Characterization of DLC Thin Films Deposited by DC-Pulsed PACVD using Methane Precursor

Seyed Mohammad Mahdi Shafiei *
Department of Mechanical Engineering,
West Tehran branch, Islamic Azad University, Tehran, Iran
Department of Mechanical Engineering,
Roudehen branch, Islamic Azad University, Roudehen, Iran
E-mail: shafiei.mohammad@wtiau.ac.ir
*Corresponding author

Hamed Raeisifard
Department of Mechanical Engineering,
West Tehran branch, Islamic Azad University, Tehran, Iran
E-mail: raeiesifard.ha@wtiau.ac.ir

Received: 28 March 2021, Revised: 8 September 2021, Accepted: 21 September 2021

Abstract: In this work, Diamond Like Carbon (DLC) thin films were deposited on aluminum alloy 6061 by Plasma-Assisted Chemical Vapor Deposition (PACVD). Nitiding prior to coated leads to appropriate hardness gradient and it can greatly improve the mechanical properties of the coatings. The composition, crystalline structure and phase of the films were investigated by Grazing Incidence X-ray Diffraction (GIXRD). Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were employed to observe the morphology and structure of the film. The DLC layer exhibited a columnar structure. The adhesion force between the film and the aluminum alloy 6061 was 30.8 Mpa. The DLC film was determined by the pull of test. The hardness of the DLC film was 12.75 Gpa. The improvement of the adhesion DLC was attributed to a less gradient hardness configuration. In addition, the mean friction coefficient of the films was about 0.2 determined by nanoindentation test. According to the results, the high and unique hardness of this coating leads to increase of the wear resistance and thus the useful life of parts.

Keywords: DLC, PACVD, Thin Film, Tribology

How to cite this paper: Seyed Mohammad Mahdi Shafiei, Hamed Raeisifard, "Characterization of DLC Thin Films Deposited by DC-Pulsed PACVD using Methane Precursor" , Int J of Advanced Design and Manufacturing Technology, Vol. 15/No. 1, 2022, pp. 65–71. DOI: 10.30495/admt.2022.1926795.1270.

Biographical notes: **Seyed Mohammad Mahdi Shafiei** received his PhD from University of Iran University of Science and Technology (IUST), Tehran, Iran, in 2015. He is currently Assistant Professor at the Department of Mechanical Engineering, West Tehran Islamic Azad University, Iran. His current research interest includes mechanical behaviour of nanostructure thin films. **Hamed Raeisifard** is Assistant Professor of Mechanical Engineering at the West Tehran Islamic Azad University, Iran, since 2014. He received his PhD from Science and Research Branch of Islamic Azad University of Iran. His current research focuses on mechanical properties and dynamics.

Research paper

1 INTRODUCTION

Aluminum alloys are preferred engineering material for automobile, aerospace and mineral processing industries for various high performing components that are being used for varieties of applications; owing to their lower weight and excellent thermal conductivity properties. Among several series of aluminum alloys, heat treatable Al6061 and Al 7075 are much explored, among them Al6061alloy are highly corrosion resistant, exhibit moderate strength and find much applications in the fields of construction, automotive and marine applications. Aluminum alloy 7075 possesses very high strength, higher toughness and is preferred in aerospace and automobile sector. Due to their high strength, fracture toughness, wear resistance and stiffness, the composites formed out of aluminum alloys are of wide interest [1-2].

The PACVD technique is an appropriate method to deposit wear and corrosion resistant hard coatings which have excellent properties for several applications. In comparison to PVD methods, it offers the possibility of homogeneous coating on work pieces with complicated shapes. Other advantages of PACVD method are the high adhesion and good morphology of the layers. Tools deposited with hard coatings, like DLC, TiCN, TiC, have already been used successfully for many industrial applications. The PACVD process is influenced by several process parameters, like discharge voltage, current density, gas pressure and gas composition and flow rate. [3–5], [16]

In recent decades, many studies in surface engineering have sought the development of coating technology on steel substrate. Coatings provide wear protection combining reduced friction, self-lubrication and resistance to chemical reactions. A promising coating that has these properties is the Diamond-like Carbon (DLC) due to its interesting properties such as wear resistance and low friction [6-7], [15]. In the present research, the influence of the CH4/ (CH4+N2) gas flow ratio on characteristics of PACVD DLC thin film on the Al6061alloy has been investigated.

