

ORIGINAL RESEARCH PAPER

The Growth of Diamond-like Carbon Nano-Structures: Investigation of the Affecting Factors

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ABSTRACT

Using DC-Plasma Enhanced Chemical Vapour Deposition (PECVD) system, the impact of pure Co on the growth of diamond-like carbon (DLC) nano-structures were investigated. In this study, Acetylene (C_2H_2) was diluted in H_2 and used as the reaction gas and Cobalt (Co) nano-particles were used as the catalyst. The effect of preparing Co catalyst at temperatures of 240°C and 350°C and growth conditions was studied. The results showed that the Co catalyst sputtering at 350°C temperature has a significant impact on purity, morphology, and synthesized diamond-like carbon nano-structures. This research was conducted to investigate the effect of catalyst preparation and growth conditions. Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy were used to characterize the diamond-like carbon nano-structures produced under different conditions.

Keywords: DLC nano-structures ; Temperature; DC-PECVD; Catalyst

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INTRODUCTION

Following the discovery of diamond-like carbon nano-structures in 1970 by Aisenberg and using the ion beam deposition (IBD) method, many major and applicable studies have been done on their synthesis for nearly three decades [1-3].

Various growth methods have been studied for generating diamond-like carbon (DLC) nano-structures [4-8] (see fig 1). These methods are divided into two types: Physical Vapour

Deposition (PVD) method and Chemical Vapour Deposition (CVD) method. The PVD method uses a solid phase as the carbon source and it is further divided into the arc, sputter, and laser Vapour deposition methods. The CVD method uses a gas which is a hydrocarbon such as acetylene and it includes radio-frequency (RF), direct current (DC) discharge, Plasma Enhanced CVD, Hot filament CVD and thermal CVD methods. It is hypothesized that hydrogen is necessary for the formation of sp^3 bond in DLC nanostructures while applying CVD method. The PVD method based on energetic

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ablation of carbon like pulsed laser deposition (PLD) demonstrated that hydrogen is not necessary for the formation of sp^3 bond [9-12]. The following table shows the various growth methods of production of diamond-like Carbon, and their salient features in terms of benefits and negative points (Table 1).

Today main techniques for the deposition of diamond like carbon nano-structures are based on plasma enhanced chemical Vapour deposition (PECVD). The most frequently used PECVD methods are radio-frequency (RF) excitation, microwave plasmas and electron cyclotron resonance (ECR) techniques. DC discharge techniques were the first methods to be applied for the deposition of DLC nanostructures or thin films. Nowadays, they are rarely used because in such systems the DC voltage is used to create the plasma and to determine the energy of the bombarding ions as well. Besides,

it is difficult to optimize such systems. However, the DC PECVD systems have the advantage that DLC nano-structures deposited by DC technique exhibit smaller stress values than the nano-structures deposited by RF PECVD technique [13-15]. The disadvantages of these depositions use high voltage, high vacuum and therefore high cost. PECVD deposition method is offered as an excellent route to grow DLC nano-structures. The PECVD method, compared with different CVD methods and PVD method, has demonstrated some obvious advantages in terms of simple setup, low vacuum and low cost and flexibility, simplicity, and the possibility of producing a large area of diamond-like carbon nano-structures. The following table shows the various methods of preparation of diamond-like Carbon, and their salient features in terms of advantages and disadvantages (see Table 1).

Table 1. Various CVD methods and their salient features

process	advantages	disadvantages
Hot filament CVD (HFC-VD) method	Inexpensive and easy to operate	High substrate temperatures, low rates (lm-m/h), difficult to scale up, film quality is not suitable for most of the applications
RF-CVD method	Inexpensive, possible to obtain higher deposition Rates.	Difficult to control, high deposition temperature, unlikely to be acceptable for most electronic and optical applications
Microwave Assisted CVD (MWCVD)	Cleaner process, easier to control and optimize	High deposition temp, low deposition rates ,rough surface topography may limit optical & electronic applications
PECVD method	Clean process, low film Damage, Possible to obtain films at high rates, High deposition rate and filling density, Low vacuum, Faster way to deposit the film large scale production high purity and density; minimize stresses and contaminations	Difficult, substrate Temperature requirements not known. Inadequate for production applications
Ion beam sputtering	Extremely good operational control, low Substrate temp.	Very low deposition rate, usable only for small area substrate
Dual sputtering beam	Same as above	Same as above
Laser ion beam technique	High deposition rates are possible	Difficult to scale up to large area, control and optimization of film properties and quality yet to be demonstrated.

