.33). Optical spectroscopy measurements in the visible range show a transmittance at 81% for a bias substrate of voltage of -75V , which correlates not only with the largest T_{auc} – gap of 1.56 eV but also with lowest sp^2 cluster of 15.25 \AA . The thicknesses of the films have been determined to be (94-147 nm) using X-ray reflectivity, and decoupled from the optical density in the transmittance data.

1. Introduction

Diamond-like carbon (DLC) thin films continue to inspire a lot of research interest due to their diverse applications and extreme properties such as high hardness, low friction coefficient, chemical inertness, high resistivity and optical transparency. For opto-mechanical applications its wide band gap and low surface roughness have made it a promising candidate for nano-mechanical resonators [1-10].

All the unique combinations of properties have extended the applications of DLC films as protective coatings for optical windows, magnetic storage disks and biomedical coatings and anti-reflection coatings [11]. The ability to tune the sp^3/sp^2 ratio and hydrogen fraction opens the way to improve the optical, electrical and mechanical properties of these materials. This further enhances their application in non-volatile memory as active layers with high scalability and low power

consumption devices [12]. In all the above cases DLC thin films are incorporated as active layer in multilayer devices, thus strain control and stress relaxation play a dominant role in the performance and life span of devices. Despite the wide range of applications. DLC thin films exhibit high compressive internal residual stress, which leads to poor adhesion, and thus limit their commercial use. Using RF magnetron sputtering under diverse substrate bias voltages provides a step towards the establishment of the correlation between microstructure and film – substrate adhesion.

2. Experimental

DLC thin films were prepared by RF magnetron sputtering system employing a 13.56 MHz radio frequency at room temperature with substrate bias voltages between (-25V and -100V). The deposition of the films was done in argon and methane gas ambient on a glass substrate (SiO₂). The RF input power density was set at 4.4W/cm² for an Ar/CH₄ ratio of 1:1 using a graphite target. The base pressure of the vacuum chamber was 3.7×10⁻⁵ mbar while the working gas pressure was set at 2.8×10⁻² mbar. The thickness and the density of the DLC films for the optical transmission were varied between 94 – 147 nm and 2.10-2.59 g/cm³, respectively, as measured by X-ray reflectivity. The microstructure of DLC thin films was studied by determining the area and intensity ratios of the D and G peaks using Raman spectroscopy after excitation with a 514.5 nm laser light source. The optical properties of the films were established using UV-vis Cary 500 spectrophotometer in the range 350-1400 nm. This technique enables the measurement of the optical transmittance of the DLC films after subtraction of the contributions of the glass substrate in the calibration.

3. Results and discussion

3.1. Raman Spectroscopy Characterization

Raman spectra of DLC thin films deposited under various substrate bias voltages are presented in figure 1. In general, the Raman spectra of the DLC thin films resembles that of disordered graphite and it constitutes of two vibrational modes, namely; the G-peak around 1580-1600 cm⁻¹ and the D-peak around 1350 cm⁻¹. These modes are assigned to the zone centre phonons of E_{2g} symmetry and the K-point phonons of symmetry, respectively [13]. The measured spectra of the DLC films were de-convoluted into distinct D- and G peaks using two Gaussian functions as shown in figure 1.

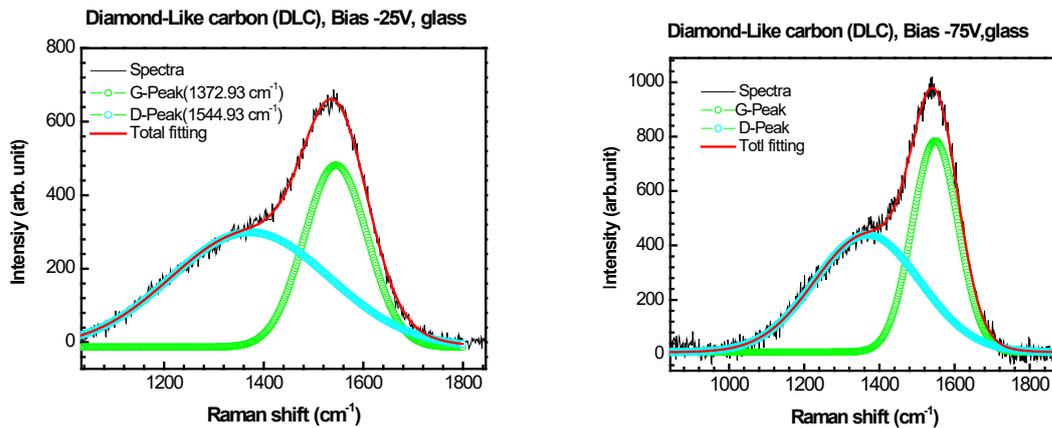


Figure 1. De-convolution of Raman spectra into distinct D- and G- peaks using two Gaussian functions for films deposited at substrate bias voltages of -25 V and -75 V.