2 EXPERIMENTAL PROCEDURE

DLC coatings with compositional gradients were deposited on an Al 6061 substrate using a PACVD coating system equipped with a voltage-controlled pulse generator.

During coating, process parameters such as gas flow ratio, wall temperature, voltage duration of pulse-on and pulse-off time and total pressure were monitored. H_2, Ar, N_2 and CH_4 gases were used as process gases for coating deposition. Total pressure was kept at 2 mbar and substrate temperature was controlled at 470°C. Plasma nitriding was used as a pre-treatment to decrease hardness gradient between substrate and coating. The processing parameters for the plasma nitriding are listed in "Table 1" . The N_2/CH_4 gas flow ratio was defined $CH_4/(CH_4+N_2)$. The crystalline structure of the coatings was determined by Grazing Incidence X-ray Diffraction (GIXRD) in the continuous scanning mode using CuKα radiation (λ = 0.154056 nm). The full-width at half-maximum (FWHM) of the Bragg peaks is used to approximate grain size based on the Scherrer formula [8].

Table 1 The PACVD parameters

Parameters	Value
Pulsed voltage	650 V
Duty cycle	33%
Temperature	470°C
PACVD time	120 min
$CH_4/(CH_4+N_2)$ flow ratio	50% , 66%
Total pressure	2 mbar
Nitriding time	120 min
Nitriding temperature	470°C

Where, D is grain size, β is the FWHM of the Bragg peak, and θ is the Bragg reflection angle. The chemical composition of the film was analyzed by X-ray Photoelectron Spectroscopy (XPS) with monochromatic AlKα radiation at the pass energy of 1486.6 eV. The film morphology studied by Scanning Electron Microscopy (SEM, VEGA-TESCAN-XMU) and Atomic Force Microscopy (AFM, DME-DS-95-50E). The Vickers hardness of the DLC coatings was measured using a micro-hardness test, within the loading range of 50 g; five micro-hardness tests were performed for each sample to obtain the average values of the hardness.

3 RESULTS AND DISCUSSION

Figure 1 illustrates the GIXRD patterns of the coatings deposited at 470◦C using the two gas mixtures. The (200) plane is revealed to be the preferred structure, deposited via kinetics-limited crystal growth [9] and under thermodynamically stable conditions because the (200) plane has the lowest energy surface in the DLC crystal. This implies that the film structure is dense because the plane (200) orientation is the densely packed plane. The GIXRD pattern also indicates an exclusively face-center-cubic (FCC) structure which is closely related to AL. Nitrogen and Carbon can be incorporated on the octahedral sites of both the hexagonal close-packed lattice of aluminum and the FCC sub lattice in DLC. In stoichiometric DLC, it is assumed that all the octahedral sites are filled with carbon [10].

DLC is a compound whose stoichiometry in AlC_xN_y can vary in the range of 0<x,y<1. Moreover, the peaks of the AlCxNy phase shift to lower angles and are close to the Al_4C_3 phase while the C relative contents reach around 45% measured by XPS. This is ascribed to the substitution of N atoms with the bigger C atoms in the solid solution.

