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INFLUENCE OF NI NANOPARTICLES ON GROWTH OF DLC FILM BY PECVD TECHNIQUE

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ABSTRACT. Plasma enhanced chemical vapor deposition (PECVD) technique is mostly used to fabricate diamond-like carbon (DLC) films on different type of substrate. Research on DLC films has been devoted to find both optimized conditions and characteristics of the deposited films on coated areas. In this work, the DLC films deposition on silicon coated Nickel layer were studied. Aluminum was used as a buffer layer, deposited directly on silicon at the room temperature. Atomic Force Microscopy was used to characterize the surface roughness and distribution function of the nickel nanoparticles. The DLC films quality was studied using Raman spectroscopy and Fourier transform infra-red spectroscopy (FTIR). The results show a lower intensity ratio of I_D/I_G for DLC films by increasing the Ni deposition time on the Si/Al/Ni substrates, providing a good quality of the DLC growth by increasing the nickel content and reducing the average roughness of the surface to less than 4 nm.

Key words: *DLC, AFM, Nickel nanoparticles*

INTRODUCTION

Diamond-Like Carbon (DLC) is a material of interest to scientists owing to its attractive properties and performances including: high hardness, smooth surface morphology, low friction coefficient, chemical inertness, biocompatibility, high optical transparency and ability to absorb photons selectivity [1-4]. Function of the existence of hydrogen atoms in their structure, DLC are categorized in two forms: hydrogenated amorphous carbon (a-C:H) and non-hydrogenated amorphous carbon (a-C). Usually, its structure is a network of sp^2 and sp^3 coordinated carbon and hydrogen atoms in different proportions. For depositing DLC coatings, the PECVD methods are available such as DC-bias, RF sputtering and pulsed-DC [4-8].

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There are a number of advantages associated with PECVD technique, making it a very attractive method for depositing DLC films, such as low deposition temperature, high deposition rate, and good control over stoichiometry, cleanliness and low particulate levels [9]. For DLC deposition, there are several problems and limitations about the substrate type. Therefore, using a suitable interlayer may help to improve the growth rate and DLC quality by increasing the rate of nucleation and adhesion to the substrate.

In the present study, DLC films were deposited on Si/Al/Ni thin films using DC-plasma of C_2H_2 and H_2 gas mixture by PECVD system. The thickness of Al and the growth conditions for DLC were kept constant in all samples. The Ni content is varied in different samples and the influence of these changes on quality of DLC was investigated. The film characterization was performed by Dektak profilometer, Atomic Force Microscopy (AFM), Raman Scattering Spectroscopy, Fourier Transform Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

AFM was typically performed on Si/Al coated thin films in contact mode on 3µmx 3µm area. Figure 1 shows 2D and 3D images of the A_1, A_3 and A_4 samples. Three dimensional images in all samples show different topography, proving different average roughness. All the experimental conditions were same for all the samples, as referred in the last part, except the deposition time for Nickel Nano Particles (NiNPs). The duration of the experiments was 40 minutes for A_1 which increases to 160 minutes at the same temperature for A_4. Therefore, as can be seen in Figure 1, the size distribution of NiNPs is nearly homogeneous for all the samples. In addition, by increasing the sputtering time, the influence of temperature results in smaller nanoparticles, which might be related to changes in the kinetic energy of the particles. Figure 2 shows the histogram of distribution of NiNP size on the surface of Si/Al substrates, calculated using WSxM 5.0 software. The maximum of number of events estimates the average of particles number and its width gives the variance of the particles diameter. Although the distribution of the particle size is sharp for A_4 and less sharp for A_3 and A_1, the full width at the half maximum of particle size distribution is not large for all of them (less than 10nm) which means the size distribution in NiNPs is of a limited range. As the Gaussian diagram shows for all samples, the distribution of the nickel nanoparticles on Si/Al substrates is nearly homogenous, but the homogeneity varies due to the effect of time duration and temperature on nickel coating. The histogram of nanoparticle distribution may be used to interpret the distribution function of particles size.

The 2D AFM image (Fig.1) and diagrams in Fig. 2 show that, by increasing the time duration in the experiments, the particle size becomes smaller and the size homogeneity increases. Using the Gaussian diagram, one can observe that the particle size of the samples is less than 10nm.