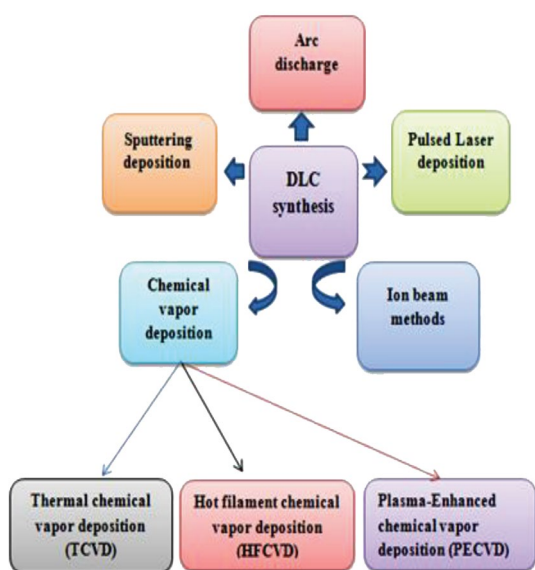


Fig. 1. Summary of different methods of synthesizing of diamond-like carbon nano-structure.

Here, Co catalyst was used for coating glass at temperatures of 240 & 350°C and the coated glass was used as the substrate for growing diamond-like carbon nano-structures with different structures. The study showed the morphology and structures of diamond-like carbons by scanning electron microscopy (SEM) and Raman spectroscopy. In this paper, we characterized diamond-like carbon nano-structures by SEM, XRD, and Raman spectroscopy.

EXPERIMENTAL DETAILS

Before the growth of diamond-like carbon nano-structure, Co catalyst was deposited onto the glass substrate. An ultrasonic bath containing ethanol and acetone was used to clean the substrates and remove any contaminants present on the surface. The sputtering Co was carried out by the DC-PECVD system at temperatures of 240°C and 350°C. Here, these were loaded into the reaction chamber and each substrate was placed on the lower electrode (cathode). Then, a pressure in the reactor of 4.2×10^{-2} Torr was pumped and acetylene plasma was used for etching the Co substrate surface for 35 minutes in the reactor prior to diamond-like carbon nano-structures deposition. In the process, the constant flow rate of 25 Sccm was considered for

acetylene gas and the pressure was kept at 5.5 Torr. After completing the etching process and before supplying the reaction gases to the reactor chamber the pressure was 3.9×10^{-2} Torr. Using the PECVD system, the growth process was carried out with acetylene and hydrogen gases as source carbon and diluting gas respectively, which were used as reaction gases for the growth of diamond-like nano-structures. The flow rates of acetylene and hydrogen gases were 10 Sccm and 100 Sccm, respectively. In this study, two growth conditions were investigated. Other growth parameters such as the gas composition and growth time were kept constant 10/100 (volumetric flow rate of H_2/C_2H_2) and 30 minutes, respectively. The typical experimental conditions are listed in Table 2.

Table 2. Typical experimental conditions for growth of diamond-like carbon nano-structures in PECVD system

Variation	Typical condition
substrate	glass
Sputtering temperatures catalyst	240° & 350°C Co
Reaction gas Source carbon gasses Reaction time Electrode distance (cm)	Ar Acetylene + H_2 30 min 2 cm

RESULT AND DISCUSSION

In this study, for the successful synthesis of diamond-like carbon nano-structures, proper sputtering techniques of the substrates played an important role. Rendering the substrate surfaces covered with grains of catalyst of a certain size were possible. In the sputtering technique, the particles were uniformly dispersed on the surface. The obtained measurements using SEM, XRD and Raman spectroscopy show the results from the analysis of (DLC) nano-structures prepared at different sputtering temperatures of 240°C & 350°C. The CVD of diamond-like carbon nano-structure on desired substrates was done under different conditions and different mixtures of gasses at various ratios

as indicated in the table below. In our method we used plasma based growth of DLCs. One of the known benefits of this method is to use plasma, which form clean surface and enhances the oriented growth of the nano-structure due to the electric and magnetic fields. On the other hand, using plasma based methods requires lower growth time because of the high energy reactive ions in plasma. Moreover, the only disadvantage of the plasma method is vacuum, which is necessary while applying the method. Table 3 shows the summary of CVD conditions reported in the introduction to grow diamond-like nano-structures by other conditions in different studies. The table provides convergent results in order to make the further investigation possible at a time.

