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Quantitative Relation between the Hamaker Constant and the Water Contact Angle with *sp*²/*sp*³ Ratio and Hydrogen Content in a Hydrogenated Diamond-Like Carbon Thin Film

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Allotropes of two crystalline carbons, diamond and graphite, are sp^3 and sp^2 hybridized, respectively. In between these two, there is an intermediate structure i.e., the mixture of sp^3 and sp^2 nanocrystalline hydrogenated diamond-like carbon (HDLC) thin films. HDLC thin films were synthesized by the biased enhanced nucleation (BEN) technique in the reactive gas-plasma process (RGPP) under the varying ratio of H_2 and CH_4 flow rates. There are numerous applications of these materials depending on their sp^2/sp^3 ratio and surface properties. The property, hydrophilic/hydrophobic nature of the film surfaces can be measured from the water contact angle on the HDLC surfaces easily which also depends on the sp^2/sp^3 ratio. In this paper, we have evaluated the sp^2/sp^3 ratio indirectly through the water contact angle of the HDLC thin film and under its annealing treatment at low pressure. The sp^2/sp^3 ratio and C1s bonding type were estimated by the XPS spectrum. The study of the surface topography of the HDLC film was made by AFM and SEM. In this study, it can be concluded that the water contact angle on the HDLC surface does not significantly affect the surface morphology. A quantitative relationship is found between the sp^2/sp^3 ratio and the water contact angle of HDLC with hydrogen content, measured by the Angus and Jansen equation, and the Hamaker constant estimated by AFM using different models.

Keywords: Diamond-like carbon, AFM, SEM, Contact angle, sp^2/sp^3 ratio, Hamaker constant.

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1. INTRODUCTION

Surface, as well as bulk material characteristics of HDLC, depend on its synthesis process, like Gas plasma chemical vapor deposition, a sputtering method, ion beam deposition, etc. HDLC does not stand for a particular composition, but it is a combination of sp^2, sp^3 hybrid crystalline, and amorphous carbon lamellar films whose property effectively depends on the synthetic nature. Depending upon the growth status hydrogen may be attached to sp^3 through a dangling bong and partially bonded with sp^2 carbon. The application of HDLC in various fields is remarkable due to its high chemical inertness, low coefficient of friction, low thermal expansion, high degree of hardness, high thermal conductivity, high water resistance, etc. [1, 2]. Some direct methods have been used to measure H-content in Diamond film like ERDA, NRA, etc., and other methods like NMR, and IR absorption can be used to monitor H-content in Diamond-like materials indirectly may compare with the NRA method [3]. But due to being time-consuming and expensive some other methods to measure the hydrogen content of HDLC may be used, such as the correlation method. HDLC mainly contains sp^2 and sp^3 sites, therefore sp^2/sp^3 ratio is the key factor to characterize the thin film property. Some well-known methods for quantitative estimation of the sp^2/sp^3 ratio of HDLC thin film, like X-ray photoelectron spectroscopy [4] [5], nuclear magnetic resonance [6], micro-Raman spectroscopy [7] Auger electron spectroscopy [8], spectroscopic ellipsometry and spectroscopic reflectometry [9], etc. Hamaker constant (A) can be defined as a convenient quantity with which the Van der Waals (VdW) body-body interactions, arising from the interaction of oscillating dipoles in the interatomic bonds of each body, manifest themselves in various aspects of behavior ranging from the determination of surface energies, adhesion properties and consequently wetting behavior of the surface of the body [10]. The formula for 'A' is given by

$$A = \pi^2 \cdot C \cdot \rho_1 \cdot \rho_2, \tag{1}$$

where ρ_1 and ρ_2 are the numbers of atoms per unit volume in two interacting bodies and C is the coefficient in the particle-particle pair interaction [11]. Since Hamaker constant is a system-specific physical constant whose value is independent [12] of the method of measurement, the value of 'A' measured by any accurate technique will agree well with that of any other accurate measurement technique. Hamaker's method and the associated Hamaker constant ignore the influence of an intervening medium between the two particles of interaction. Comparison of the result of 'A' by all methods for HDLC samples can be correlated with the sp^2/sp^3 ratio and wettability of the samples.