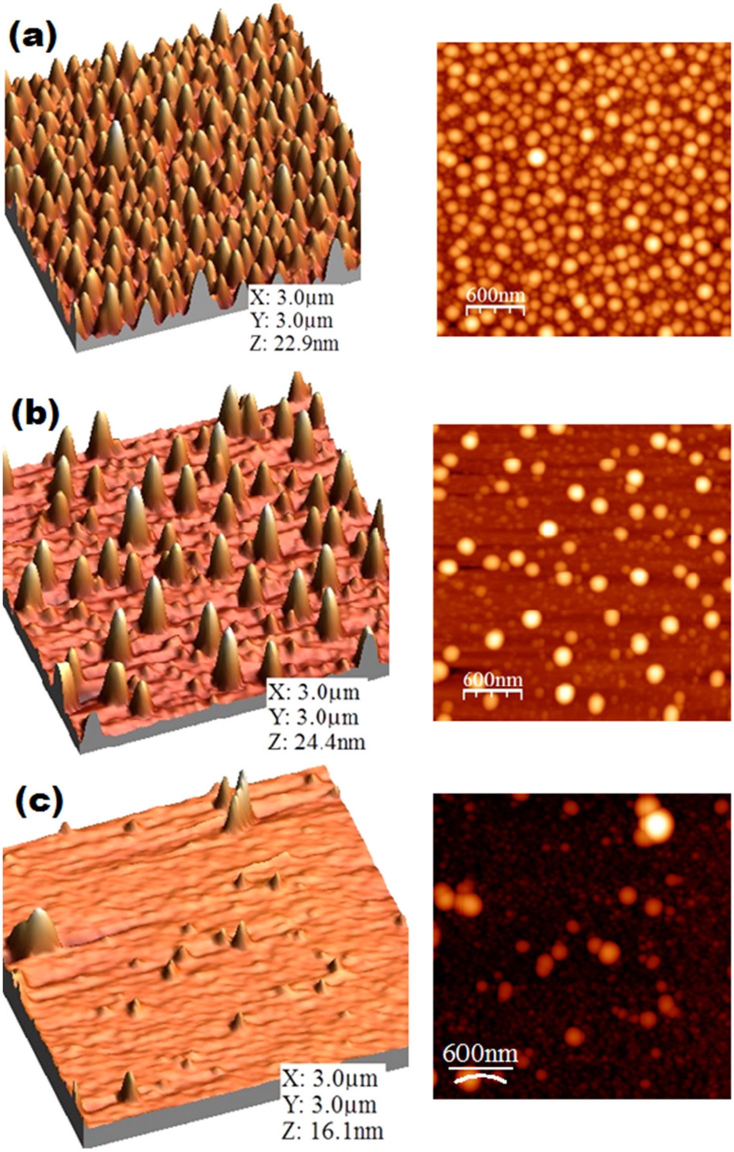

Figure 1. Two and three dimensional AFM images: (a) A_1, (b) A_3 and (c) A_4

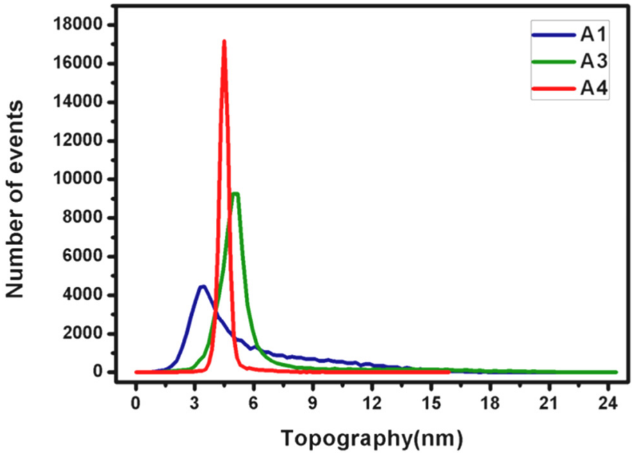

Figure 2. Histogram of NiNPs distribution on Si/Al substrates

The results of surface analysis are listed in Figure 3. The average roughness and RMS roughness of the surface decrease by increasing the Ni sputtering time duration [4]. In addition, the height changes, obtained from the 3D AFM images of Fig.1 using WsXM software are shown here.