Catalyst preparation

A catalyst was used to optimize and test the parameter on glass substrates. The nano-particles were sputtered according to the desired deposition condition. This was done to generate the most suitable and auxiliary experimental results to form uniform diamond-like carbon structures. As seen in figures 2a and 2b, respectively, in order to show the distribution of Co nano-particles on the glass substrates at temperatures of 240°C and 350°C, SEM images

obtained from the surface of the prepared substrates were used. At 240°C the particles were not uniformly dispersed on the surface of the glass substrate. Although the particles were discretely deposited on the surface, some aggregations were observed (see figure 2a). But at 350°C temperature, Co nano-particles were distributed uniformly throughout the substrate (see figure 2b). Furthermore, more nano-particles were aggregated but still there were particles discretely deposited on the surface. When the heating temperature was increased to 350°C, an increase in the density of nano-sized Co particles was observed. Figure 2b shows homogeneous distribution of the nano-particles with the size of the particles being around 150 nm.

Due to the elevated temperature, the Co particles were seen to agglomerate into relatively smaller particles and the spacing between them was found to be very small. The migration of Co particles on the glass surface can be considered as a reason for agglomeration. Based on our present work, we discovered that the nano-sized Co particle suitable for diamond-like carbon nano-structures growth could be fabricated on glass substrate. At temperature of 350°C, the Co particle morphology determines the quality of the diamond-like carbon growth as to be discussed later.

Table 3. Summary of CVD conditions reported in the literature to growth diamond- likes carbon structures

Temperature substrate	Method of growth	gasses	Time of growth	Substrate	Reference
770°C	MWCVD	Methane/ Nitrogen	420 min	Glass- Si	17
200°C	DC-PECVD	H ₂ - Acetylene	40-80-120-160 min	steel	33
350°C	RF-PECVD	H ₂ - Methane	30 min	Si	19
600-700°C	HFCVD	H ₂ - Methane	10min	Si	35
600° C	TCVD	Organic compound	-	Si	28

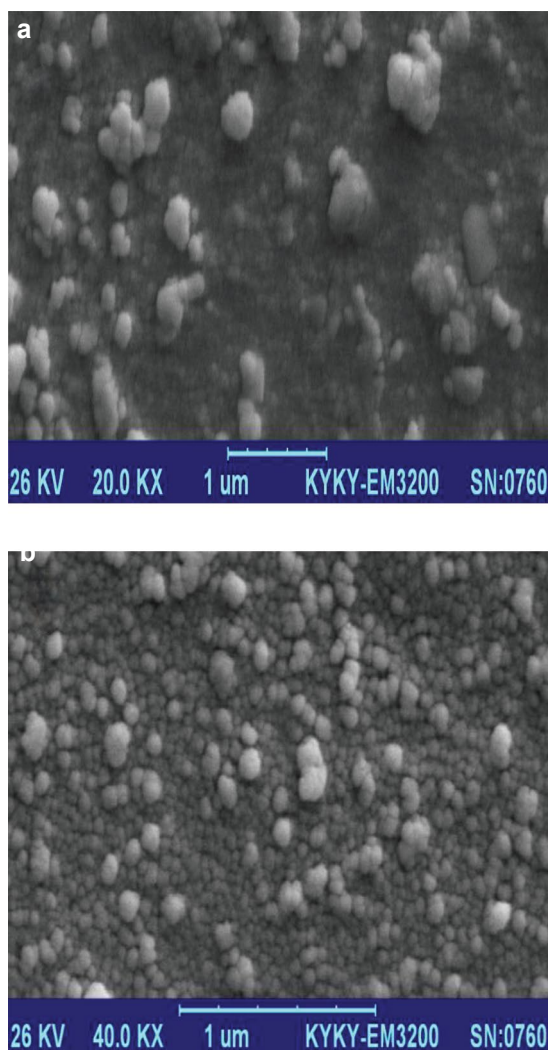


Fig. 2. The morphology of Co particles sputtered by PECVD system in two different temperatures, (a) 240°C and (b) 350°C on glass substrates

Here, AFM images were taken from the surface of prepared substrates show distribution of Co nano-particles on the glass substrates in the temperature of 240°C and 350°C in figures 3a and 3b, respectively. In the 240°C, nano-particles did not distribute uniformly throughout a substrate (Fig. 3a) but in the 350°C, particles were uniformly dispersed on the surface. Although particles discretely were deposited on the surface, some aggregations were observed (see Fig. 3b). Furthermore, nano-particles were aggregated more, but particles discretely deposited on the surface.

