Effect of Substrate Temperature on the Properties of Diamond-like Carbon Deposited by PECVD in Methane Atmosphere

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Abstract

Diamond-like carbon thin films were prepared at different substrate temperatures by using DC-PECVD at 1×10^{-1} Torr in methane atmosphere. The DC-PECVD system was reconstructed for getting higher substrate temperature up to 560°C. Raman spectroscopy has been used to study the effect of chemical bonding of the films and the deposition rate is studied too. The deposition rate is decreased with the increasing substrate temperature. The Raman main band is due to the lattice vibration of sp^2 bonded carbon atoms (graphite band or G band). If the size of the graphite domains decrease, a low frequencies modulation corresponding to the disorder zone of graphite that corresponding to D peak. The sp^3 bonded carbon increased as the substrate temperature increase from 27°C to 200°C. The result also showed that I_D/I_G ratio decreased with increasing amount of sp^3 fraction as the temperature is increased up to 200°C.

Keywords: Diamond-like carbon, DC-PECVD, temperature.

Introduction

In recent years, there is a significant interest in diamond-like carbon (DLC) because of their unique properties [1,2]. DLC films are beginning to find their way into many industrial wear applications. Because of its high hardness, chemical inertness, optical transparency, and its wide band gap semiconductor, recently, it has been use as protective coating in area such as for optical windows, antireflectcoating for Si solar cell and protective coatings on copper mirror for automobile industry purpose [3-5]. In electronics field, DLC films currently use as a material for microelectrochemical system (MEMs). Carbon has two main categories, namely diamond and graphite. Carbon forms a great variety of crystalline and disorder structures because it is able to exist in three hybridization, sp^3 (dominating bond in diamond), sp^2 (dominating bond in graphite) and sp^1 [6]. The properties of DLC has been characterised by the volume friction of the sp^3 bonds which can be controlled by film deposition mechanisme. Therefore there were many research on properties of DLC grown by various deposition condition [7]. The effect of substrate temperature may also play an important role [8]. Surface reactions are temperature depends and different species may have different resident time. According to J. Robertson subplantation model [9], a low energy ion will not have enough energy to penetrate the surface, so it will just stick to the surface and remain in the lowest energy state, which for carbon is sp^2. If the ion energy is higher than the penetration threshold, it has a probability to penetrate the surface and enter the surface interstitial site. This will increase the local density. The local bonding will than reform around that atom according to this new density.

In this paper we investigate the influence of the substrate temperature on the deposition rate and Raman scattering of DLC films deposited using PECVD technique in pure (99.5%) methane atmosphere under different substrate temperature of 25°C, 30°C, 100°C and 200°C while the other parameters remain constant.

Materials and Methods

Diamond-like carbon films were deposited using plasma enhanced chemical vapour deposition (PECVD) in methane, CH_4 (99.5%) atmosphere. During all deposition, the distance from anode to substrate holder (cathode) was kept at 4cm while the gas pressure and flow is 1×10^{-1} Torr and 9sccm accordingly. Silicon substrates were placed on 6.8-cm diameter stainless-steel cathode fed by a. d.c (1.2 kV) power supply. All substrate were cleaned in acid chromic and deionised water.

The heater of this homemade PECVD system was reconstructed by for getting high substrate temperature. A 1.2m coiled 2.0525-mm diameter Kantal 1 wire was used as a heating element. Heating element was placed in the grooving ceramic inside the heater. The substrate temperature was measured by thermocouple.

Raman spectra of the deposited films were obtained using 200NIR FT-Raman (Perkin Elmer) spectroscopy. Samples were scan for 30 times with $8cm^{-1}$ resolution using 10mW Nd:YAG laser Spectra were recorded at 1250 to $2500cm^{-1}$. Peak positions, amplitudes and surface areas for each peak were measured. Integral intensity I_D/I_G ratios were calculated from the ratio of the area of *D* and *G* peak which is significant the sp^3/sp^2 ratio in the films. The thicknesses of the films were measured using ellipsometer with 623nm He-Ne laser as light source.

Results and Discussion

The new heater of the PECVD system can heat the substrate up to 560°C. The parameters of making high temperature substrate heater can be explained by resistance equation R=(ρl)/A, where R = resistance, ρ = resistivity, l = length, A = cross section area, and material-temperature equation $R=R_{ref}[1+\alpha(T-T_{ref})]$, where R= conductor resistance at temperature T, R_{ref} = conductor resistance at reference temperature T_{ref}, usually 20°C, but sometimes 0°C, α = temperature coefficient of resistance for the conductor material,T= conductor temperature in °C, T_{ref} = reference temperature that α is specified at for the conductor material.

The shape of the heater casing is fix, result on the fixing of the length of heating element coil. According to material-temperature equation, for metals, α is a positive number, meaning that resistance increases with the increasing temperature. Based on resistance equation, for getting high resistance at constant wire length,l and resistivity, ρ the cross section area, A should be small seems that resistance, R is inverse with A for constant ρ and l. Using small diameter (2.0525mm) Kantal A1 wire as a heating element, helps to generate high temperature.