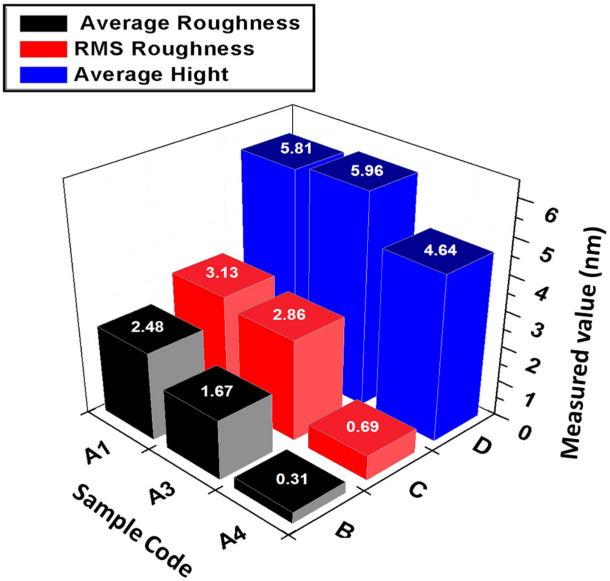

Figure 3. Histogram of the roughness of Ni coating on Si/Al substrates for different sputtering time durations and its height changes

In our previous work [4], the mechanism of adhesion is categorized into mechanical interlocking and chemical bonding, respectively. Mechanical interlocking can be seen as locking by friction and locking by dovetailing [4, 10]. As our group reported elsewhere [4], by decreasing the roughness, the surface becomes smoother. Due to the high degree of chemical bonding and good friction coefficient of Ni nanoparticles layer in this case, there is more adherence to the substrate surface and Nickel nanoparticles [4]. The AFM images show that, by increasing the deposition duration, the NiNPs size was reduced, therefore the surface becomes smoother, which can increase the possibility of mechanical interlocking and also the solubility of carbon atoms in NiNPs. The model of mechanical interlocking was described elsewhere [4].

Raman spectroscopy [11] is a standard nondestructive technique used to evaluate the quality and structural properties of DLC coatings. Fig.4 (a)-(d) shows the Raman spectra of our grown DLC films. These spectra contain typical two broad peaks (see Fig. 4), the so-called G (labeled ‘G’ for graphite) and D (labeled ‘D’ for disorder) peaks [12]. The G peak is attributed to the graphite-like layers of sp^2 micro domains, while the D peak is due to the bond-angle disorder in the sp^2 graphite-like micro domains induced by the linking with sp^3-C atoms as well as the finite crystalline sizes of sp^2 micro domains [13-15]. The results of the Raman study are listed in Table 1.

Table 1. Results of the Raman study for all substrates

Sample Code	**D Band (cm^{-1})**	**G Band (cm^{-1})**	**I_D/I_G**
A_1	1455	1564.49	1.43
A_2	1455.11	1562.44	1.25
A_3	1451/05	1550.94	0.59
A_4	1459.68	1563.67	0.52

The position of G lines and the intensity ratio of D peak and G peak, I_D/I_G, can be correlated with the sp^2/sp^3 bonding ratio, graphite cluster size, and disorder in these threefold coordinated islands [14]. The Raman analysis shows the ratio I(D)/I(G) values for the DLC coatings in the range 1.43 for A_1 and 0.52 for A_4 substrates. A lower intensity ratio I_D/I_G is connected a with higher overall sp^3 content. Therefore, we can infer that the DLC films deposited on A_4 substrate have a more sp^3 content [15-17].