The quantitative correlation between sp^2/sp^3 ratio and water contact angle of carbon-based materials diamond (100 % sp^3 site), amorphous hydrogenated carbon thin film (a-C, up to 60% sp^3 sites), amorphous carbon (a-C, up to 90% sp^3 sites) made by Ostrovskaya et al., 2002. Another interesting observation was shown by Mattia et al., 2006, that a correlation exists between water contact angle and graphitization of HDLC by thermal annealing. In this study, a relation between the sp^2/sp^3 ratio and water contact angle is made quantitatively to evaluate the sp^2/sp^3 ratio by the water contact angle, and Hamaker constant. The hydrogen content of HDLC can be obtained from this relation using the Angus and Jansen equation. The surface

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morphology with the surface roughness and surface cluster of the HDLC thin films was measured by AFM and SEM images to glorify the effect of the sp^2/sp^3 ratio with water contact angle.

2. EXPERIMENTAL

A simple preparation [2] of HDLC thin films in reduced pressure biased enhanced nucleation (BEN) method at normal temperature in an asymmetrically capacitive RF (13.56 MHz) combined tool, involves the following two steps: (1) etching of mirror-polished Si(1 0 0) substrate of 20 mm diameter for 1200 s in pure hydrogen (flow rate ~ 500 cm^3/min) plasma, at a pressure of 0.0193 kPa, produced by 30 W RF power-producing dc self-negative bias (~ – 200 V), to remove the oxide layer from the surface of Si(1 0 0) and (2) in situ BEN process using He (flow rate ~ 1500 cm^3/min) plasma produced by 50 W RF power-producing dc self-negative bias (~ – 200 V), with H_2 (flow rate ~ 500 cm^3/min) and CH_4 (flow rate ~ 50 cm^3/min) gases at a total pressure of 0.0756 kPa and at substrate temperature ~ 287 K, for 1800 s deposition time. The as-prepared film was annealed with the constant temperature at 200 °C, 400 °C, and 700 °C for ~ 1800 s at low pressure in presence of Oxygen and cooled to ~ 25 °C. An atomic force microscope (AFM) topography of the sample was obtained in noncontact mode with Si_3N_4 cantilever by a multimode scanning probe microscope (Agilent AFM 5500 series system, USA) having a multipurpose small scanner with a low coherence laser (1 mW power, 670 nm wavelengths (< 50 μm), scan range XY: 0-10 μm; Z: 0-2 μm noise level: XY < 0.1 nm RMS, Z < 0.02 nm RMS. Scanning electron microscope (SEM) (FEI Quanta 200) was used in order to capture the microstructural image of the prepared sample to examine the surface morphology. X-ray Photoelectron Spectroscopy (XPS; England Thermo VG-Scientific inc, Sigma Probe) is used to find C1s type of the bonding and sp^2/sp^3 ratio. To deconvolute the C1s line by curve fitting sp^2, sp^3, CO peaks, and 100% Gaussian is applied. Contact angle measurements were performed by using contact angle (CA) goniometer of ramé hart instrument co. USA (model 250). A small drop of deionized water was placed on the surface of the cleaned HDLC sample using a micropipette, and contact angle was measured using the menu based DROPimage Advanced v2.4 software in situ. The contact angle was measured at least ten times with different drops in order to increase the reproducibility of measurements. Hamaker constant was estimated by using the parametric tip model and by the jump-into-contact method.

3. RESULTS AND DISCUSSION

Fig. 1 indicates the AFM topography of HDLC thin film in as-prepared and in different temperatures. The calculated root means square (rms) values of the as-prepared, annealed surfaces at 200 °C, 400 °C, and 700 °C is 2.3 nm, 2.7 nm, 2.2 nm, and 1.8 nm, respectively. From the RMS values of the surfaces, it may conclude that there is no monotonic trend in changes of the surface due to annealing. A few changes of rms of these HDLC samples suggest surface roughness is not

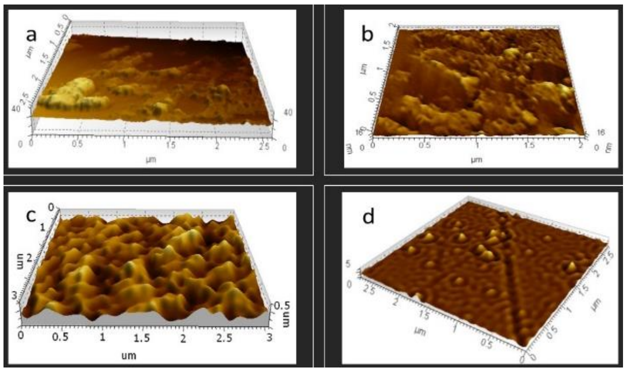

Fig. 1 – AFM images (a) as-prepared, rms: 2.3 nm (b) at 200 °C, rms: 2.7 nm (c) at 400 °C; rms: 2.2 nm and (d) at 700 °C; rms: 1.8 nm of DHLC samples

