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ScienceDirect

Procedia Engineering 97 (2014) 1452 – 1456

Procedia Engineering

www.elsevier.com/locate/procedia

12th GLOBAL CONGRESS ON MANUFACTURING AND MANAGEMENT, GCMM 2014

Detailed Raman study of DLC coating on Si (100) made by RF-PECVD

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Abstract

Radio frequency (RF) plasma enhanced chemical vapour deposition (PECVD) technique was used to make a diamond like carbon (DLC) coating on silicon (100) substrate. The deposition was carried out using C_2H_2 as the process gas, at different temperatures, 25°C (room temperature) and 300°C with constant power and flow rate. Characterization techniques such as ellipsometry and Raman spectroscopy were used to characterize these samples. Raman analysis of DLC coatings at different temperature is carried out in detail for two different excitation wavelengths i.e. 514 and 785 nm and, results are presented in the paper. Blue-shiftis observed in both D and G peaks of Raman spectrum with increase in deposition temperature, which indicates the formation of compressive strain in high temperature deposited DLC coatings. Dispersion in both D and G peaks is observed for different excitation wavelength suggesting that the coating is hydrogenated DLC. The degree of hydrogenation of the DLC coating appears to decrease with respect to the deposition temperature. Nano-indentation study shows a marginal increase in hardness with increase in deposition temperature.

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*Keywords:*DLC; PECVD; Silicon, Raman; Nanoindentation

1. Introduction

Diamond like carbon (DLC) is a mixture of sp^2 and sp^3 hybridization of carbon, where sp^3 hybridization is more dominant, therefore has diamond like characteristics [1-3]. DLC coatings showed good mechanical, optical, electrical, chemical and tribological properties and can be used in applications for antireflective coatings for solar cells, IR optical materials, wear resistant and low friction coatings, orthopedic implants etc [4-8]. DLC coating is deposited by physical and chemical process such as sputtering and microwave (MW) and Radio Frequency (RF) process respectively [9-11]. Different process parameters such as reacting gases, bias voltage etc., can be used for the deposition of DLC films [12-14] in the chemical process.

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Selection and peer-review under responsibility of the Organizing Committee of GCMM 2014
doi:10.1016/j.proeng.2014.12.428

Based on degree of hydrogenation, properties of the DLC coatings such as hardness, coefficient of friction (COF) and antireflectivity can change. Therefore Hydrogenation plays an important role in the biomedical application to reduce cytotoxicity and COF in the DLC coatings [15-17].In this paper hydrogenated tetrahedral amorphous carbon (ta-C:H) coating were developed on a silicon substrate using plasma enhanced chemical vapour deposition (PECVD) technique using RF power. Raman analysis is useful technique to understand carbonaceous materials such as DLC [18,19]. In this paper, detail Raman studies were carried out to with excitation laser of 514 and 785 nm to understand the DLC coating.

2. Experimental details

DLC films were deposited on the single sided polished silicon (100) substrates. The deposition system consists of a 13.56 MHz RF- PECVD system of Roth&Rau, Germany, model: HBS 500. DLC films were coated on silicon (100) substrates. The substrates were first cleaned by soap water, distilled water and in the end, by isopropyl alcohol in an ultrasonic bath. Before deposition, the substrates were cleaned in argon (Ar) plasma at a flow rate of 300 sccm and a constant bias voltage of 400 V for 20 minutes.DLC deposition was then carried out with 100 sccm of C_2H_2 as process gas in a constant power mode with RF power of 200 W and at an operating pressure of $2.0x10^{-3}$ mbar. The deposition temperatures were varied at 25ºC (RT) (Sample name - Si RT) and 300ºC (Sample name - Si 300) to study the effect of deposition temperature on the structural and mechanical properties of the DLC coating.

Film thickness and refractive index of the DLC film were determined by J.A. Woollam, MX 2000X ellipsometer in the wavelength of 400 - 1000 nm. Raman analysis of the DLC films was carried out by Seki Technotron, STR 300 Raman spectroscope with 514 and 785 nm monochromatic light. Hardness and Young's modulus were studied by nanoindenter of Agilent make of model G200.

3. Results and discussions

From the ellipsometry result it is found out that thickness of DLC coatings is decreasing with respect to the deposition temperature, which means that the DLC process is falling in the depletion region (table 1).

Table 1. Table for thickness vs deposition temperature variation of the DLC coating process.