Our results indicate that the centroid of the D-peak occurs in the vicinity of (1369.32-1373.49 cm⁻¹) and this corresponds to intensity I_D/I_G and area ratios in the range (0.55-0.63) and (1.28-1.59), respectively. The results further show a decrease in the D-peak position and I_D/I_G ratios with increasing substrate bias voltage. This is attributed to the increase in sp³ fractions in the films which represent the bonding configuration responsible for the formation of more diamond-like carbon films.

The relationship between I_D/I_G and cluster size defined by equation (1) is an appropriate indication on the formation of DLC thin films;

$$I_D/I_G = C(\lambda)L_a^2 \quad (1)$$

where $C(\lambda)$ is the constant dependent on wavelength and L_a is cluster diameter or in-plane correlation length. It is therefore evident that the I_D/I_G ratio decreases with decreasing cluster (L_a) size of the sp^2 bonds. Applying a DC bias voltage to the silicon substrate in ambient CH_4/Ar was observed to optimize DLC nucleation resulting in the highest fraction of sp^3 bonds at -100 V, however nucleation can also be determined by the space charge effects which can lead to a higher sp^3 fraction at lower bias voltage as was observed at (-75 V)[14]. In the CH_4 , the H/C ratio is significant, since the hydrogen fraction changes the properties of the films. A typical signature of hydrogenated samples is the increasing photoluminescence background with increasing H content shown in figure 2. This background generally overshadows the Raman signal of a-C:H around 40- 45 at.% of H. The ratio between the slope m of the fitted linear background and the intensity of the G-peak, $m/I(G)$, is used as a measure of the bonded H content as shown in figure 2. The bonded hydrogen in DLC was thus estimated using equation (2) and the results included in Table 1. Note that this expression is valid for $H > 20$ at. % [15].

$$H[at. \%] = 21.7 + 16.6 \log \left\{ \frac{m}{I(G)} [\mu m] \right\} \quad (2)$$

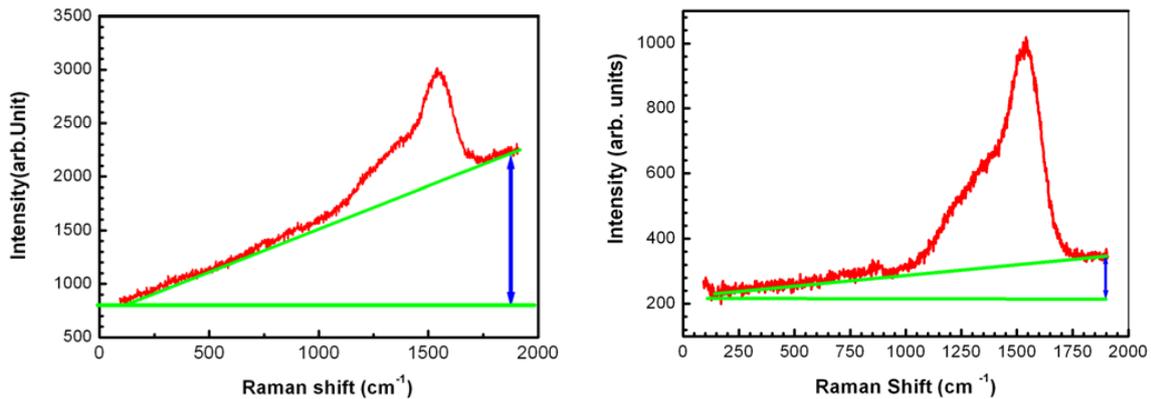


Figure 2.The ratio between the slope m of the fitted linear background and the intensity of the G-peak, for -25 V and -75 V.

A summary of the Raman spectroscopy results is presented in Table1. It is observed that the substrate bias voltage increases the hydrogen content in the DLC films up to -75 V, beyond which (at -100 V) a decrease in the amount of hydrogen occurs. This decrease could be attributed to re-sputtering effects arising from plasma etching. Indeed the thickness of the DLC thin films deposited at -100 V is 99 nm compared to 147 nm, that of films deposited at -75 V. This implies that the films deposited on the glass can be classified as diamond-like carbon which has the value between 20 - 40% of hydrogen [16].

Table 1. Different parameters of DLC thin films obtained from the Raman spectra at 514 nm.