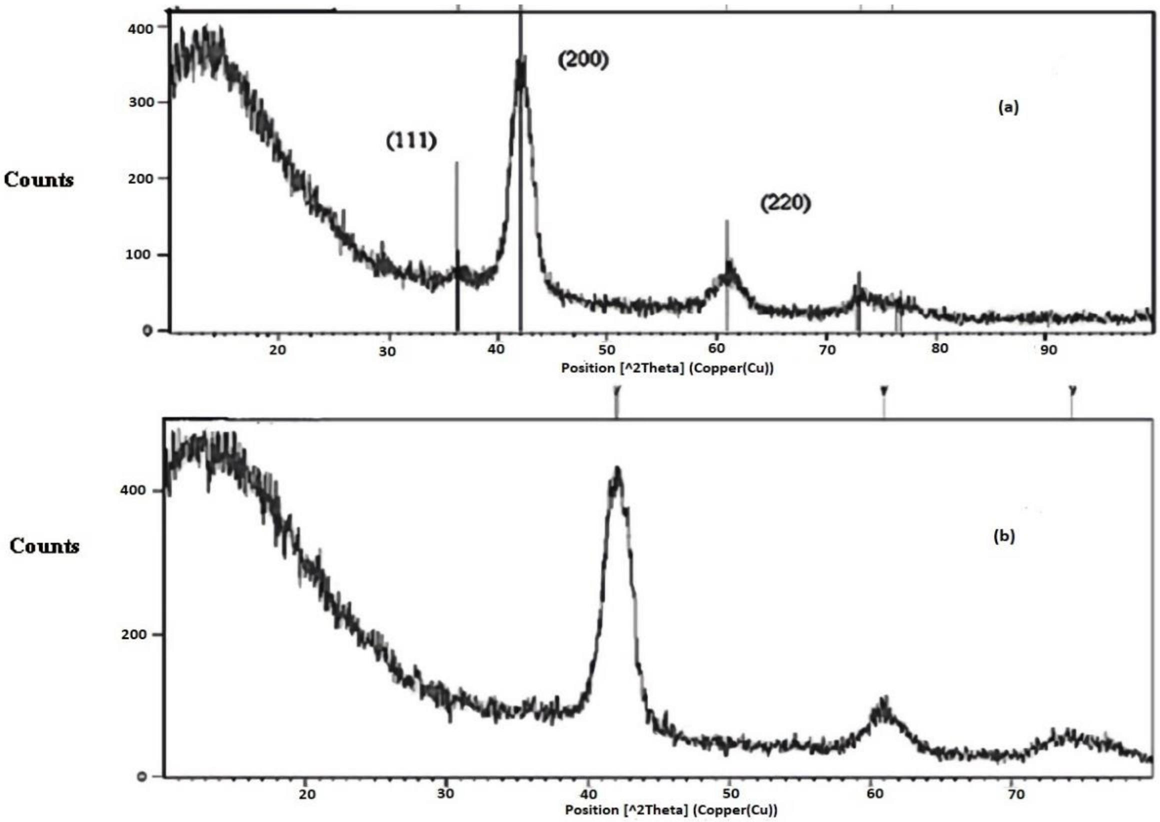


Fig. 1 GIXRD patterns acquired from the $Al_4C_xN_y$ coatings using the two gas mixtures CH_4/ (CH_4+N_2).a) 0.66 and b) 0.5.

Figure 1 also shows that by increasing the flow ratio from 50% to 66%, the (220) plane is thermodynamically stable relative to the (200) plane and the broad peak of the (200) plane in "Fig. 1b" indicates that the grain size increases by increasing the flow ratio. Hence, the specific surface of DLC decreases. Only for a CH_4/ (CH_4+N_2) gas flow ratio of 0.5, the color of the DLC layers is dark brown. At higher gas flow ratio, it becomes increasingly black [11]. The later layers mentioned are not stoichiometric. When the gas flow ratio was %50, the C/N ratio was 0.43 with $AlC_{30}N_{70}$ stoichiometric composition ("Fig. 1a"). By increasing the gas flow ratio to %66, the C/N ratio changed to 2.33 and $AlC_{70}N_{30}$ stoichiometric composition ("Fig. 1b"). The $AlC_{30}N_{70}$ possesses a face-centered cubic (FCC) lattice with a_o=0.4258 nm and grain size of 28.6 nm but the $AlC_{70}N_{30}$ possesses a face-centered cubic (FCC) lattice with a_o=0.4287 nm and grain size 44.37 nm, so lattice parameter decreased with increasing gas flow ratio. This is in agreement with relation (eq.1) proposed by Li Yuanbing et al for AlC_xN_{1-x} [12].

$$a = 0.4235 + 0.007x(nm) \tag{1}$$

The residual stresses of the samples were determined by X-ray measurements. The surface residual stresses of DLC layers are -28.74 MPa for %66 and -23.42 MPa for %50. The residual stress values increase with increasing flow ratio. The crystallite percents were determined by X-ray diffraction. The crystallite percents of DLC layers were %76 for % 66 gas flow ratio and %85 for % 50. Also films deposited at low CH_4/N_2 ratios were much more crystallite than those deposited at high ratios.