Figure 1 shows the deposition rate, R_d is an approximation made from the films thickness (nm)/time. It can be seen that the deposition rate is decrease with the increasing of substrate temperature. This result is also obtained by previous reseracher [10,11]. The deposition rate is decreased with increasing substrate temperature. This can be explained by Frenkel equation:

$$\tau = \tau_o \exp(-\frac{E_{act}}{\kappa T})$$

Where,

- τ = residence time of particle on the substrate surface
- τ_0 = smallest possible adsorption time (τ_0~10^{-12} –10^{-13}s)
- E_{acts} = activation energy,
- T = substrate temperature and
- κ = Boltzmann constant

The temperature depended of growth rate is described with model of adsorbed layer promote by Robertson [9]. A low energy ion will not have enough energy to penetrate the surface, so it will just stick to the surface and remain in its lowest energy state, which for carbon is sp^2. In this surface state, when they closed the opened bond at the surface at which they chemisorb, new chemical bonds can be formed between the adsorbate and the growing layer.

As the temperature increase the residence time of the physisorbed species decrease exponentially. The resulting decrease of the coverage leads to the reduced rate of cross-linking by ions and so the deposition rate decrease with increasing temperature

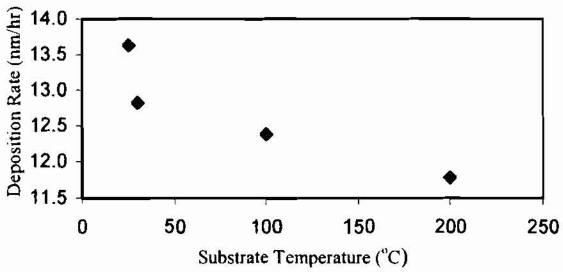

Figure 1: Deposition rate of DLC films as a function of substrate temperature

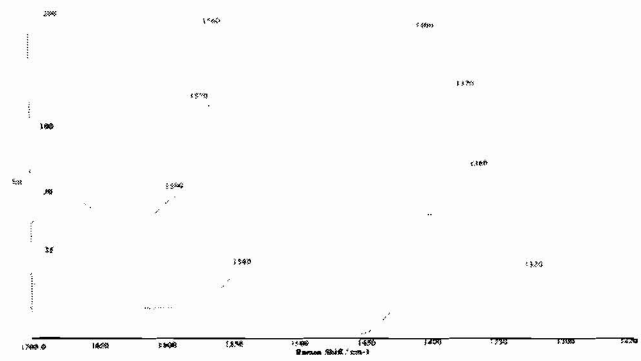

Figure 2: Raman Spectra of the DLC films deposited at different substrate temperatures

The Raman spectra of the DLC films deposited under different temperatures are shown in Figure 2. The *G* peak shift to higher wavenumber, 1590 cm^{-1} at temperature 30°C and then moves downwards with the increasing of substrate temperature. The *D* peaks position shift to a higher wavenumber 1320-1400 cm^{-1}. I_D/I_G slightly decrease with increasing of substrate temperature as Figure 3.

Table 1: Position of G and D peaks, and I_D/I_G ratio of DLC films prepared at 25, 30, 100 and 200°C

Samples	G peak (cm^{-1})	D peak (cm^{-1})	I_D/I_G Ratio
S1	1540	1320	1.5309
S2	1590	1360	1.3940
S3	1570	1370	0.9750
S4	1560	1400	0.8368

The Raman main band is due to the lattice vibration of sp^2 bonded carbon atoms (graphite band or *G* band). If the size of the graphite domains decrease, a low frequencies modulation corresponding to the disorder zone of graphite that corresponding to *D* peak. Increasing in the amount of sp^3-bonded atomic sites in amorphous carbon result in a shift of the *G*-band position to lower frequencies. Thus, the up shift in the *G* position from 1540 to 1590cm^{-1} indicates the increasing of sp^2-bonded carbon. On the other hand, the downwards shift of G-position from 1590 to 1560cm^{-1} indicates that sp^3 bonded fraction is increases as the substrate temperature increase from 30 to 200°C. High values of I_D/I_G ratio at substrate temperature of 25°C indicates that there is a low percentage of sp^3-bonded carbon in the deposition films. With increase of substrate temperature up to 200°C the I_D/I_G ratio decrease with increasing amount of sp^3 fraction.

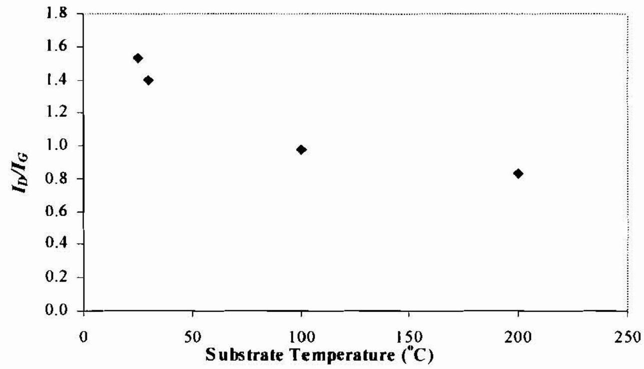

Figure 3: Variation of I_D/I_G ratio with substrate temperature for DLC films

Conclusion

In this work, we studied the parameter of making a heater and bonding of DLC. The deposition rate is strongly dependent on the substrate temperature are qualitative agreement with the adsorbed layer model. The resistance and metal-temperature equation is important to determine the heating temperature. The increasing of temperature can reduce the sp^3 bonding of the DLC films. A much more detail study of higher (>200°C) work will be discussed in other publications.

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