

MECHANICAL AND STRUCTURAL CHARACTERIZATION OF DLC PREPARED BY PECVD TECHNIQUE

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Abstract: *Diamondlike carbon (DLC) films have been explored extensively in the past due to their highly attractive properties. However, the high level of internal stress developed during growth, calls for stress relieving process where structural and mechanical properties changes takes place. In the present study, the DLC is deposited on Si substrate using PECVD process and mechanical & structural changes during the post heat treatment process of DLC are investigated by using nanoindentation and Raman spectroscopy. Increase in hardness value confirmed the conversion of sp^2 to sp^3 structure while heat treatment.*

1. INTRODUCTION

Diamond-like carbon (DLC) films have attracted considerable technological interest because of their unique combination of properties, such as extreme hardness, optical transparency, high electrical resistivity and chemical inertness [1, 2]. Potential applications of the films include protective antireflection coating for IR optics, silicon solar cell, and coating for the reduction of wear, abrasion and corrosion [3, 4].

The thin film deposition conditions for DLC films usually result in deposited films with a high intrinsic residual stress between the substrate and the film. The presence of large residual stresses leads to film failure and restricts the thickness of DLC films that will adhere to substrates. The residual stresses in fillms can be removed by annealing at a suitable temperature for a sufficiently long time. Experimental investigations by Sullivan et al. [5] and Friedman et al. [6] indicate that residual compressive stresses can almost be completely eliminated in tetrahedral amorphous carbon films by vacuum annealing of the films to 600 °C. In the case of DLC films based on hydrogenated amorphous carbon (a-C:H), attempts to anneal out residual stresses at temperatures above 300°C results in structural changes that degrade some of the desired properties expected from DLC films.

This thermally induced structural modification of

the (a-C : H) films has to be properly monitored and controlled if the desired properties of the films are to be retained after annealing to remove residual stresses. The above stated structural changes in hydrogenated DLC films is associated with the effusion of hydrogen from the films and thermal graphitisation [7]. Attempts to improve the thermal stability of DLC (a-C:H) films and therefore facilitate annealing to relieve residual stresses at relatively high temperatures has involved modifying the films with additives like transition metals or silicon [4]. We report here our investigation of the structural and mechanical changes in thermally annealed DLC (a-C:H) by Raman spectroscopy and nanoindentation.

2. EXPERIMENT

2.1 Film Deposition

DLC films on silicon substrate of sample size 20mm×20mm×0.75mm shown in fig. 01 were prepared by PECVD equipment (Roth & Rau, Germany, model: HBS 500). The substrates were pre-cleaned with soap water, distilled water and with isopropyl alcohol in an ultrasonic bath for 15 minutes at 35°C by using ultrasonic cleaning machine (model: S 70H ELMASONIC). Prior to deposition the substrates were cleaned in argon (Ar) plasma at a flow rate of 300 sccm and constant bias voltage of 400 V for 20 minutes. DLC deposition was carried out with C₂H₂ (Acetylene) as process gas in a constant power mode with RF power of

200 W and at an operating pressure of 1.40×10^{-3} mbar. Five samples were prepared with target of film thickness 1micron under the same operating condition (Table-01)

2.2 Thermal Treatment

The internal stresses induced during the DLC growth are processed for post thermal treatment at different cycles to investigate the structural & mechanical properties changes. This process is carried out by using ceramic furnace under controlled inert atmosphere, both heating and cooling rates of $5^{\circ}\text{C}/\text{min}$ and they are soaked for 2 hours at different annealing temperature i.e 150°C , 200°C , 300°C and 400°C .

2.3 Characterization

The DLC film thickness is measured by ellipsometry (MX 2000X) and after thermal treatment of DLC film the structural changes & mechanical properties are characterized by Raman spectroscopy (Seiki Tecnotron, Japan) &

nanointendor (Agilent G200, USA) respectively.

3. RESULTS AND DISCUSSION

The Raman Spectra and nanoindentation results of DLC films (a-C:H) prior to thermal treatment and after thermal annealing are as shown in Fig. 02 and table 03. The variation of $I(D)/I(G)$ ratios of the DLC films with annealing temperature is shown in table 02. After annealing the sample at 150°C a slight decrease in $I(D)/I(G)$ ratio was observed with respect to the as-deposited films. The increase in $I(D)/I(G)$ ratio becomes more significant as the annealing temperature is increased from 200°C to 400°C as shown in table 02.

