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Oxygen doping effect on the wettability of diamond-like carbon thin films

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ABSTRACT

Diamond like carbon (DLC) thin films as a great coating to protect biomedical tools and optical devices are being developed. Modifying the surface properties, such as wettability, is necessary in some application. In this research, oxygen doping effect on the DLC films wettability was investigated. Oxygen doped diamond-like carbon (DLC) thin films were deposited by the RF-PECVD method with different oxygen concentrations in feeding gas (0.0, 1.9, 3.8, 5.6, 7.4 and 9.1 vol%). The film's structure was studied by Raman spectroscopy (RS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The chemical composition was determined by a combination of elastic recoil detection analysis (ERDA) and Rutherford backscattering spectroscopy (RBS). Surface roughness and morphology of the films were analyzed by an atomic force microscopy (AFM). Wettability of the films was characterized by measuring the contact angles of the films with water. The results showed that by increasing the incorporation of oxygen into the films' structure, the contact angles of water with films were reduced. The increase in the oxygen content of the films, from zero to 11 at%, caused to reduce water contact angles from 78.4° to 66.0°. By adding the oxygen into the film's structure, C=O and C=C bonds content increased in the films. Due to the more polarizability of C=O and C=C bonds in comparing with C–C and C–H bonds, a polar component of films' surface energy was increased by adding the oxygen to the films' structure. The surface roughness of the un-doped and doped DLC films were so low (less than 1 nm) that they had no roles in the films' surface energy. Doping the DLC films with oxygen caused to increase wettability, without no significant change in the morphology and surface roughness.

1. Introduction

Diamond-like carbon (DLC) is an attractive material due to its unique properties, such as high mechanical hardness, high wear resistance, chemical inertness, low friction coefficients and optical transparency. DLC thin films are suitable for use as protective coatings for biomedical tools and optical devices [1–2]. Wettability of DLC film is a main property in these applications that is depended on surface energy and roughness. In some applications, it is necessary to tailor surface properties of DLC film, such as wettability. Doping or alloying of the DLC film with light elements (B, Si, O, N, and F) and metals is a common method to tailor its properties [3]. Due to the addition of dopant elements into DLC films, the hydrogen content and the ratio of sp^2/sp^3 sites are changed in the film structure, and consequently all properties of these films are affected [4–7]. Already, the incorporation of light elements such as nitrogen [4,8], silicon [5,9], boron [6,10], phosphors [11,12] and fluorine [7,13] into DLC film's structure has been studied. Oxygen as a light element dopant which have the ability to modify surface properties has been considered rarely [14–15]. To the best our knowledge, only Grischke et al. [15] has studied the

wettability of oxygen doped a-C:H films which had been deposited using a gas mixture of acetylene and oxygen (C_2H_2/O_2). The DLC thin films are prepared by various deposition methods, such as ion beam, sputtering, cathodic arc, pulsed laser, and plasma enhanced chemical vapor deposition (PECVD) [1]. Diamond-like a-C:H is a class of DLC films and usually is deposited by PECVD methods [16]. Radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) is a common method for deposition of this DLC film class. The advantages of RF-PECVD method are low-cost deposition, ability to deposition on large area and complex shape substrates, low temperature process (less than 250 °C), high deposition rate and good adhesion to many substrates [17]. Pressure of chamber, power (or bias voltage) and kind of hydrocarbon feeding gas are principle variables of RF-PECVD method. The change of each variable cause to change of DLC films' hydrogen content and ratio of sp^2/sp^3 sites, and consequently to change mechanical, electrical, optical and surface properties of DLC films [18]. In our previous works, the optical and mechanical properties of oxygen doped a-C:H films have been studied [19,20]. In this study, the wettability of doped a-C:H films with different oxygen concentrations were studied. The films were deposited by RF-PECVD method using a gas mixture of

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ethane, argon and oxygen ($\text{CH}_4/\text{Ar}/\text{O}_2$). Then, the correlation between structure and wettability of the films, and the effect of surface roughness on the films' wettability were studied.

2. Experimental details

A RF-PECVD apparatus (Plasma Fanavar Amin Co., Iran) was used to deposit oxygen doped a-C:H films. A mixture of methane (CH_4), Argon (Ar), and oxygen (O_2) was also used as feed gas. The ratio of 9 sccm: 1 sccm: X sccm ($X = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) between the CH_4 : Ar: O_2 was selected. More details about deposition processes has been reported in previous work [17]. In order to investigate the film's structure, Raman spectra of the films were acquired by a dispersive Raman spectrometer with 4 cm^{-1} resolution (Thermo Nicolet Almega). The films were excited by a visible light beam with 532 nm wavelength. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the bonding into film's structure (Bruker Tensor 27). The IR absorption spectra in the range of 400 to 4000 cm^{-1} were collected with 2 cm^{-1} resolution, and then were normalized and deconvoluted into sub-peaks by a mathematical software. Elastic recoil detection analysis (ERDA) and Rutherford backscattering spectroscopy (RBS) were simultaneously used to determine the chemical composition with precision of $\pm 1 \text{ at}\%$. The films were analyzed by irradiation of a $1.8 \text{ MeV } ^4\text{He}^+$ beam which generated by the 3 MeV single-end Van de Graaff accelerator. The RBS spectra were obtained using a SB detector at an angle of 165° with respect to the incident beam. The ERDA spectra were obtained by irradiating the target at an incident angle of 30° . The water contact angles of the films were measured by an optical contact angle measurer instrument (DataPhysics-OCA 15 plus). Each measurement was repeated three times and the average was reported. The measurement accuracy was 0.1° . Morphology and roughness of the films were acquired by an atomic force microscopy (Bruker Nano Inc.) in contact mode with precision of $\pm 0.1 \text{ nm}$.