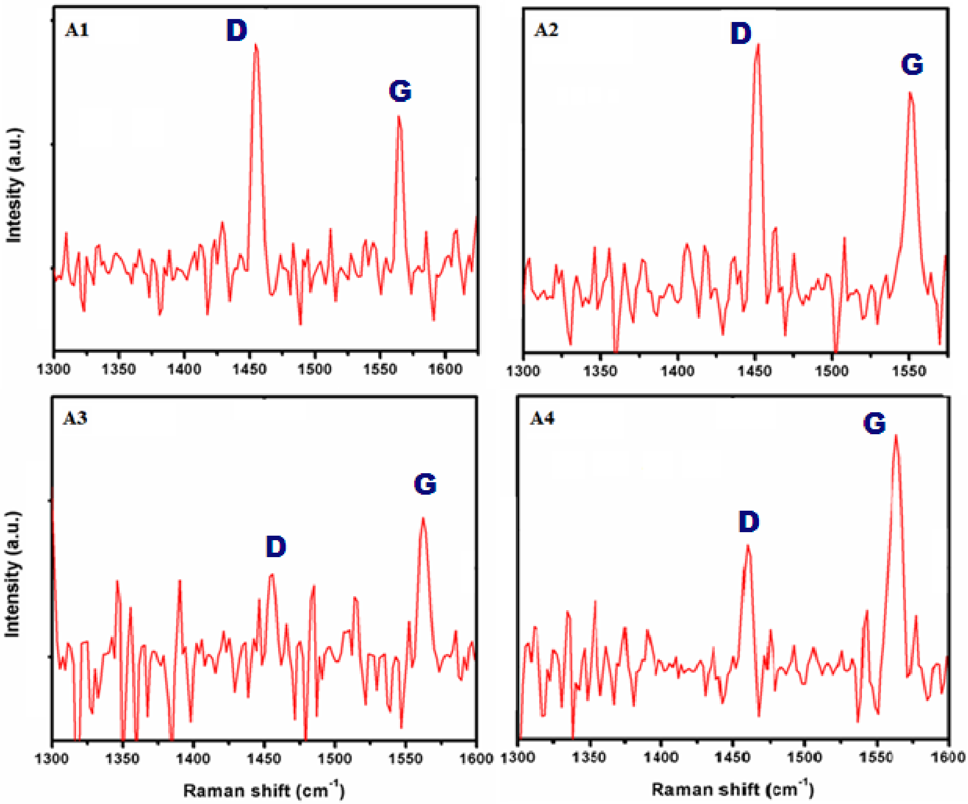

Figure 4. The Raman spectra of DLC films deposited on A_1, A_2, A_3 and A_4 substrates

Fourier Transform Infrared Spectroscopy (FTIR) is a widely used technique to analyze the bonding states of DLC films. Typical FTIR absorption spectra of DLC coatings deposited on our substrates are shown in Figure 5. The band appearing at 905.03 cm^{-1} is assigned to sp^2 CH_2 olefinic bonds. The peak near 1231.12 cm^{-1} could be related to sp^2/sp^3 C-C bonds and the weak peak near 1295.19 cm^{-1} may arise due to CH (olefinic) bond in sp^2-type carbon. The other absorption peaks are listed in Table 2. The C-H stretching vibration region, observed at 2800-3200 cm^{-1} in the FTIR spectra of DLC films, is very important to explain the electrical and nano-mechanical properties of these films [4,16]. The peak located at around 2862.70 cm^{-1} is attributed to sp^3-CH_n (n=1, 2, 3) symmetric stretching vibration modes, while the peaks at approximately 2966.80 cm^{-1} are associated with asymmetric stretching modes. The peak originated at 3292.90 cm^{-1} represents sp^1 CH bonds.

Table 2. Characteristic sp^n CH$_m$ (n and m=1, 2, 3) vibration modes of DLCs grown on Si/Al/Ni: A$_2$ and A$_3$

Sample	Wave numbers (cm^{-1})	Bond type
A$_2$, A$_3$	905.03	(olef) SP^2 CH$_2$
	1231.12	SP^2/SP^3 C-C
	1295.19	(olef) SP^2 CH
	1375.28	SP^3 CH$_3$
	1440.50	SP^3 CH$_2$
	2862.70	SP^3 CH$_n$ (n=1,2,3)
	2966.80	SP^3 CH$_2$ (asymmetric)
	3292.90	SP^3 CH$_3$ (asymmetric)

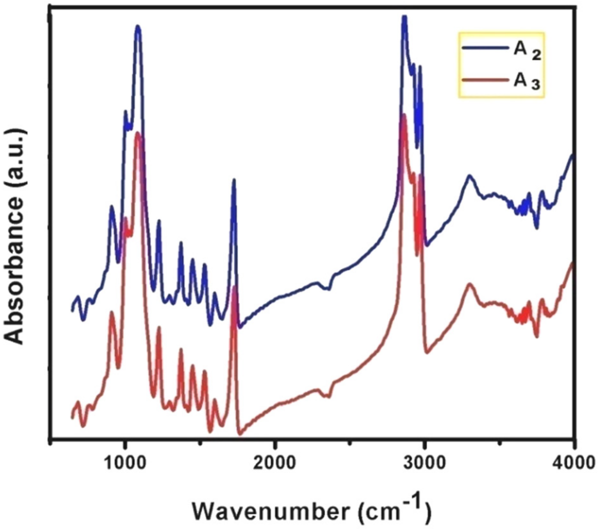

Figure 5. FTIR absorbance spectra of DLC films deposited on Si/Al/Ni substrates

These results suggest the films grown on Ni coated silicon substrates have a DLC structure, in good agreement with the Raman analysis. Typical scanning Electron Microscopy (SEM) of the surface coating for A$_4$ is shown in Figure 6. The DLC layer of the sample were segregated in order to measure the thickness which was done typically, using Microstructure Measurement software (See Fig.6 (II)).