Substrate bias voltage (V)	D-peak (cm^{-1})	Area ratio (I_D/I_G)	Height ratio (I_D/I_G)	Sp ³ /sp ² (± 0.05)	Hydrogen (at.%)
-25V	1372.93	1.59	0.63	1.07	22.15
-50 V	1369.32	1.45	0.59	1.21	31.27
-75 V	1367.76	1.28	0.55	1.33	38.19
-100V	1373.49	1.51	0.61	1.13	32.52

3.2. Optical spectroscopy

The UV-vis transmission spectra of DLC thin films at various substrate bias voltages (from -25 V to -100 V) are shown in figure 3(a). The dependence of transmission on the optical constants and the film thickness is decoupled from the measurement. Thus the values presented represent the percentage transmission from the intrinsic properties of the DLC film deposited at various substrate bias voltages. The highest transmittance is observed for films deposited with a bias voltage of -75 V, which corroborates with the presence of more sp³ fractions in the films. Using Beer’s law, Tauc’s relation and the Fermi-golden rules for interband transitions, the dispersion of absorption coefficient is extracted as shown in figure 3(b). The plot of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ of DLC films prepared at different bias voltages on the substrate is based on a direct allowed transition to estimate the Tauc gap, and the results are shown in Table 2, where the largest Tauc gap occurs for the films prepared at -75 V bias, owing to the higher sp³ fraction.

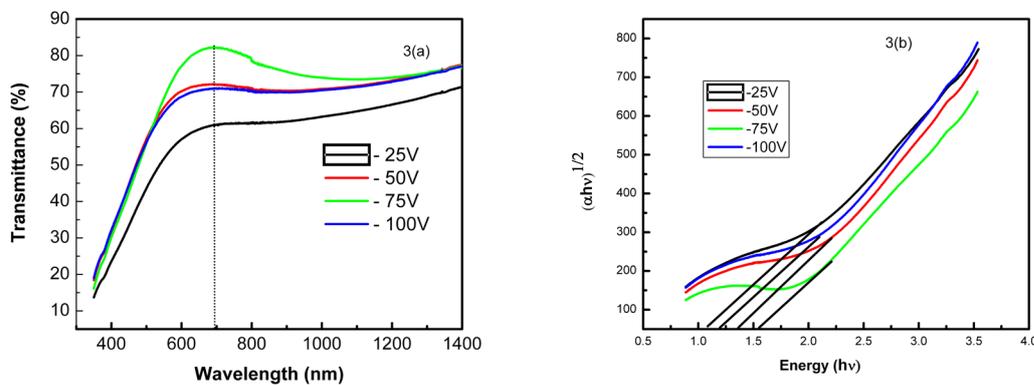


Figure 3 (a) Transmittance versus wavelength and (b) the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$.

Table 2. The mixture of optical property and Raman spectroscopy results for the biased DLC films.

DLC films	Transmission (%)	Tauc gap PL (eV)	Cluster size Height (Å)
-25V	58	1.10	17.00
-50 V	69	1.37	16.24
-75V	80	1.56	15.25
-100 V	66	1.20	16.57

The linear extrapolation in fig 3(b) from the straight line to the energy axis gives the Tauc gap of the films under diverse substrate bias. The optical band gap (E_g) of the films has been determined to be: 1.10, 1.37, 1.56 and 1.20 eV, corresponding to the substrate bias voltages of -25 V, -50 V, -75 V and -100 V, respectively. The results in Table 2 show that the Tauc-gap increases with increasing sp^3 fractions, corresponding to more diamond like films tending to be optically transparent, for which the cluster size of DLC thin film is less than 2 nm. The values of Tauc gap determined in this work are in agreement with those reported for a-C:H (1- 2 eV) [15]. The Tauc- gap is mainly determined by the C sp^2 hybridization clusters embedded in the amorphous carbon medium [16] and thus the increase in the Tauc- gap is expected for decreased fraction of sp^2 cluster sizes as shown in Table 2.

4. Conclusion

The present work has shown that DLC films had been successfully deposited onto a glass substrate at room temperature using graphite target and ambient Ar/CH₄ using a radio frequency (RF) magnetron sputtering. The dependence of structural evolution of DLC films as a function of the substrate bias voltage has been demonstrated by a combination of Raman spectroscopy and X-ray reflectivity, where an amorphous matrix evolves into a predominantly sp^3 bonded system with sp^2 chains. Raman and UV-visible spectra further corroborate this evidence indicating that increasing substrate bias voltage leads to the reduction of the cluster size of sp^2 rings, creating more sp^2 chains and the sp^3 bonds. It is thus expected that as fraction of sp^3 bonds increases, the films will also exhibit stronger mechanical characteristics, thus this project will be extended to employ Brillouin scattering technique to measure the Young's modulus of these DLC films.

5. References

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