Sample Name	Thickness (nm)
Si RT	528.38
Si 300	500.34

Raman spectrum for different deposition temperatures is shown in Figure 1. Raman data is deconvoluted and shown in Table 2.Both D and G Raman peaks are found to be blue shifting with respect to the deposition temperature of DLC processing. It is concluded that high deposition temperature leads to increase in compressive stress. FWHM value of both G peak is found to be decreasing, while D peak is found to be increasing with increase in the deposition temperature. Ad/Ag (peak area ratio of D and G peaks) ratio is found to be increasing, with respect to the deposition temperature, which suggests that ring structure concentration is getting increased with respect to linear structure.

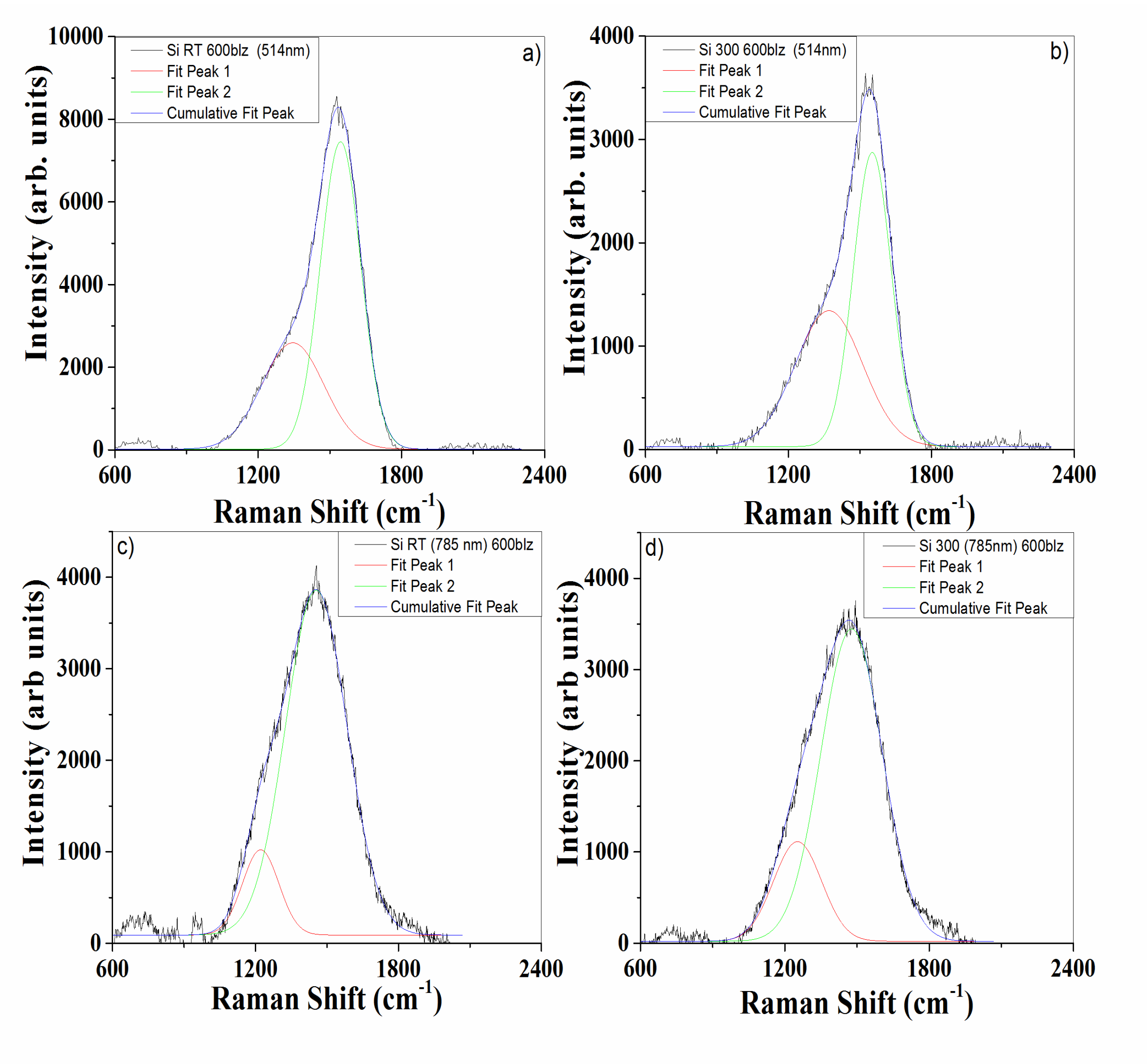

Fig. 1. Raman spectrum of DLC coating collected at excitation wavelength of 514 nm and deposited at (a) room temperature; (b) 300°C and, at excitation wavelength of 785 nm and deposited at (c) room temperature; (d) 300°C