Figure 2 presents the XPS spectra of N 1s and C 1s of the DLC film. In the Al spectrum, two peaks of Al 2p are found at 462.7 and 468.4 eV. The N 1s spectrum exhibits a weak peak at 394.6 eV, which corresponds to the N–Al bonds. The weak electronegative of C element, involved in the AlCN film formation, would slightly increase the binding energies of Al–N. The C 1s spectrum consists of three peaks at binding energies of 281.5, 283.4 and 285.2 eV.

The peak at 281.5 eV is assigned to the Al–C bonds. The peaks at 283.4 eV and 285.2 eV are assigned to the sp2–C and sp3–C bonds, respectively. The C 1s binding energies of pure graphite (284.3 eV) and diamond (285.3 eV) measured under the same conditions are cited for comparison. It is also seen from "Figs. 2 and 3" that the peak at 281.5 eV occupies a large fraction of the total C 1s spectrum compared with the other peaks, indicating that a large fraction of C atoms is bonded to Al atoms, and a little of C atoms exist as amorphous carbon. That is in agreement to GIXRD pattern. Figure 2a shows that chemical composition is $AlC_{0.426}N_{0.544}O_{0.03}$ for 50% and $AlC_{0.453}N_{0.51}O_{0.038}$ for 66% ("Fig. 3"). Therefore, the XPS spectra offer similar chemical composition for both cases while they were different from GIXRD patterns because the XPS spectra are very sensitive to surface analysis.