a key factor of the water contact angle between HDLC and water. Fig. 2 shows the SEM images of as-prepared HDLC thin film and annealed HDLC in different temperatures. The surface morphology is rather smooth, and some cluster-like structure is seen for as-prepared as well as annealed samples. That's mean the surface roughness is not the key factor, but the film property is the critical factor of the wettability of the HDLC thin films [13]. XPS study was conducted to highlight the chemical bonding, sp^2/sp^3 ratio and to find the occurrence of oxygen-containing groups in HDLC thin film for as-prepared as well as in annealed state at different temperatures. The result was specified in Fig. 3. XPS of HDLC demonstrated C and O signals corresponding to the binding energy (eV). A prominent peak of C signal is observed with a binding energy of 285.5 eV, which is owing to the C–H, C=C and C–C groups. The peak concentrated at the binding energies of 534.5 eV can be assigned to the C=O and C– O bonds.

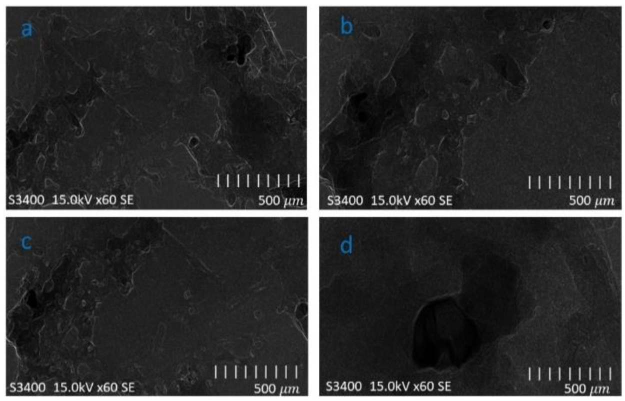

Fig. 2 – SEM images of the sample: (a) as-prepared, (b) at 200 °C, (c) at 400 °C, and (d) at 700 °C temperatures

This CO may arise due to impurity in as-prepared and due to the presence of oxygen at the annealed time in the annealed HDLC samples. The water contact angle could reduce due to the hydrophilic property of oxygen-containing groups. The water contact angles of as-prepared and annealed HDLC at 200 °C, 400 °C, and 700 °C is 43.5°, 54.5°, 57°, and 63° respectively is shown in Fig. 4. This result shows that the HDLC surfaces becoming hydrophilic to more hydrophobic in nature due to thermal annealing which is leading to graphitization [14] of the sample. For as-prepared and annealed HDLC at 200 °C, 400 °C, and 700 °C the sp^2/sp^3 ratio is 1.87, 3.25, 5.56 and 6.98 respectively. This correlation between sp^2/sp^3 ratio and annealed temperature is like some literature [15].

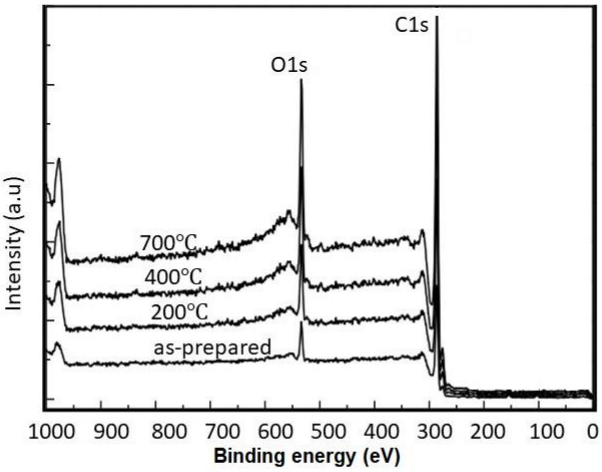

Fig. 3 – XPS spectra C1s and (b) O1s of as-prepared and annealed HDLC thin film.

