Dedicated to Professor Mircea Diudea
on the Occasion of His 65th Anniversary

THICKNESS EVOLUTION OF NICKEL NANO LAYER ON THE MICROSTRUCTURE AND ADHESION STRENGTH OF DLC FILMS

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ABSTRACT. Diamond-like carbon (DLC) films are metastable amorphous hydrogenated or non-hydrogenated forms of carbon, with excellent properties that make them reliable to use in various fields of science and technology. However, poor adhesion of DLC films to the substrate limits their performance. Using an interlayer is one of the methods to reduce the stress in films and improve the adhesion. In this study, different thickness of the nickel nano layers was deposited on the silicon substrates as an interlayer for the growth of DLC films. The Ni nano layers with the thickness of 10, 20, 40 and 80 nanometers were deposited on the substrates by DC magnetron sputtering while DLC films were synthesized by plasma enhancement chemical vapor deposition (PECVD) system with a mixture of argon and methane gases as the precursors. Morphology and the surface roughness of Ni interlayers were investigated by atomic force microscopy (AFM) which showed low surface roughness changing with thickness of interlayer. For the characterization of DLC films, Raman spectroscopy was used; it proved high degree of diamond-like character for the films grown on 10 nanometers nickel interlayer, as given by the ratio of I_D to I_G. FE-SEM (Field emission scanning electron microscopy) cross-section images of DLC films showed increasing of the thickness of DLC films by increasing of nickel nano layer thickness. The adhesion strength also was investigated by the nanoscratch test.

Keywords: Nickel Nano Layer, Diamond-Like Carbon film, Adhesion Strength, Raman Spectroscopy

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INTRODUCTION

Diamond like carbon (DLC) is a metastable form of amorphous carbon containing a mixture of tetragonal sp^3 and planar sp^2 carbon–carbon bonds [1]. The ratio of sp^3 to sp^2 bonds present in DLC films, largely affects their overall properties [1, 2]. DLC coatings have excellent properties like high hardness, high band gap, low friction coefficient, chemical inertness, wear resistance and biocompatibility [2-4]. Poor adhesion of DLC films to the substrate is the main limitation for their wide applications which is due to the presence of high internal compressive stress in the film and high diffusion of carbon into the substrate [3, 5]. Using a metal interlayer such as Cr, Ti, Al and Ni between the DLC and Si substrate is a one of the strategies to overcome this limitation [5-9].

In this work, the nickel nano interlayer was selected as an interlayer between DLC film and silicon substrate and various thicknesses of the Ni thin films were sputtered on the substrates. Plasma enhancement chemical vapor deposition (PECVD) technique [10] was applied for synthesis of DLC films. The results illustrate that the thickness of Ni nano layer is very effective in the microstructure and adhesion strength of DLC films.

RESULTS AND DISCUSSION

After the deposition of Ni layer, atomic force microscopy (AFM) was adopted to investigate the surface morphology and surface roughness of the layer. The AFM images of Ni layers are shown in Figure 1; they were named S_1, S_2, S_3 and S_4 according to their Ni layer thickness (10nm, 20nm, 40nm and 80nm, respectively).

Surface roughness of the substrate is one of the important parameters which could be characterized by atomic force microscopy in terms of RMS roughness [11]. In this study, the WSxM 5.0 software was used to measure the roughness and make the histogram of distribution of nano metal particle sizes. The results of RMS are shown in Figure 1, for each sample; one can see the increse of roughness by increseaing the thickness of Ni nano layer. The histogram of distribution of Ni nano particle sizes on the surface (shown in Figure 2) indicates a homogenous distribution for all the samples.