3. Result and discussion

The Raman spectroscopy is a non-destructive and routine method for characterizing the bonding structure of carbon films [21]. Unlike diamond and graphite Raman spectra, the DLC Raman spectra appear to form of wide peak, which are located in the range from 1000 to 2000 cm^{-1} . Here, the Raman spectra of all films had this feature that has been shown previously [20]. The wide peak of DLC film is created by overlapping two peaks, G (graphite) and D (disorder). The G peak is resulted from stretching mode of all pairs of sp^2 sites (both olefinic and aromatic), whereas the D peak results from breathing mode of all pairs of sp^2 sites which are only located in aromatic rings [1]. Three important factors which fully depended on the DLC film structure, can be extracted from DLC Raman spectra [22]. These factors are position of G peak, full width at half maximum (FWHM) of G peak, and ratio of D peak intensity to G peak intensity (I_D/I_G). In order to extract these factors, the Raman spectra of DLC films were decomposed into two Gaussian line shape peaks (G and D peaks). The extracted factors from two peaks are shown in Table 1. Elastic recoil detection analysis (ERDA) and Rutherford backscattering spectroscopy (RBS) were together

Table 1
Variation of G-peak position, G-peak width and I_D/I_G ratio extracted from Raman spectra.

Flow rate of oxygen in precursor gas (sccm)	G-peak position ($\pm 4 \text{ cm}^{-1}$)	G-peak width ($\pm 4 \text{ cm}^{-1}$)	I_D/I_G ratio (± 0.01)
0.0	1518	175	0.30
0.2	1528	162	0.53
0.4	1550	160	0.71
0.6	1576	143	0.94
0.8	1531	172	0.39
1.0	1545	170	0.47

Table 2
Chemical composition of the DLC films that were derived by the ERDA and RBS methods.

Flow rate of oxygen in precursor gas (sccm)	Element ($\pm 1 \text{ at}\%$)		
	C	H	O
0.0	70	30	–
0.2	70	26	4
0.4	76	17	7
0.6	81	8	11
0.8	75	21	4
1.0	75	19	6

carried out to determine the concentration of hydrogen, oxygen and carbon exactly, and to investigate the uniformity of element distribution in the films' structure. The chemical composition of all films is shown in Table 2. By increasing the oxygen concentration in feeding gas up to 0.6 sccm flow rate, the oxygen concentration into DLC films were raised up to 11 at%. The extracted Raman factors were also changed simultaneously with the change in films' chemical composition. By increasing the oxygen concentration in the films, the G peak position and I_D/I_G ratio were increased, and the width of G peak was decreased. The change of G peak position toward higher wavenumber indicated that the film's structure was varied from olefinic to aromatic. The G peak position was shifted from 1518 to 1576 cm^{-1} by incorporation of 11 at % oxygen in the film's structure. Also, increase in the I_D/I_G ratio indicated an increase in size and number of clusters, and decrease in chain-like groups [22]. Therefore, the size and number of graphite clusters were increased by increasing the oxygen incorporation in the film's structure [19,23]. Olefinic sites (chain-like) possess more carbon-hydrogen bonds in comparison to aromatic sites (rings), therefore, it can be predicted that by increasing the oxygen concentration into film, and the change of structure, the film's hydrogen concentration will be reduced. The ERDA-RBS results showed that there is an inverse relationship between hydrogen and oxygen concentration of the films. With attention to Raman factors (Table 1), it can be seen that the doped DLC film in 11 at% oxygen, possessed highest proportion of sp^2 sites in the structure, in comparison to other films [22]. Furthermore, the ERDA-RBS results demonstrated that oxygen was uniformly distributed into film's structure, and concentration of oxygen, carbon and hydrogen at different depths of films was constant.

In order to characterize the bonding in the film structure, the ATR-FTIR spectroscopy was used. The IR spectroscopy is the common method for characterizing the bonding into the DLC films' structure. The stretching, vibration frequencies of carbon-hydrogen bonds are located in the range from 2800 to 3300 cm^{-1} while that of carbon-carbon bonds are located at lower wavenumbers, around 1600 cm^{-1} [23–25]. Stretching modes of carbon-hydrogen bonds are divided into three zones, the $\text{sp}^1\text{C-H}$ modes in the center of 3300 cm^{-1} , the $\text{sp}^2\text{C-H}_n$ modes in the range from 2975 to 3085 cm^{-1} and the $\text{sp}^3\text{C-H}_n$ modes in the range from 2850 to 2955 cm^{-1} [24]. The normalized absorption spectra were extracted from ATR-FTIR spectra for all DLC films. Two major absorption peaks were seen in the normalized absorption spectra that are shown in Fig. 1. One absorption peak, which was located in the range from 2800 to 3000 cm^{-1} had a

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