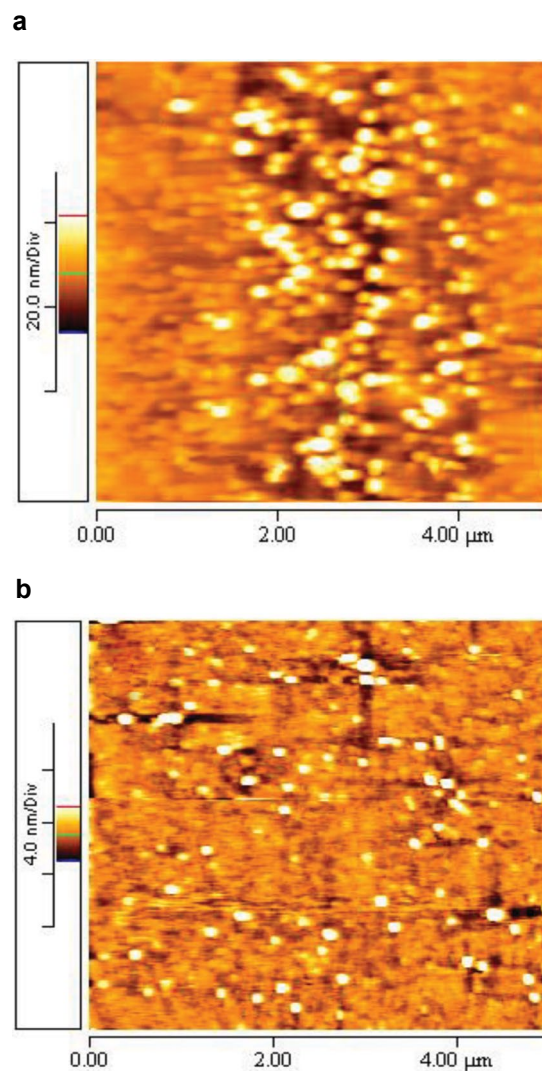


Fig. 3. AFM images of deposited Co nanoparticles on glass: (a) 240°C (b) 350°C.

Growth conditions

In research works, one of the most widely used methods to characterize diamond and carbon nano-structures is Raman spectroscopy [15-16]. Raman analysis was used to characterize the quality of diamond-like carbons synthesis, type bonding, and structures. In the previous studies, the first-level Raman spectrum of diamond has a single peak at 1332 cm^{-1} with a single peak at about 1580 cm^{-1} that confirmed the desired nano-structure in experiments [17-18]. The Raman spectra of diamond-like carbon structures included two peaks around $1345\text{--}1415\text{ cm}^{-1}$ and $1570\text{--}1590\text{ cm}^{-1}$ [19-21].

In this study, the impact of sputtering temperature of Co catalyst on the quality of the deposited diamond-

like carbon nano-structures were investigated. This parameter is essential in determining the structure, morphology and quality of deposited products. We have measured Raman analysis of nano-structures prepared on glass substrates by DC-PECVD system. The Raman spectra of the deposited diamond-like carbon nano-structures obtained from Co catalyst on glass substrates are shown in Fig. 4.