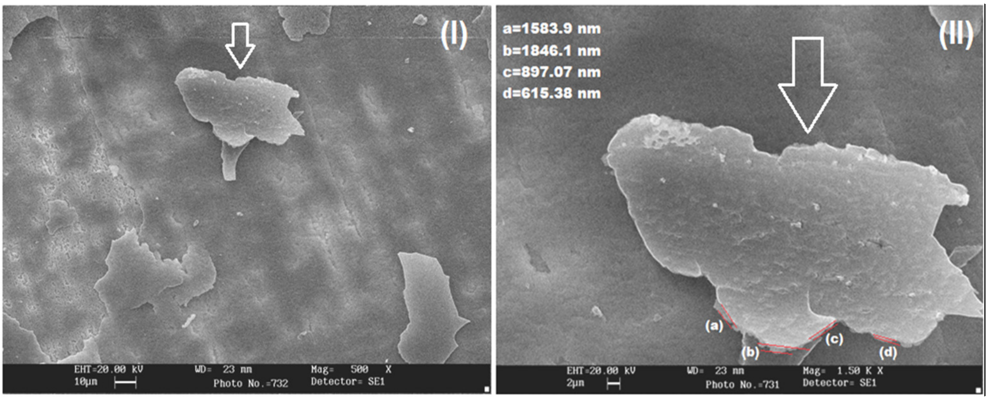

Figure 6. Typical SEM images of DLC deposited on Si/Al/Ni (A_4)

CONCLUSIONS

In this study, DLC films were deposited on Si/Al/Ni substrates. The Al thickness and DLC experimental conditions have been kept constant for all samples but the Ni deposition time was increased from 40 min to 160min. The AFM results show that the particle size distribution of NiNPs was nearly homogeneous for all the samples. In addition, by increasing the sputtering time, the influence of temperature on the nanoparticles growth resulted in smaller size, which might be related to changing in the kinetic energy of the particles; as a consequence, the reduction of average roughness of the substrate surface was observed. The RMS roughness of the surface decreased and the surfaces become smoother with increasing the NiNPs deposition time.

Raman analysis enabled evaluation of the intensity ratio I_D/I_G for the DLC coating on the realized substrates A_1 to A_4. The results have shown that by reducing the surface roughness a lower intensity ratio I_D/I_G can be obtained, in connection with a higher overall sp^3 content and the sp^2 phase organized rather in chain structures. As a result, high quality DLC films have been obtained.

EXPERIMENTAL SECTION

The multilayer was synthesized on P-type silicon wafers (100) in the size of 5×5 mm. The substrates were cleaned in acetone and rinsed with ethanol prior to deposition. Two methods were used for deposition of multilayer:

DC magnetron sputtering and planar DC sputtering. DC magnetron sputtering was performed with Argon gas for Al deposition at $2x10^{-2}$Torr for 1 minute at room temperature. The system consists of two coaxial cylinders, used as the cathode (inner one) and anode (outer one) [17]. The plasma current was obtained at 200mA and 600V, respectively. A nearly uniform magnetic field, parallel to the axis of the cylinders, was generated by a coil around the outer cylinder [17]. Fig. 7 shows the thickness measurement of the Al thin film by Dektak3 profilometer. The thickness of the as-deposited Al layer was about 540nm.

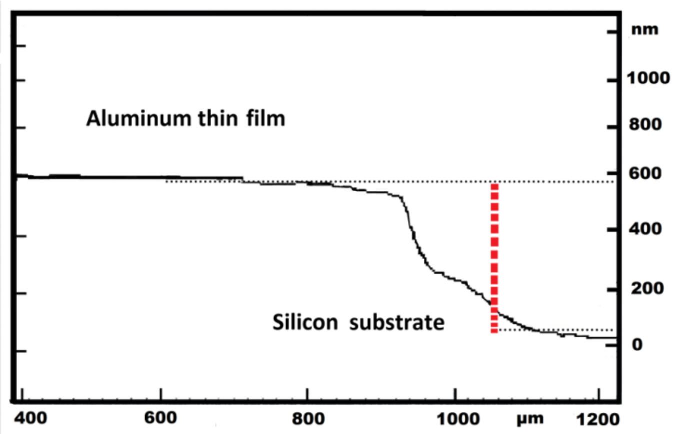

Figure 7. DEKTAK profilometer result, showing the thickness of Al nanolayer

A planner DC sputtering was applied for Nickel sputtering on Si/Al substrates using Ar gas. The temperature does not exceed 200°C during the experiment. The experimental conditions for nickel sputtering were listed in Table 3.