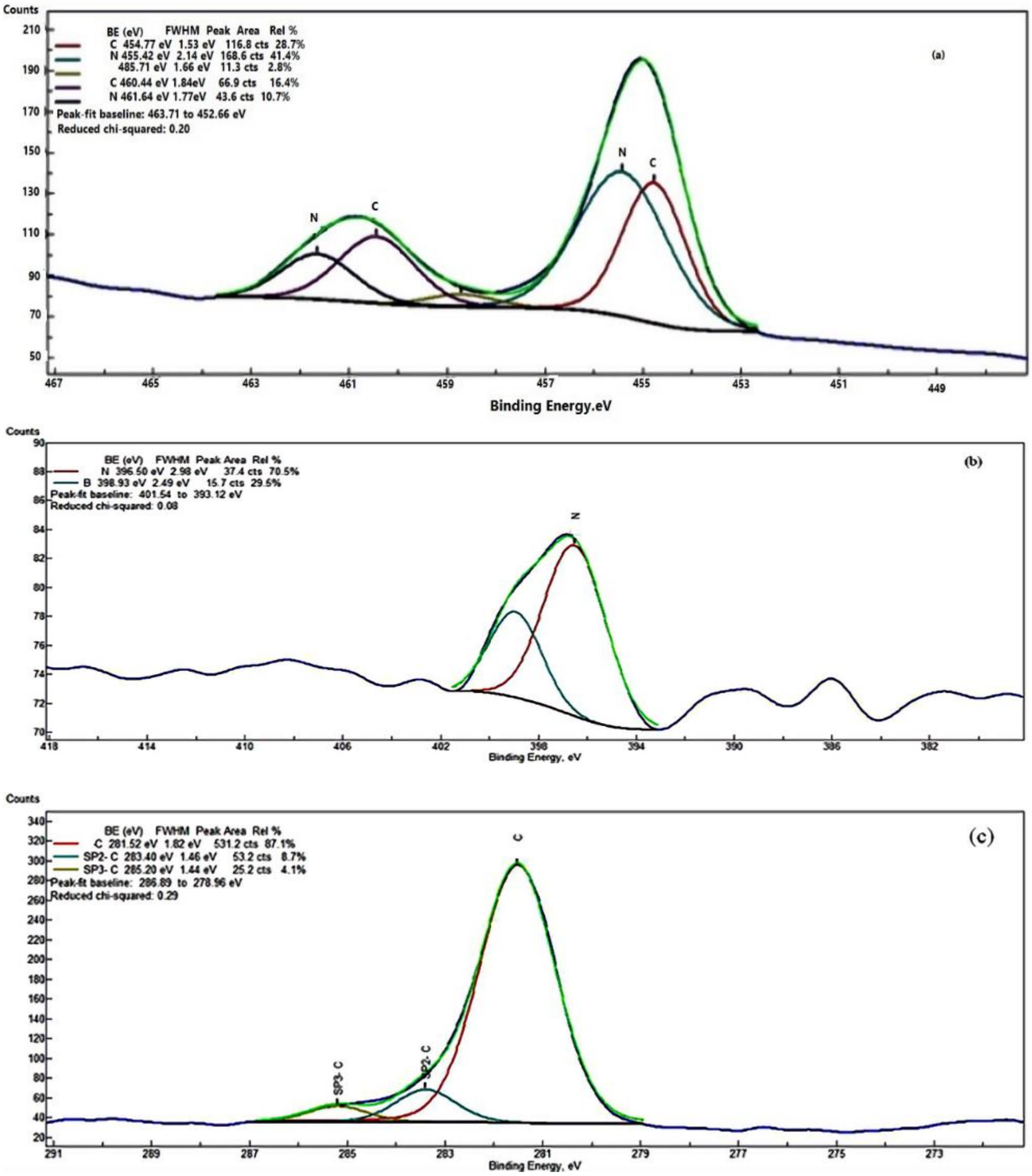


Fig. 2 XPS spectra of: (a): Al 2p, (b): N 1s. and (c): C 1s for the film for CH_4/ (CH_4+N_2) gas flow ratio 66%.