Wild and Koidl [8] have proposed that the evolution of hydrogen during thermal annealing of (a-C:H) takes place by the desorption of hydrogen and hydrocarbon from the edges of the sp^2 dominated clusters and effusion through a network of boundaries decorated by hydrocarbons. According to Tang et al. [9,10] the

Table 1: Operating Conditions for DLC by PECVD

S. No	PARAMETERS	RANGE
1	Radio frequency discharge	13.56MHz
2	RF Power	200W
3	Pre-cleaning gas	Argon (Ar)
4	Working gas	Acetylene (C_2H_2)
5	Flow rate	100 sccm
6	Deposition temperature	30°C
7	Deposition time	125 min
8	Film thickness	1 micron
9	Number of sample	5 samples

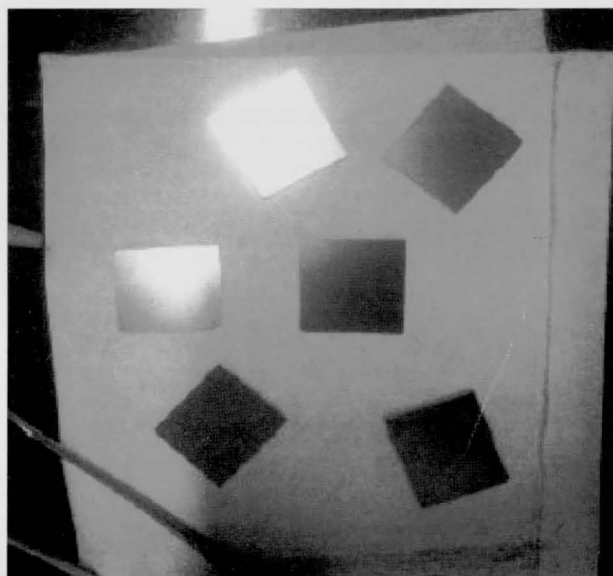


Fig 1. Si Substrate for DLC Film Preparation

Table 2: Effect of Annealing Temperature on Structural Changes (ID/IG ratio)

S.NO	Annealing temperature ($^{\circ}\text{C}$)	G- peak position (cm^{-1})	D – peak position (cm^{-1})	ID/IG Ratio
1	150	1483.02	1082.352	0.322
2	200	1481.46	1144.963	0.451
3	300	1498.56	1180.129	0.541
4	400	1496.96	1170.109	0.569
5	As deposition condition	1487.67	1178.46	0.442

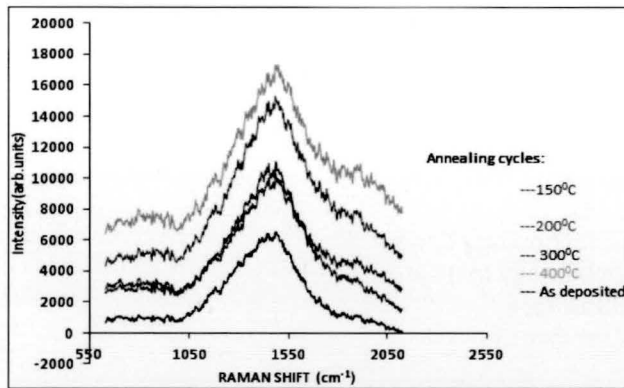


Fig 2. This Figure Shows Raman Spectra of a 1µm a-C:H Film on Silicon Prior to, and After Annealing for 2 h in a Ceramic Furnace at 150°C, 200°C, 300°C and 400°C

Table 3: Effect of Annealing Temperature on Mechanical Properties (Hardness) of DLC

Sample identification	Annealing temperature (°C)	Hardness (GPa)
1	150	33.29
2	200	32.44
3	300	33.26
4	400	34.63
5	As deposited condition	27.70

initial increase in I(D)/I(G) ratio with annealing temperature which we have also observed in our (a-C:H) film indicates that the average cluster size decreases rapidly beyond a threshold which they identified for the (a-C:H) to be 450°C.

Whilst we agree with the suggestion of Tang, et al. [9, 10] regarding the changes in the structure of (a-C:H) with increasing annealing temperature, their explanation of the changes responsible for the initial increase in I(D)/I(G) ratios with increasing annealing temperature does not seem to be directly related to the expected changes in sp²:sp³ ratio. Our study is in agreement with the proposal of A. A. Ogwu, et al [11] regarding the desorbed hydrogen and hydrocarbon from the edges of sp² clusters in (a-C:H) during the initial annealing stages go into sp³ bonding configuration and is clearly evidenced from increase of hardness of DLC film as shown in table 3.

4. CONCLUSION

Thermally annealed diamond like carbon (DLC) films have been characterized by Raman spectroscopy and nanoindentation. The structural modifications in these films show a dependence on the annealing temperature based on Raman spectroscopy. The mechanical characterization reveals the increase of hardness which is in line with assumption made by A.A. Ogwu et al., regarding the desorbed hydrogen and hydrocarbon from the edges of sp² cluster in (a-C:H) during the initial annealing stage go in to sp³ bonding configuration leading to initial increase in I(D)/I(G) ratios.

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