Table 2. Deconvoluted Raman data of the DLC coating deposited at different deposition temperatures and excitation wavelengths

Sample name.	G peak position (cm^{-1})	FWHM (G) (cm^{-1})	D peak position (cm^{-1})	FWHM (D) (cm^{-1})	A_d/A_g
Si RT (514nm)	1545	199	1345.3	306.2	0.53
Si 300 (514nm)	1551.8	186.6	1370.2	333.3	0.83
Si RT (785nm)	1455	304.5	1221.6	179.7	0.15
Si 300 (785nm)	1477.4	300.1	1252.6	235	0.25

Dispersion of both G and D peaks are studied in different excitation wavelengths of 514 and 785 nm, to study the variation of deposition temperature over structural property of the DLC coatings (Figure 2). Dispersion takes place when peak shift occurs at different excitation wavelength, which is generally associated with disorder in the system [18,19]. We calculated the dispersion using the below equation:

$$\Delta G = G(@514nm) - G(@785nm) \quad (1)$$

$$\Delta D = D(@514nm) - D(@785nm) \quad (2)$$

Where, ΔG and ΔD are difference of Raman peak position of D and G peaks respectively.

More dispersion in G peak confirms the formation of DLC coating. However, D peak also appears to shift with the excitation wavelength, which is indication of hydrogenation of the DLC coating. The dispersion seems to reduce for D and G peaks when the deposition temperature is raised to 300°C. It means that both hydrogenation and disorder in the DLC coating is reducing with the increase in the deposition temperature. Similar results are obtained through non-Rutherford backscattering (non-RBS) and elastic recoiling detection analysis (ERDA) where, hydrogen to carbon ratio was calculated for the DLC coating at room temperature is found to be 32:68, which decreases slightly at deposition temperature of 300°C to 30:70.

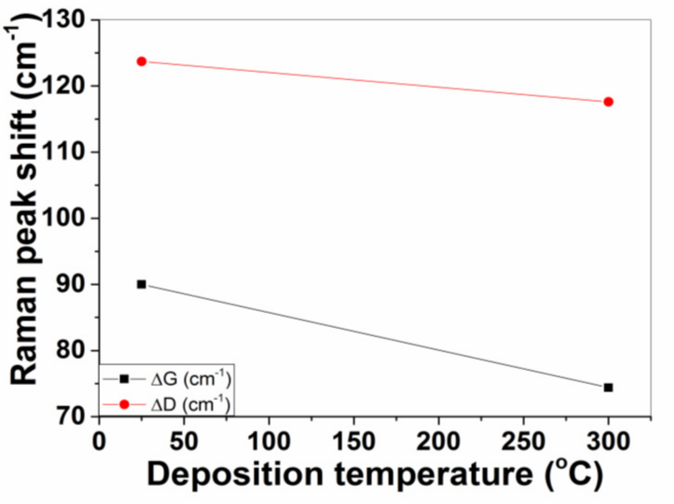

Fig. 2. Dispersion study of D and G peak position using different excitation wavelength laser of 514 and 785 nm.

Table 3. Hardness and Young's Modulus as a function of the deposition temperature in the DLC coating process.

Sample Name	Hardness (GPa)	Young's modulus (GPa)
Si-RT	30.12	232.2
Si-300	31.36	271.2

Nanoindentation analysis shows increase in the hardness and Young's modulus with increase in the deposition temperature. The data is consistent with the Raman results that reveals the increase in deposition temperature leads to decrease in disorder, hydrogenation and, increase in ring structure content and compressive strain, which helps in increasing the hardness and Young modulus of the DLC coating.

4. Conclusions

The DLC coating made by RF power PECVD process is found out to be disordered and partially hydrogenated based on detailed study of Raman analysis. With the increase in the deposition temperature, it is observed that disorder and hydrogenation slightly gets reduced and compressive strain is getting increased. Ad/Ag ratio is also found to be increasing with the deposition temperature, which indicates the increase in ring structure content with respect to linear structure content. Overall structural properties contribute to the increase in hardness of the DLC coating.

5. Acknowledgement

Authors express acknowledgement to Prof. Muralidhar Ghantasala, Western Michigan University, USA, and Prof. S. Mohan, Nano Innovation Chair, CMTI, for their valuable guidance in conducting the DLC experiments and analysis of the results.

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