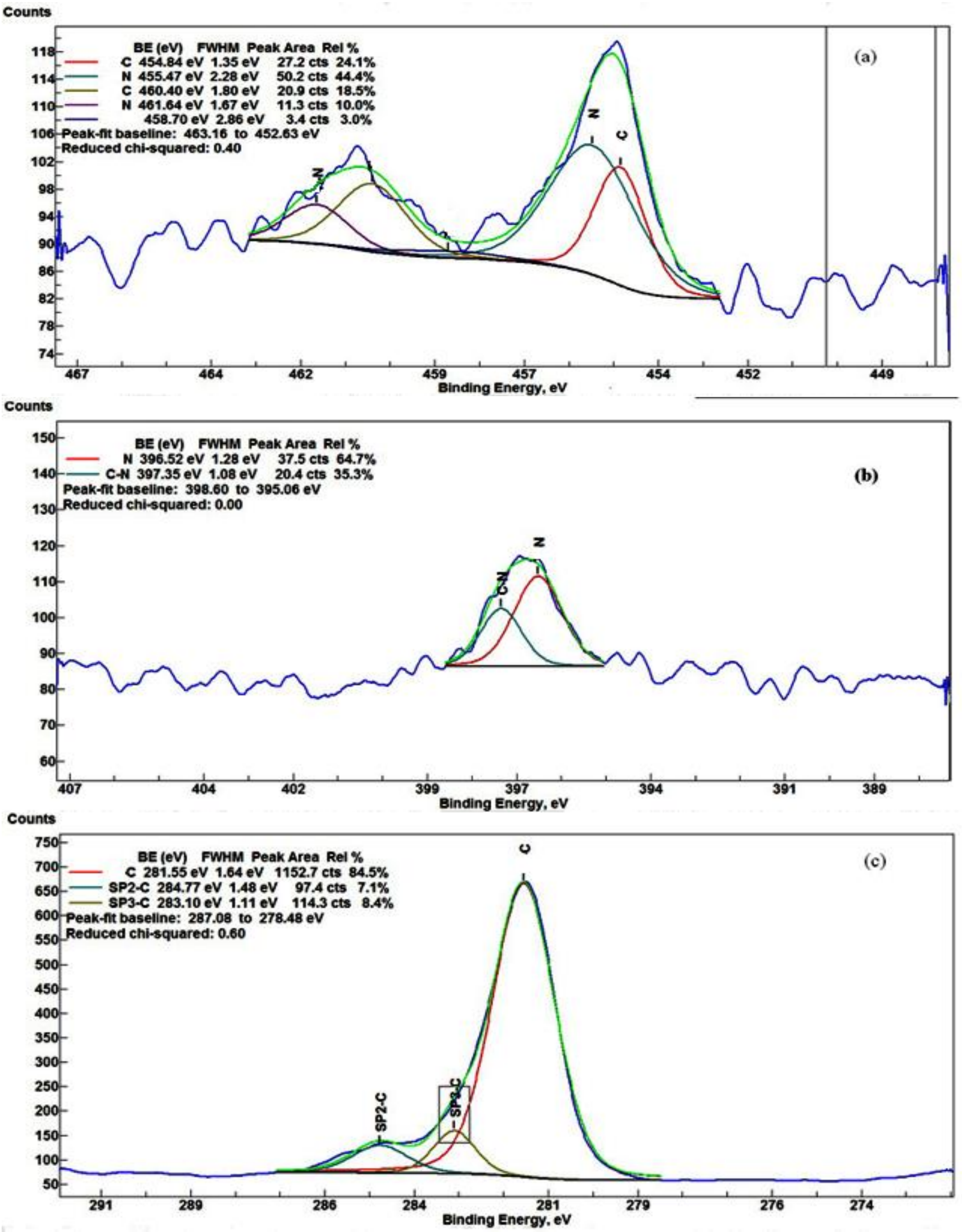
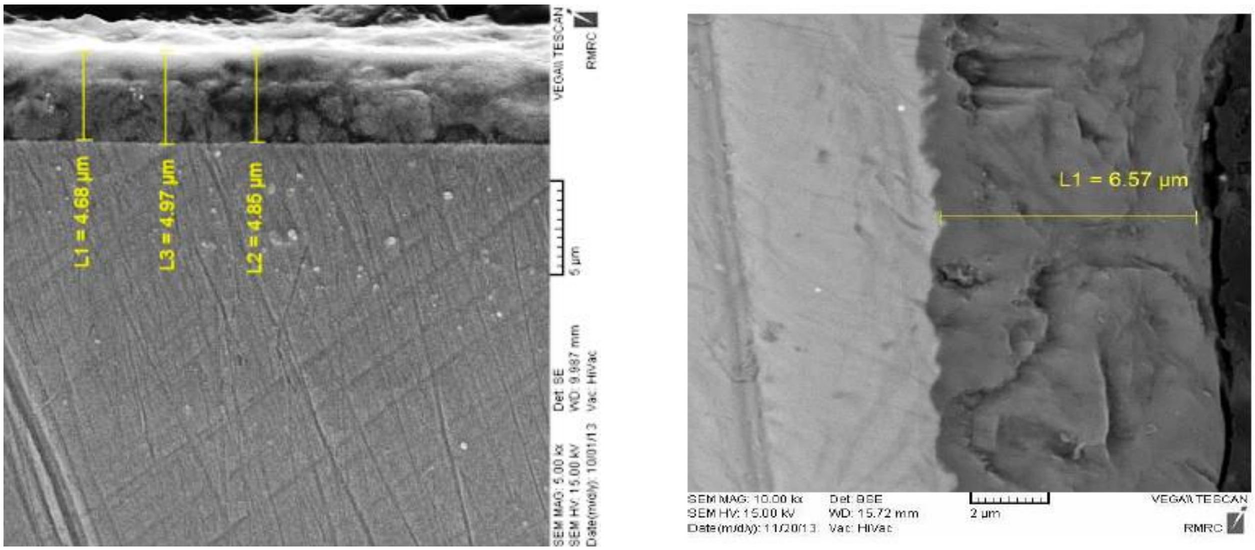


Fig. 3 XPS spectra of: (a): Al 2p, (b): N 1s, and (c): C 1s for the film for CH_4/ (CH_4+N_2) gas flow ratio 50%.