Table 3. Experimental conditions for nickel sputtering on Si/Al substrates

No.	Sample	Temperature (°C)	Ni Deposition time (min)
A_1	Si/Al/Ni	200	40
A_2	Si/Al/Ni	200	80
A_3	Si/Al/Ni	200	120
A_4	Si/Al/Ni	200	160

Diamond-like Carbon films were produced in a DC-PECVD system. Figure 8 shows the schematic diagram of the PECVD system.

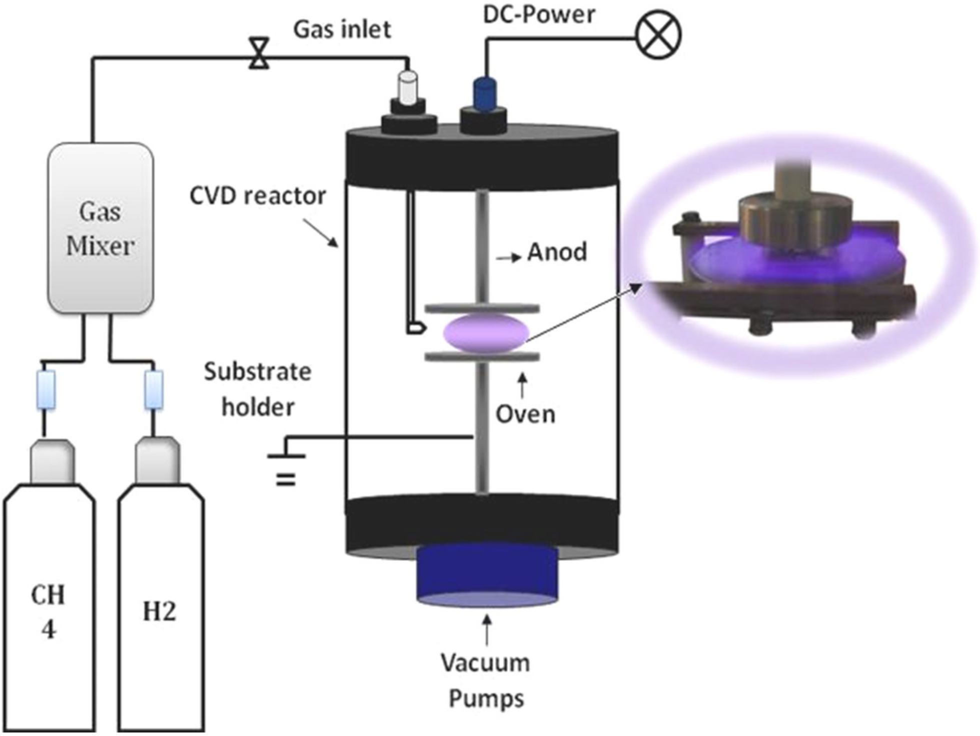

Figure 8. Schematic diagram of the PECVD system

The pretreated substrates were mounted into an oven in the center of PECVD chamber. The cathode was fed by a DC power supply. The DLC films started to be deposited using acetylene for 50 minute (80 sccm gas flow at 10 Torr and a discharge voltage of 100 V). After, the experiment was continued with the C_2H_2/H_2 mixture plasma with 15% flow ratio, during 120 minutes. The voltage was kept constant at 450V and the pressure inside the chamber was 12 Torr. Temperature was reached to 300°C. The schematic form of the deposited layers was shown by a model in Figure 9.

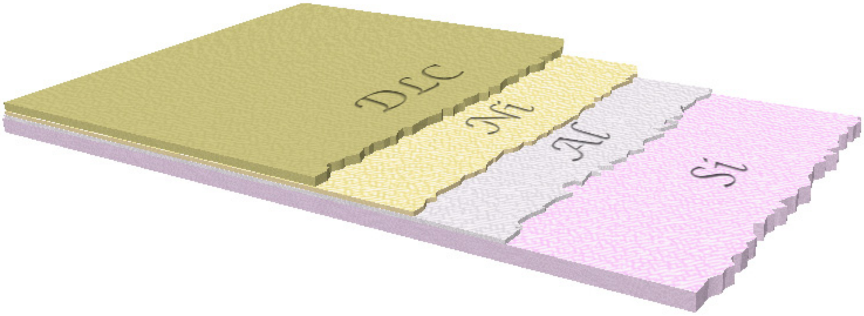

Figure 9. A schematic image of the DLC coated on Si/Al/Ni substrate

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