Table 1 – Comparative study among Hamaker constant, water contact angle, hydrogen content and sp^2/sp^3 ratio

Sample	Water contact angle	A by jump into contact (10^{-19} J) (Eq. (5))	A by sphere flat method (10^{-19} J) (Eq. (4))	Hydrogen content (at. %)	sp^2/sp^3
as-prepared	43.5°	19.09 ± 0.44	14.37 ± 0.51	38.80	1.87
200 °C	54.5°	6.37 ± 0.32	4.79 ± 0.31	34.90	3.25
400 °C	57°	5.0 ± 0.37	3.67 ± 0.51	28.03	5.56
700 °C	63°	4.1 ± 0.35	3.50± 0.44	26.36	6.98

C. Argento (1996) and then Achintya Singha (2007) elaborately discussed force-distance relation with parametric tip model by AFM. Their model assumes the tip of the cantilever to be a cylinder followed by a conical section and a spherical cap. The model is completely defined by two parameters: the tip radius R and the cone angle γ. According to this parametric tip-model, the total van der Waals force on the probe due to a flat surface is [16]:

$$F_V\left(h_j\right)=\frac{AR^2\left(1-\sin\gamma\right)\cdot\left(R\sin\gamma-h_j\sin\gamma-R-h_j\right)}{6h_j^2\left(R-h_j-R\sin\gamma\right)^2}+\frac{A\tan\lambda\left(h_j\sin\gamma+R\sin\gamma+R\cos 2\gamma\right)}{6\cos\gamma\left(h_j-R-R\sin\gamma\right)^2}, \quad (2)$$

where the first term corresponds to the contribution of the spherical cap and the second term originates from the cone component of the tip. We have used Si_3N_4 cantilever measured force constant about (0.765 N/m), tip radius ≈ 10 nm and cone angle ≈ 0.365 radians. The Hamaker constant values obtained from Eq. (2) for as-prepared and annealed HDLC at 200 °C, 400 °C, and 700 °C are given in Table 1.

Soma Das et al. reported the Hamaker constant can determined from the deflection of the cantilever at the "jump-into-contact" using the force constant of the cantilever and the tip radius of curvature by the following equation (3) [17].

$$A=\frac{24k_c h_j^3}{27R_t}, \quad (3)$$

where we have used actual cantilever deflection height for attraction = (h_j) Rt = tip radius ≈ 10nm, k_c = measured force constant about (0.765 N/m) and the Hamaker constant values were obtained from Eq. (3) Achintya Singha (20007) for HDLCs sample.

The influence of sp^2/sp^3 ratio on the water contact angle of HDLC thin film is shown in the Table 1. Ostrovskya et al. mentioned the a-C:H thin film properties may vary with the deposition techniques and with the different measurement techniques. The mentioned water contact angle on as-prepared a-C:H is ~ 55° but for our case it is 43.5° measured by the menu-based DROPimage method.

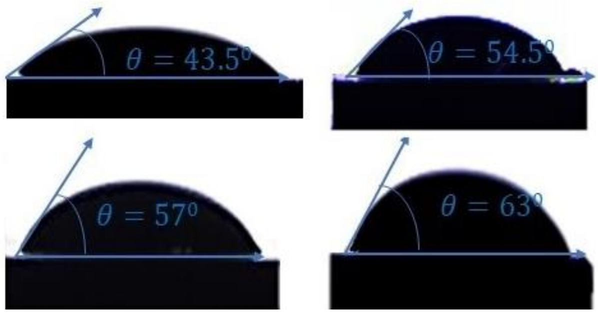

Fig. 4 – Water Contact angle on (a) as-prepared (b) at 200 °C, (c) at 400 °C, and at 700 °C temperatures

Angus and Jansen estimated the sp^2/sp^3 ratio for the random covalent network cluster of hydrogenated diamond like carbon which contains solely sp^2 and sp^3 carbon sites by using the following equation [18].

$$\frac{sp^2}{sp^3}=\frac{8-13x_H}{6x_H-1}. \quad (4)$$

From Table 1, it is clear, with the increase of water contact angle the sp^2/sp^3 ratio also increases. It is a reasonable due increase of graphitization of HDLC by thermal annealing in different temperatures. Another cause of the increase of the water contact angle on the annealed HDLC is the polar part of the water drop on the hydrophobic dispersive surface of HDLC. The measured Hamaker constant is correlated with the sp^2/sp^3 ratio shown in Table 1. Again, the hydrogen content and sp^2/sp^3 ratio of HDLC are correlated. Due to this good agreement of correlation if one obtained sp^2/sp^3 ratio, then using Angus equation [19], hydrogen contain HDLC can be calculated to remove time consumption and expenditure of elastic recoil detection (ERDA), nuclear reaction analysis (NRA), Rutherford backscattering (RBS) methods [20] etc. The hydrogen contained in the atomic percentage of HDLC thin film is shown in Fig. 5. From Fig. 5, it is seen that the