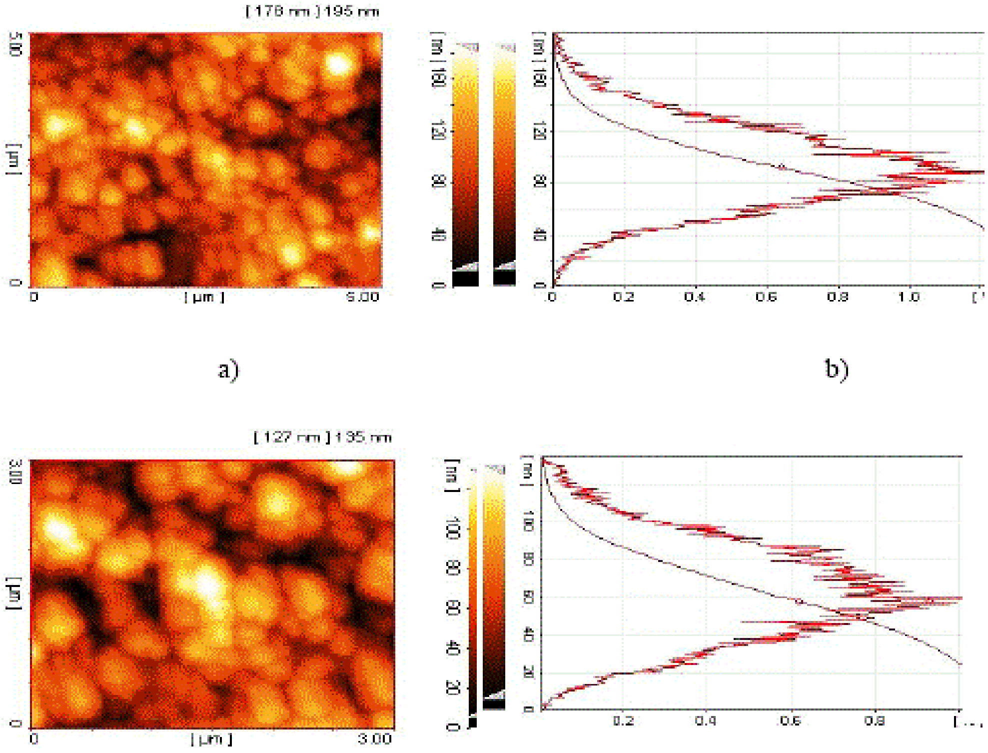
SEM images show the thickness of layer plus the rate of growth, both of them decreased by increasing gas flow from 6.57 μm to 4.83 μm (“Fig. 4”).

Figure 5 shows the AFM images of the AlCN layers. High CH_4 gas flows led to a high surface roughness of the AlCN layers, as can be seen in the “Fig. 5 (b)”.



(a) **(b)**

Fig. 4 SEM images of deposited AlCN thin films for CH_4/ (CH_4+N_2) gas flow ratio: (a): 66%, (b): 50%.



a) b)

Fig. 5 Morphology of AlCN thin films via the CH_4/ (CH_4+N_2) gas flow ratio, evaluated by AFM: (a) 50%, (b): 66%.

A dense AlCN layer is grown in 50% but not in 66%, where the AlCN layer has a relatively rough structure. Increasing roughness could be due to the fact that the assisting ions lead to significant damage and preferential sputtering effects, mainly during the deposition of the AlCN film. The effects are rather significant, inducing rougher surfaces and the disappearance of the previous texture. Figure 5 shows that films deposited at low CH_4/N_2 ratios are much more homogeneous than those deposited at high ratios. Most of deposited particles size is around 55 nm at low CH_4/N_2 ratios while it is approximately 90 nm at low CH_4/N_2 ratios [13-14].

The hardness values of the AlCN coatings deposited at a temperature of 470 °C with various flow ratios are illustrated in “Fig. 6”, showing a hardness value of 2038 $HV_{0.05}$ for the flow ratio of 50% to a hardness of 1896 $HV_{0.05}$ for the flow ratio of 66%. It means that the hardness of the AlCN coatings decreased as the flow ratio increased. The reduction of hardness can be attributed to two reasons. When the flow ratio increases, the grain size of the AlCN coatings is increased, resulting a decrease in the hardness of AlCN coating. Furthermore, during the growth of the grain size, the chlorine atoms can diffuse into high angle grain boundaries, after exceeding the solubility limit of chlorine in the AlCN lattice [11]. Thus, the hardness of the thin films is decreased.