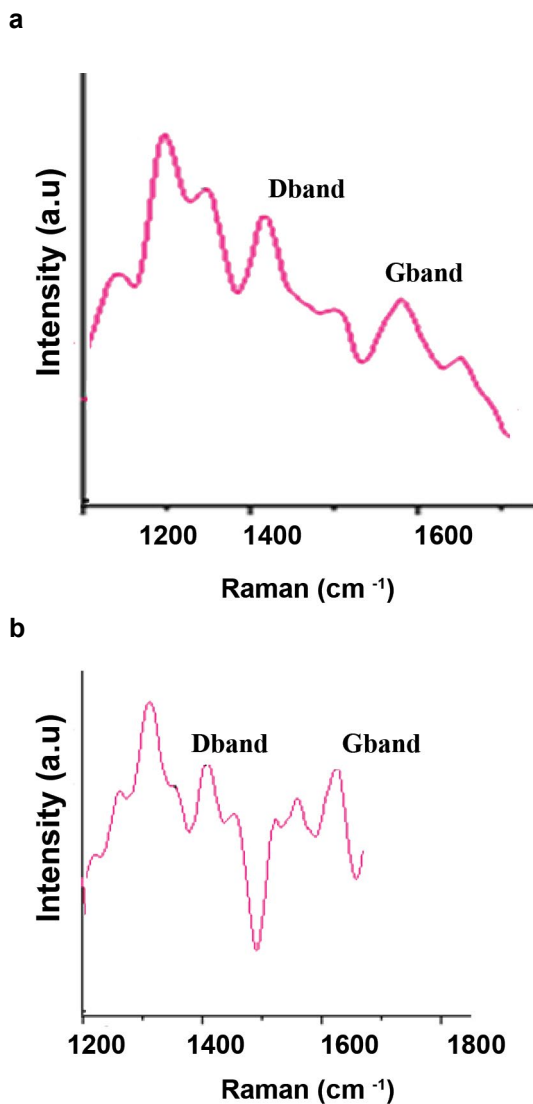


Fig. 4. The Raman spectra of diamond-like carbon nano-structures deposited by PECVD system in two temperatures of Co sputtering (a) 240°C and (b) 350°C.

In both figures, the 1330 cm⁻¹ feature can be readily assigned as the first-order Raman mode of sp³-type C-C stretching. The feature at 1403 cm⁻¹ and 1595 cm⁻¹ correspond to sp³-type

amorphous carbon and sp²-type amorphous carbon, respectively. It should be noted that the spectra obtained from CVD carbon films generally focused on the appearance of the first-order Raman mode of diamond (sp³-type bonding) at 1330 cm⁻¹. According to other papers, features of carbon, diamond-like carbon and the diamond nano-structures appear in the Raman spectra in the spectral range of 1320 cm⁻¹ to 1600 cm⁻¹ in research works [22-24]. They are associated with carbon structures such as graphite (sp²-type bonding) and amorphous carbon. In fact, the PECVD system was used to synthesize this nano-structure. A schematic diagram of the reaction chamber of the PECVD system is shown in Fig. 5.

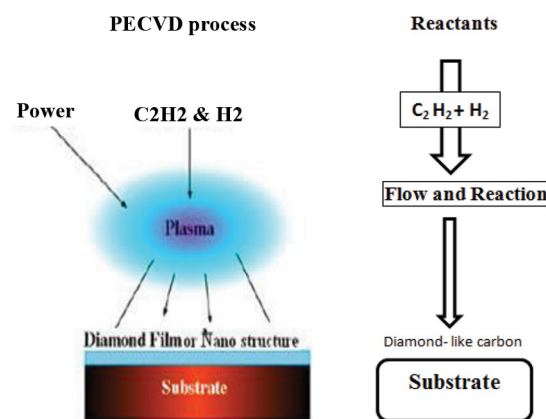


Fig. 5. The Plasma CVD process for diamond-like carbon nanostructure grown on glass substrate.

Effect of deposition time

Like Raman spectroscopy, X-ray diffraction (XRD) is considered as a powerful and important technique to provide a fingerprint presence of a diamond phase and other carbon nano-structures [25-27]. In addition to Raman spectroscopy, XRD analysis can be utilized to confirm that diamond synthesis has been achieved by the Co catalyst. We studied the change of diamond-like carbon nano-structures morphology in this work. The XRD profiles of diamond-like carbon nano-structures made by C₂H₂-H₂ plasma in various sputtering temperatures is shown in Fig. 6. An increase in the intensity of the peak at 2θ=43/15° was considered as the most obvious change. This peak corresponds to the diffraction of the diamond (111) plane [28-29]. The presence of the diamond (111) peak in

XRD patterns clearly shows that the diamond-like carbon nano-structures are mainly composed of sp^3 carbon frameworks. This was consistent with the interpretation of the Raman spectra made in the study. In both figures, we observed three peaks of diamond-like carbon structures that correspond to $2\theta=43.15^\circ$ which could be determined by the reflection (111) plane of diamond. It can be said that with Co catalyst in the desired conditions, diamond structures and carbon-base structures may be produced. This study demonstrated the feasibility of preparing diamond-like carbon structures by this catalyst. Then we found that the sputtering of catalyst had a significant, effective and extraordinary impact on the produced diamond-like carbon nano-structures.