Figure 3 presents the cross-sectional FE-SEM images of DLC films deposited on Ni nano layer and Si without an interlayer. In the absence of Ni, a very thin layer, with thickness of about 14nm was formed (Figure 3(a)). The Ni layer promotes the thickness of DLC film from 114nm to 728 nm, function of the Ni layer thickness (Figures 3 (b to e)); this fact proves the catalytic activity of Ni in adsorption and surface diffusion of carbon atoms to precipitate and form the DLC film [5, 12].
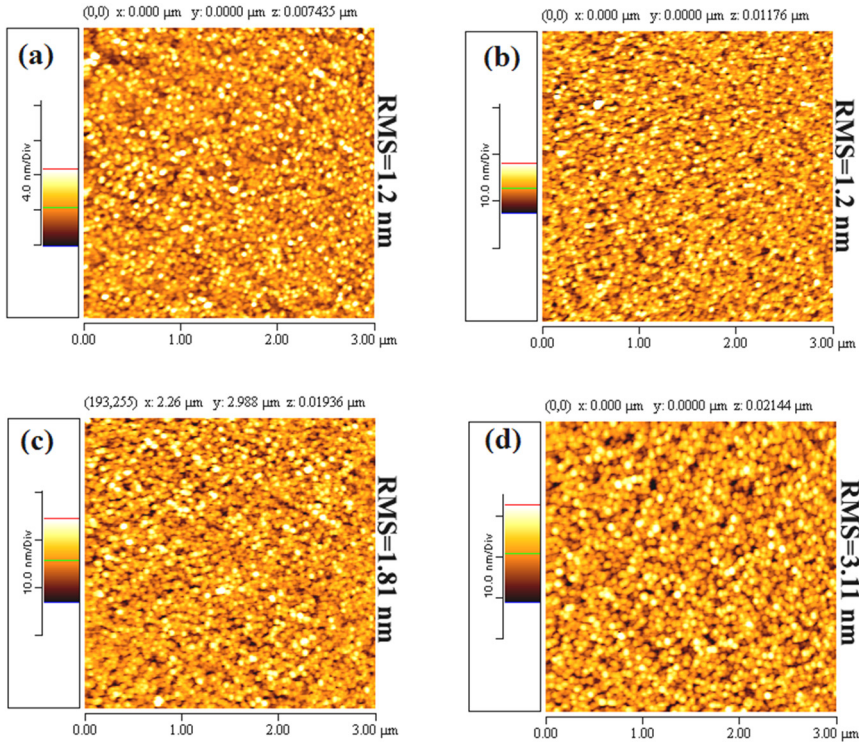
Figure 1. AFM images of a 3×3 μm^2 area of surface (a) S_1, (b) S_2, (c) S_3 and (d) S_4. The RMS surface roughness of each sample was inserted in right of each image.
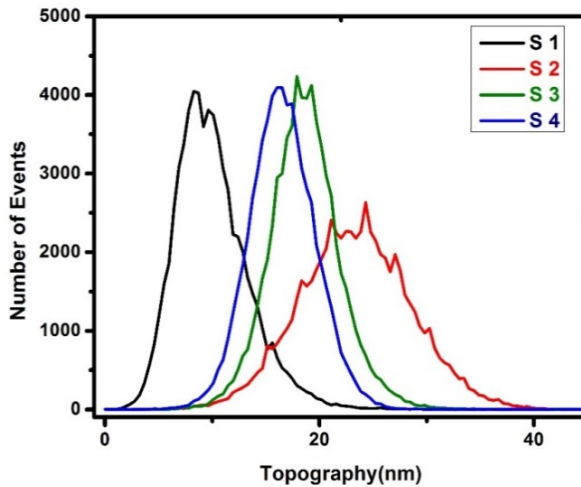

Figure 2. Size distribution of nickel nano particles on the surface of silicon substrate.
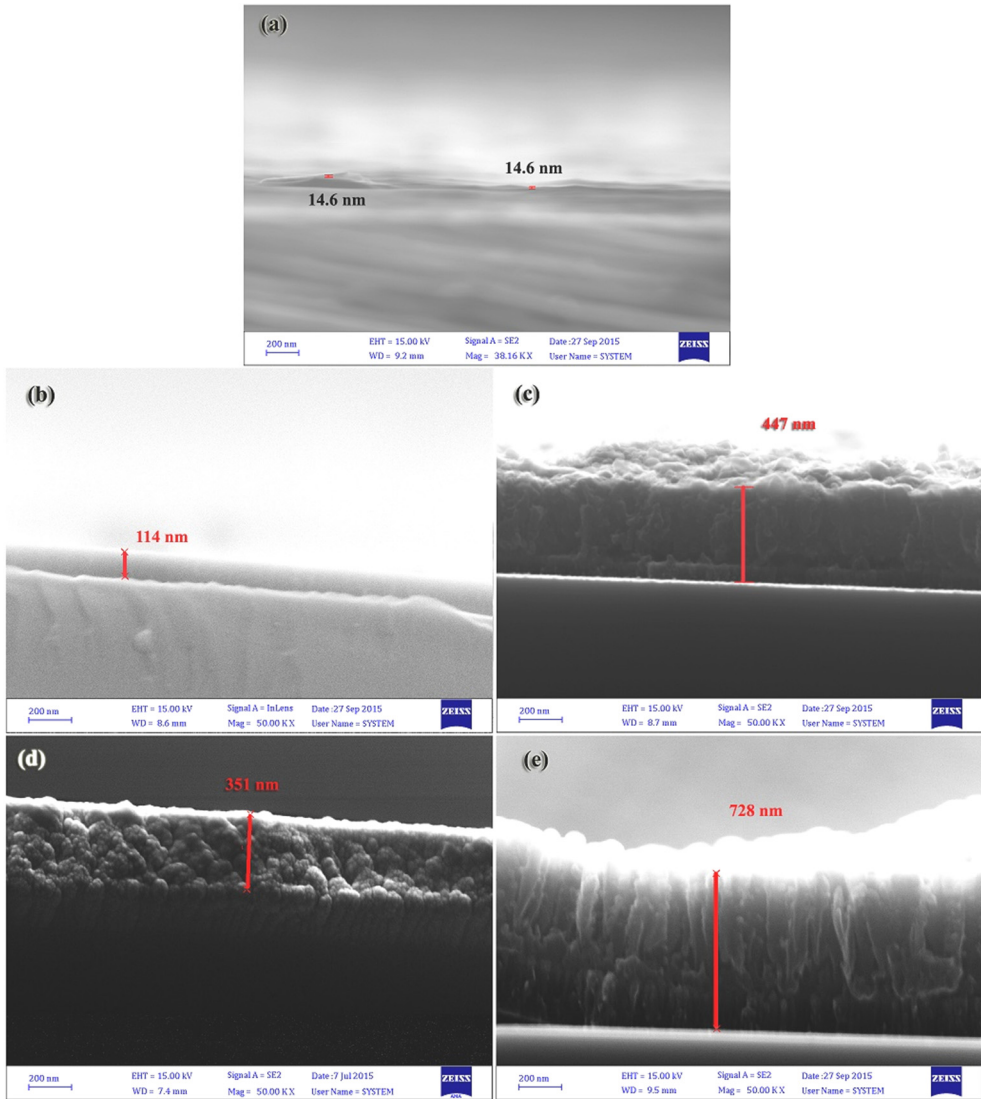
Figure 3. FE-SEM morphology of DLC films grown on the substrate (a) without interlayer, and with interlayer thickness of (b) 10nm, (c) 20nm, (d) 40nm and (e) 80 nm.