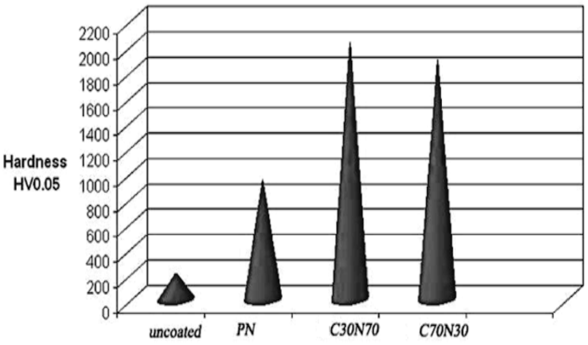


Fig. 6 Hardness values of AlCN coatings in various flow ratios.

4 CONCLUSIONS

The following conclusions can be drawn from this research:

- $AlC_{30}N_{70}$ stoichiometric composition was obtained in 0.5 gas flow ratio and $AlC_{70}N_{30}$ for 0.66 which were different from XPS results.

- XPS peaks indicate that a large fraction of C atoms are bonded to Al atoms, and a low fraction of C atoms exist as amorphous carbon.

-The films grown, using plasma-assisted processes at lower flow ratios, were generally fine-grained and had a denser structure.

- It was found that the rate of growth decreased with increasing the flow ratio.

- Finally, it was found that the surface hardness decreased with increasing the flow ratio due to decreasing in grain size and diffusion of chlorine in grain boundary.

COMPLIANCE WITH ETHICAL STANDARD

This study was funded by University of West Tehran Islamic Azad Branch. Conflict of interest: The authors declare that they have no conflict of interest.

REFERENCES

[1] Chintaiah, N., Ravi kumar, S. T., International Journal of Science, Engineering and Technology Research (IJSETR), Vol. 7, 2018, pp. 2278 -7798.

[2] Casati, R., Vedani, M., A Review, Vol. 1, 2014, pp. 65-83.

[3] Rie, K. T., Gebauer, A., Woehle, J., Tonshoff, H. K., and Blawit, C., Surf. Coat. Technol., Vol.74-75, 1995, pp. 375–381.

[4] Hedenqvist, P., Olsson, M., Wallen, P., Kassman, A., Hogmark, S., and Jacobson, S., Surf. Coat. Technol. Vol. 41, 1990, pp. 243–256.

[5] Sundgren, J. E., Thin Solid Films.Vol. 128, 1985, pp. 21–44.

[6] Rie, K. T., Gebauer, A., and Woehle, J., Surf. Coat. Technol., Vol. 60, 1993, pp. 385–388.

[7] Ishii, Y., Ohtsu, H., Adachi, T., Ichimura, H., and Kobayashi, K., Surf. Coat. Technol., Vol. 4, 1991, pp. 279–283.

[8] Cullity, B. D., Elements of X-Ray Diffraction, 2nd ed, Addison Wesley., 1978, pp. 154-196.

[9] Niederhofer, A., Bolom, T., Nesladek, P., Moto, K., Eggs, Ch., Patil, D. S., and Veprek, S., J. Surf. Coat. Technol., Vol. 183, 2001, pp. 146–147.

[10] Tadahiro, W., Materials Science Forum, Vol. 638-642, 2010, pp. 368-373.

[11] William, D., Melo, S., José Rubens, G. C., and Vladimir, T. A., J. Materials Research. Vol. 16, No. 3, 2013, pp. 603-608.

[12] Yuanbing, L., Nan, L., Guozhi, R., Jianwei, L., and Xiaohui, L., Materials and Design., Vol. 28, 2007, pp. 969–972.

[13] Jones, B. J., Mahendran, A., Anson, A. W., Reynold, A. J., and Bulpett, R., J. Frank. Diamond and Related Materials, Vol. 19, 2010, pp. 685.

[14] Vinod Babu, C., Yaradi, M., and Teja Thammineni, D., Materials Science and Engineering, Vol. 390, 2018, pp. 012079.

[15] Zangh, H., Yan Tang, S., Raremetals., Vol. 29, 2010, pp. 528.

[16] Kenneth, H., Helena, R., Anssi, L., Kim, W., Sture, H., Staffan, J., Urban, W., Souza, M., and Per, S., Wear, Vol. 267, 2009, pp. 2142–2156.