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Influence of consumed power on structural and nano-mechanical properties of nano-structured diamond-like carbon thin films

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ABSTRACT

Mixed Ar–C_2H_2 plasma was characterized by VI probe for estimating the actual consumed power (CP) in the plasma and its effect on diamond-like carbon (DLC) thin films deposited at different CPs in the range 16–85 W. The structural properties of the films were examined using variety of spectroscopic and microscopic techniques, such as Fourier Transform Infrared spectroscopy, X-ray Photoelectron Spectroscopy, Micro-Raman Spectroscopy and Atomic Force Microscopy. The film deposited at 36 W CP showed the formation of nano-structure, creation of optimum sp^3/sp^2 bonding ratio and excellent nano-mechanical properties with the maximum hardness of ~28.2 GPa. However, the nano-mechanical properties of the films got altered with the variation of CP, which is attributed to the changes seen in the structural properties. These findings show that high quality DLC films with higher hardness can be deposited by monitoring and controlling the process parameters of the plasma.

1. Introduction

Apart from diamond and graphite, hydrogenated amorphous carbon (a-C:H), also called diamond-like carbon (DLC), is an important member of carbon family. It is a metastable form of carbon that holds both diamond-like sp^3 and graphite-like sp^2 bondings. Owing to its unique structure, DLC films show excellent electrical, optical and mechanical properties because of which they have gained significant scientific and industrial attention [1–9]. In DLC films, π–π^* bonded sp^2 clusters are embedded in amorphous sp^3 matrix [1,9–11]. The sp^3 bonding maintains the mechanical properties and sp^2 bonding controls the electrical and optical properties. So variation in sp^3 and sp^2 bondings tunes the properties of DLC thin films. The change in sp^3 and sp^2 bondings can be obtained by varying the deposition parameters such as power, pressure, flow rate, thermal annealing, introduction of foreign elements (N, Si and metals), etc. Since the presence of hydrogen help stabilizing the diamond-like bonding, bonded hydrogen concentration plays an important role in hydrogenated DLC thin films. Various spectroscopic techniques are available for the structural analysis of the DLC films. Among them X-ray photoelectron spectroscopy (XPS) [12,13] and Raman spectroscopy [14] are very important techniques. XPS probes the chemical bonding and sp^3 and sp^2 contents [15], whereas Raman spectroscopy provides information about the microstructure of DLC films. Besides these two techniques, Fourier transform infrared (FTIR) spectroscopy is also an important technique, which provides information about various vibrations of C with C and H. The FTIR is also used to determine bonded hydrogen concentration. Hence, all of these three spectroscopic techniques (XPS, Raman and FTIR) provide complete structural information of DLC films, which may further help understanding the change in their properties.

As the name suggests "diamond-like carbon", there is predominant interest on the mechanical properties of these films. Though DLC films can be deposited using plasma enhanced chemical vapor deposition (PECVD) [16], sputtering [17,18], pulsed laser deposition [19] and filtered cathodic vacuum arc (FCVA) [12] techniques, low temperature processing, simple operation and large area deposition characteristics make PECVD the better technique for the deposition of hydrogenated DLC thin films [20,21]. However, as far as hardness is concerned, PECVD deposited DLC films are considered to be moderately hard with hardness close to 20 GPa [22]. Hence, an enhancement in the hardness of PECVD deposited DLC films remains an issue. The reliability of PECVD process for depositing DLC films with high hardness coupled with other desired properties can be easily possible by monitoring the hydrocarbon

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plasma by VI probe. This provides better understanding of the plasma phase during the deposition, extracts the actual deposition conditions and helps understanding the structure of the deposited films. By meeting the optimum conditions, hard DLC films may be deposited by PECVD process. We have shown the usefulness of VI probe to extract the plasma parameters for the growth of DLC and silicon films [23,24].

It is observed that in RF-PECVD process certain amount of power is consumed in plasma irrespective of all the applied powers. Although matching network is used to avoid this situation, still the actual CP is different from the applied power due to its consumption in different regions of plasma [25–31]. Beneking [25] has proposed a theoretical model for the power dissipation mode in the plasma through the dependence of plasma impedance on rf current at various frequencies. He understood that the applied power is consumed in different plasma regions, such as sheath region for ion acceleration and bulk region for stochastic heating. After Beneking's theoretical investigation of power dissipation mode as a function of current and frequency [25], Godyak et al. [26,27] discussed the power dissipation mode in different regions of the plasma as a function of pressure and rf current. You et al. [28–30] have performed experiments on the power dissipation mode under different conditions of magnetic field, pressure and frequency, and observed similar behavior of plasma or power dissipation mode as that observed by Beneking [25] and Godyak et al. [26,27]. Apart from these, self-bias is also found to be an important parameter that controls the properties of the plasma as well as carbon films. Recently, Ishpal et al. [23] have discussed the power dissipation mode as a function of self-bias for hydrocarbon plasma. This is clear that the applied power can be consumed in bulk of the plasma as well as in the sheath region. Therefore, it becomes very important to monitor the actual CP in the plasma for replicating the a-C:H films with desired properties. In the present work, we report the characterization of Ar–C_2H_2 plasma by VI probe for determining the actual CP and its influence on the structural and nano-mechanical properties of the films.