Raman Spectroscopy is a non-destrutive and important technique for determining the bonding types in DLC film [13, 14]. Usually, amorphous carbon thin films exhibit two main Raman bands (D and G) in the wavenumber region of 1000–1800 cm^{-1}. The Position and the relative intensity of G and D are important factors in the properties of DLC [8, 15]. Figure 4 and Table 1 show the Raman spectra and their results, respectively.
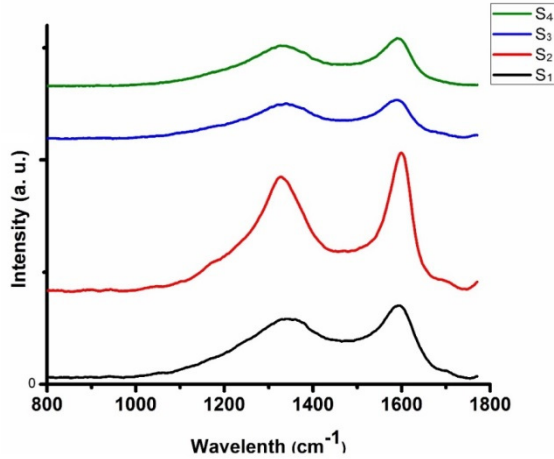
**Figure 4.** Raman spectra of DLC films grown on S_1, S_2, S_3 and S_4.

As can be seen from Table 1, the intensity ratio of the D to G bands (I_D to I_G) changes with the thickness of interlayer. The lowest value of I_D/I_G is for sample S_1 which had the lowest thickness of Ni layer. The ratio of I_D/I_G is correlated to the sp^2/sp^3 ratio in the DLC films, and a lower intensity ratio (I_D/I_G) can be interpreted as corresponding to higher sp^3 content [16]. The Raman spectra also show the G peak positions shifted upwards in all the samples. This is indicative of lower amount of internal compressive stress [17]. Thus, the results obtained from shifting of G peak position and I_D/I_G ratio value exhibit an enhancement in diamond-like character which S_1 sample has the highest degree of diamond-like character (sp^3 bonding) and lowest value of sp^2 carbon clustering.

Table 1. Raman spectra data of DLC films deposited
at different thicknesses of Ni nanolayers

	D band Position (cm^{-1})	G band Position (cm^{-1})	I_D/I_G
S_1	1345	1592	0.84
S_2	1329	1597	0.85
S_3	1337	1587	0.92
S_4	1332	1591	0.87

Mechanical properties of the films were studied using the nano scratch test [18, 19]. The AFM surface morphology of the scratch track on the DLC film of S_1 and S_2 can be seen in Figure 5. The surface roughness of S_1 is lower than that of S_2 and a narrower scratch track and lower residual wear depth