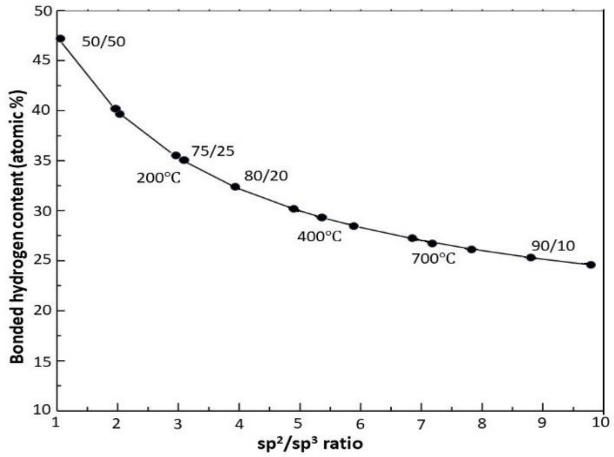

Fig. 5 – Correlation curve between sp^2/sp^3ratio and bonded hydrogen content

hydrogen content decreases with the sp^2/sp^3 ratio due to oxidation of the surface bylosing hydrogen under thermal annealing [18]. This method may be a highly influential method to obtain hydrogen contain irrespective of the preparation technique of the HDLC because from the water contact angle, the sp^2/sp^3 ratio can be measured, and then using the Angus equation hydrogen content can be calculated indirectly.

4. CONCLUSIONS

For the water contact angle of the HDLC surface, the surface roughness is not the key factor but dehydrogenation from HDLC thin film by thermal annealing is effective to increase the hydrophobic nature. However, this hydrophobicity arises due to the increasing of sp^2 character on the HDLC surfaces during the thermal annealing. During thermal annealing at low pressure, some oxidation (formation of some C=O groups) also takes place, but thermal graphitization (dehydrogenation) overcomes this effect on water contact angle. From this potential influence of sp^2/sp^3 ratio on the water contact angle and Hamaker constant, one can readily able to estimate the Hydrogen content in HDLC thin films indirectly when complex and expensive measurement technique is not accessible.

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Кількісне співвідношення між константою Гамакера та кутом контакту з водою із співвідношенням sp^2/sp^3 та вмістом водню у тонкій плівці гідрогенізованого алмазоподібного вуглецю

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Алотропні фази кристалічного карбону, алмазу та графіту, гібридизовані відповідно як sp^3 та sp^2. Між цими двома знаходиться проміжна структура, тобто суміш тонких плівок нанокристалічного гідрогенізованого алмазоподібного вуглецю (HDLC) sp^3 і sp^2. Тонкі плівки HDLC були синтезовані методом зміщеної посиленої нуклеації (BEN) у реактивному газоплазмовому процесі (RGPP) при варіюванні співвідношення швидкостей потоків H_2 і CH_4. Існує безліч застосувань цих матеріалів залежно від їхнього співвідношення sp^2/sp^3 та властивостей поверхні. Властивість гідрофільної/гідрофобної природи поверхні плівок можна легко виміряти за кутом контакту з водою на поверхнях HDLC, який також залежить від співвідношення sp^2/sp^3. У роботі ми оцінили співвідношення sp^2/sp^3 опосередковано через кут контакту з водою тонкої плівки HDLC та під час її відпалу при низькому тиску. Співвідношення sp^2/sp^3 та тип зв'язку C1s оцінювали за спектром XPS. Дослідження топографії поверхні плівки HDLC виконано методами AFM та SEM. Можна зробити висновок, що кут контакту з водою на поверхні HDLC істотно не впливає на морфологію поверхні. Виявлено кількісний зв'язок між співвідношенням sp^2/sp^3 і кутом контакту з водою плівки HDLC зі вмістом водню, виміряним за рівнянням Ангуса та Янсена, та константою Гамакера, оціненою за допомогою AFM з використанням різних моделей.

Ключові слова: Алмазоподібний вуглець, AFM, SEM, Кут контакту, Співвідношення sp^2/sp^3, Константа Гамакера.