2. Experimental details

The DLC films were deposited using an asymmetric capacitively coupled RF-PECVD. The power electrode (cathode) of the system was made much smaller than the ground electrode (anode), which includes the wall of the chamber. An MKS VI probe (model VI probe 350) was used to examine the actual CP as a function of applied power. The probe was attached to the power electrode after the matching network. All the films were deposited at different CPs ranging from 16 W to 84 W at a frequency of 13.56 MHz. Before the deposition of films, the chamber was evacuated down by a turbo molecular pump backed with a rotory pump to a pressure of $\sim 4 \times 10^{-5}$ Torr. Then, a mixture of argon and acetylene gases in the ratio 1:2 was injected to achieve a working partial pressure of 0.1 Torr. The schematic of deposition system used in present work can be found elsewhere [23].

The thicknesses of the DLC films were determined using Talystep (Rank Taylor and Hobson) thickness profile-meter, and the relevant data is given in Table 1. The surface features, such as topography, particle size and root mean roughness, were examined using atomic force microscope (AFM) (Nanoscope Veeco-V). The X-ray photoelectron spectroscopy (XPS) measurements were carried out using Perkin-Elmer (model no. 1257) with monochromatic X-ray radiation of Mg Kα (1253.6 eV). The XPS general survey scan was acquired using a 100 eV pass energy at a step of 1.0 eV, whereas the C 1s core level spectra were acquired at 0.05 eV step with a pass energy of 60 eV. A grounded metal clamp was used for the charge compensation generated on the surface of the sample during the measurements. Renishaw InVia micro Raman spectrophotometer with visible light (514.5 nm) as an excitation source was used for the structural analysis of the films. The nano-mechanical properties of the films were determined using high resolution IBIS nanoindentation (M/S Fisher-Cripps Laboratories Pvt. Ltd., Australia) having diamond Berkovich indenter at a maximum indentation load of 5 mN.

Table 1
XPS peaks positions of DLC films as a function of consumed power.

Consumed power (W)	Binding energy (eV)/FWHM (eV)/%area		
	sp^2C	sp^3C	C=O
16	284.3/1.17/38.30	285.3/1.61/55.22	287.3/1.53/06.47
36	284.4/1.15/29.90	285.4/1.50/59.85	287.0/1.87/10.25
55	284.1/1.16/28.13	285.1/1.53/61.02	286.6/1.82/10.85
84	284.5/1.30/31.39	285.5/1.76/57.56	287.5/2.12/11.05

3. Results and discussion

3.1. Thickness and deposition rate

The thickness of DLC films deposited at CPs of 16 W, 36 W, 55 W and 84 W were found to be 326 nm, 333 nm, 328 nm and 337 nm, respectively. The effort was made to maintain the thickness of each sample almost identical by changing the deposition time. This can be seen from Table 1 that there is only 11 nm difference in the thickness of all the samples. In order to examine the role of actual CP to the thickness, the deposition rate for each sample was determined, which was found to increase from 46.6 nm/min to 55.5 nm/min with the increasing CP from 16 W to 36 W. This is attributed to the consumption of most of the power in bulk region and sufficient decomposition of hydrocarbon precursor that leads to generation of more carbon ions. However, after 36 W power the deposition rate started to decrease and found to be 43.7 nm/min and 37.4 nm/min at CPs of 55 W and 84 W, respectively. Overall we found gradual change in deposition rate with the actual CP. Explaining deposition rate in plasma processed thin films has always been a subject of debate. Voulgaris et al. [31], while studying the effect of actual consumed power on the discharge, observed similar type of effect on the deposition rate of silicon oxide thin films in the presence of TEOS/O_2 for 13.56 MHz and 27.12 MHz frequencies. They found deposition rate initially increased due to the enhanced electron density, which caused higher electron impact on gas molecules to produce more radicals for the deposition. They also observed saturation in the deposition around 20 W power. The deposition rate was decreased beyond this power due to different deposition paths, which produced radicals that do not contribute to the thickness. In the present study, we have also observed gradual change and saturation of deposition rate, but at somewhat higher power of ∼36–55 W, beyond which the deposition got decreased. Such a behavior of the deposition rate in the present study could be due to similar mechanism as discussed in literature [31,32]. Another reason for this behavior of deposition rate may be the introduction of argon along with hydrocarbon (C_2H_2), which we employed during the deposition of DLC by RF-PECVD. Though C_2H_2 contributes to the thickness, Ar ions simultaneously bombard the growing species, etch the softer species and densify the structure. Thus, the deposition is a consequence of the competition between growth and etching. At higher power, the films become softer, the etching effect dominants over growth rate and leads the lower deposition rate.