were formed indicating better mechanical properties. The friction coefficients of DLC films obtained from nanoscratch test were also illustrated (Figure 5,c) which demonstrate a lower value for the film grown on 10 nanometers Ni interlayer (S_1).
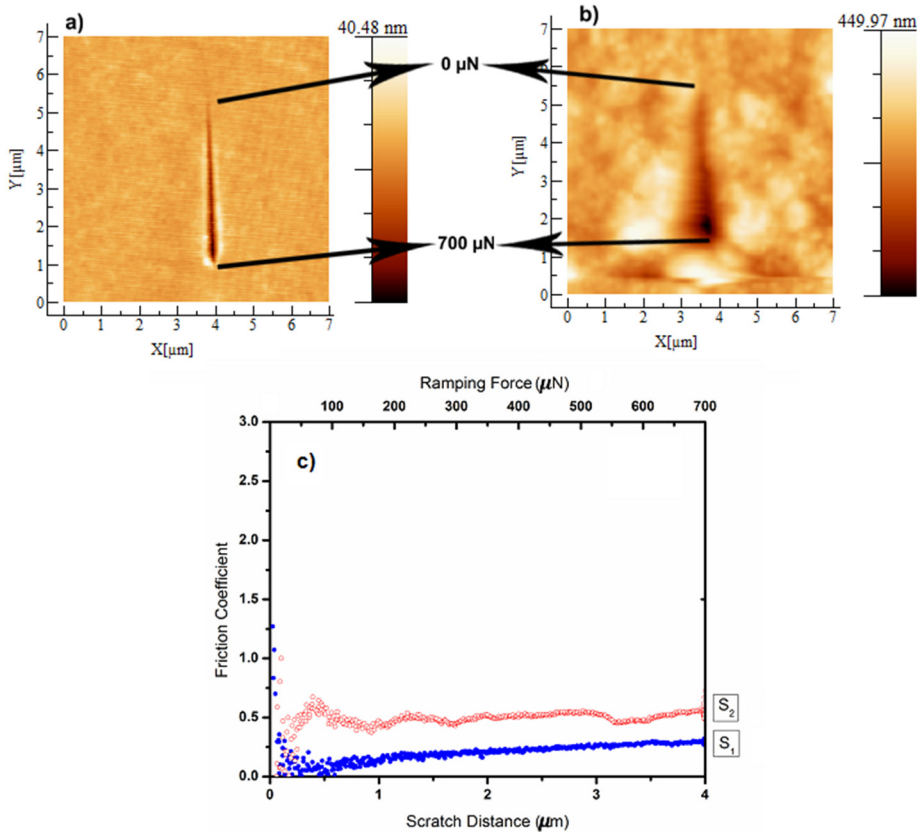
Figure 5. AFM images of the nano scratch test on a) S_1 and b) S_2; c) Changing of friction coefficient during ramping force and scratch distance for S_1 and S_2.

CONCLUSIONS

Different thicknesses of nickel nano layers, from 10 to 80 nanometers, were used for the growth of DLC films on silicon substrates. The morphology study of Ni nano layer showed a low surface roughness with homogeneous size distribution of Ni particles, which increased with the thickness of Ni layer. The FE-SEM images represented thicker DLC films formed with increasing

the thickness of Ni nano layer. Raman study revealed minor changes in the value of I_D/I_G ratio of DLC films; the ratio had the lowest value for S_1, indicating lower sp^2 fraction and better mechanical properties than other samples. Nanoscratch test confirmed the Raman results and showed better adhesion of DLC film on 10 nanometers Ni layer, which also had a lower surface roughness and friction coefficient.

EXPERIMENTAL SECTION

Silicon (p-type (400)) wafers were used as the substrate for deposition of the DLC films and were cleaned ultrasonically in ethanol, acetone and deionized water, each of them for 15 minutes, to rinse the contamination from substrates. Nickel nano layer was deposited on substrates by DC sputtering magnetron (Pishtaz Engineering Co. High Vacuum Technology Center (ACECR-Sharif University. Branch-Iran)) at 10^{-5} Torr base pressure in thickness of 10, 20, 40 and 80 nanometers. For the growth of DLC films, DC-plasma enhanced chemical vapor deposition (DC-PECVD) chamber [10] was exhausted to 10^{-5} Torr. At first, methane was introduced to the chamber for 30 minutes with a flow rate of 20 sccm. Then a mixture of methane and argon (25 vol. % CH_4) was inserted to the system with a total flow of 40 sccm. The growth temperature was 300∘C and duration of growth was 60 minutes.

The topographical and surface roughness of the Ni nano layers were studied by atomic force microscopy (AFM, XE-NSOM, in contact mode). The morphology and thicknesses of DLC films were studied using Zeiss Sigma VP field emission scanning electron microscopes (FE-SEM). Raman spectroscopy (Nd:YAG laser with wavelength of 532 nm) was used to measure the atomic bonds of DLC films. The nanoscratch tests (A Hysitron Inc. TriboScope® Nanomechanical Test Instrument) were performed to measure the DLC film's adhesion to the substrate. Each scratch test was performed by moving the probe (Berkovich indenter) laterally in a distance of 4 μm while concurrently ramping the normal force from 0 to 700 μN [20].

ACKNOWLEDGMENTS

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