Aghaie et al. [28] showed that the diamond like carbon film was grown by hot filament chemical Vapour deposition (HFCVD) technique. They investigated the quality of the DLC films grow on the substrates that were coated with various metal nanocatalysts (Au and Ni). Khalaj et al. [33] investigated the quality of the DLC films grown on stainless steel substrates using different thickness of the nickel nanoparticle layers on the surface. Nickel nanoparticles were sputtered on the stainless steel substrates at 200°C by a DC-sputtering system. Atefi et al [36] investigated the effects of different substrate temperature and nitrogen etching gas on the synthesis of Nano Crystalline Diamonds (NCDs). They prepared all samples by HFCVD system. Substrate temperature was controlled by thermocouple in contact with substrate holder, between 550 and 650°C . The results showed nano-crystalline diamond films and diamond nanocrystals grown on substrate under various temperatures with different crystalline structures.

Effect of Hydrogen

It was concluded that H_2 (flow rate 100 Sccm) had a significant and effective impact when the C_2H_2 plasma was used to produce diamond-like carbon nano-structures. It should be noted that H_2 not only helps produce plasma effectively, but also has a direct impact on the structural and chemical properties of the diamond-like carbon nano-structures. This research work tries to study the role of hydrogen by chaining the diluting gas from hydrogen to Ar. Ar was used instead of hydrogen under different identical experimental conditions to conduct this experiment (C_2H_2 flow rate 10 Sccm, 3.9 Torr pressure and Ar flow rate 100 Sccm). Raman spectra of C_2H_2 -Ar system is shown in Fig. 7. No diamond peak at 1332°C was obtained for C_2H_2 -Ar system.

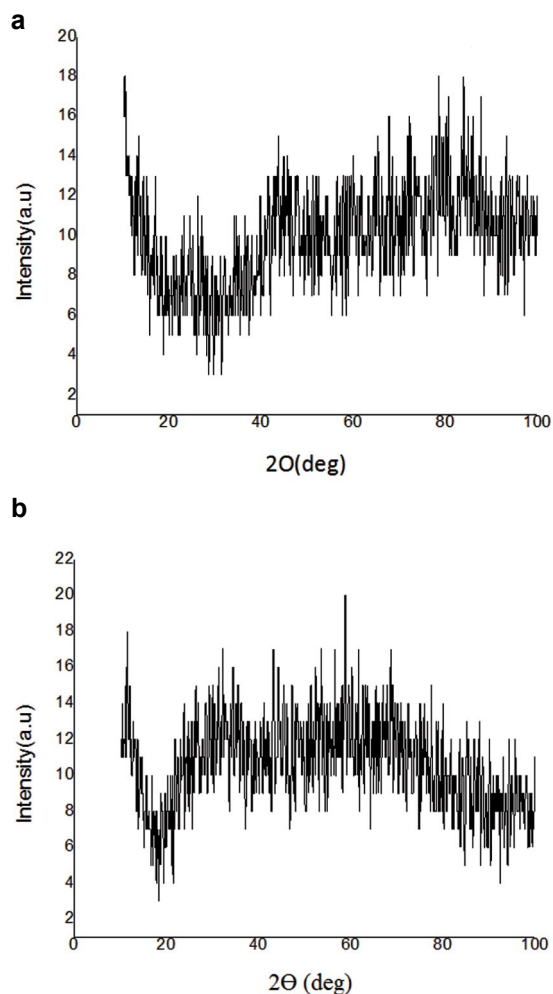


Fig. 6. XRD spectra of diamond-like carbon nano- structures deposited on Si substrate at temperatures of (a) 240°C and (b) 350°C by Co catalyst.

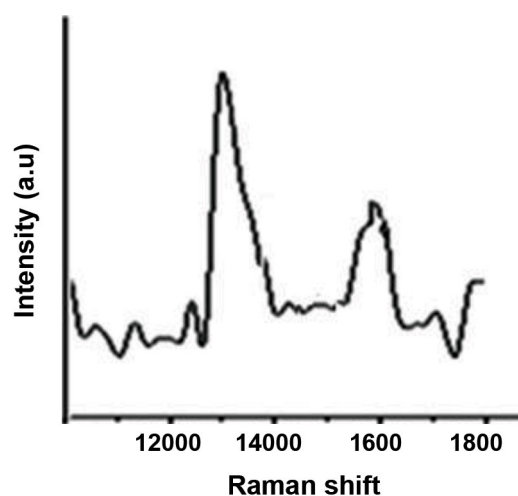


Fig. 7. The Raman spectra of C_2H_2 -Ar system by PECVD method.

The emission of hydrogen atomic radicals, excited hydrogen of molecules and hydrogen atoms was adsorbed on the substrate of glass and thermally decomposed to form diamond-like carbon nano-structures. Other nano-carbon structures such as diamond and graphite were studied in order to investigate the important role of H_2 . Unfortunately, there is no clear mechanism for growth of diamond-like nano-structures. The effective role of H_2 gas can be considered as a promoter of the acetylene decomposition to synthesize the diamond-like carbon nano-structures. The properties of diamond-like nano-structures are strongly connected to their hydrogen concentration, which have a significant impact on the synthesis of this nano-carbon structure [30-31]. Thus, the study of hydrogen content is of great relevance to achieve a good control over diamond-like nano-structures such as optical, electric, mechanical and surface properties [32-33].

Morphology of diamond-like carbon

It was reported that diamond-like carbon nano-

structures deposited by Plasma-enhanced CVD system will have very good surface; therefore, we concluded that an examination of the detailed morphological features of diamond-like carbon structures is only very easy by SEM [34-35].

Fig. 8 shows the SEM Micrographs of the film I (Fig. 8a) and film II (Fig. 8b) taken in contact mode. This figure shows the protrusions ranging from nano to micrometer in size of diamond-like carbon nano-structures deposited by Co catalyst on glass substrates. In this study, sputtering temperatures of Co catalyst have a significant impact on the composition of nano-structures and diffusion mechanism of diamond-like carbon nano-structure. Figures 8a and 8b show SEM micrographs of diamond-like carbon nano-structures synthesized at 240 °C and 350 °C, respectively. It should be noted that growth parameters were the same for both the samples, diamond-like carbon nano-structures were grown on both substrates, but interestingly, types of diamond-like carbon structures were not same because of different nucleation conditions.

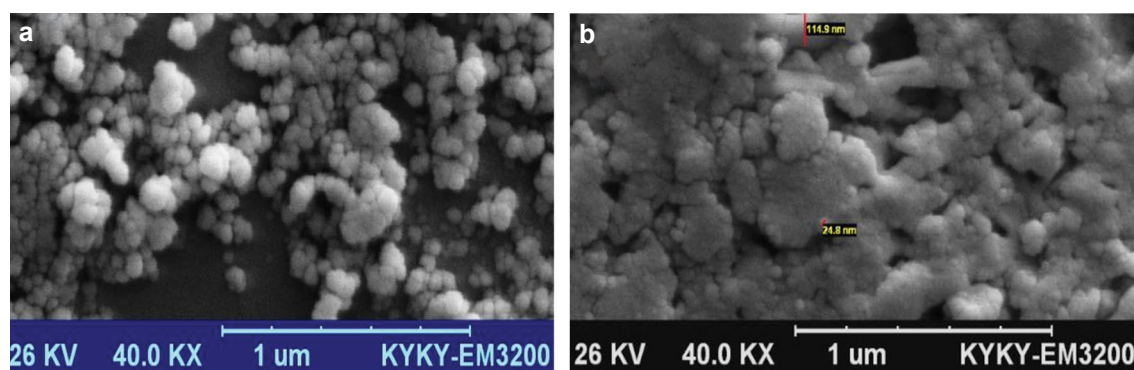


Fig. 8. SEM Morphology of diamond-like carbon synthesized by Co Catalyst in (a) 240°C and (b) 350°C temperature.

CONCLUSION

The PECVD method is a powerful technique to deposit high quality diamond-like carbon nano-structures. By using Raman and other analysis, the bonding structure and morphological features and purity of the diamond-like carbon structures, which depend on the sputtering Co catalyst and other factors, were investigated systematically. It was concluded that the highest deposition rate of the diamond-like carbon structures achieved under the optimum deposition conditions, was approximately at a temperature of 350°C. Compact

and uniform structures were observed by SEM. In this work, the impact of temperature on sputtering Co nano-particles was evaluated. It was understood that a temperature of 350°C is most suitable for sputtering Co catalyst and synthesis of diamond-like carbon nano-structures. The diluting gas H_2 was found to have a significant impact on depositing diamond-like carbon nano-structures.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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