# Influence of 'sp ${ }^{2}$ / $\mathbf{s p}^{3}$ ratio' on Hamaker Constant and Surface Energy of Hydrogenated Diamond Like Carbon Surface 

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#### Abstract

A series of Hydrogenated Diamond Like Carbon films were synthesized based upon bias enhanced nucleation (BEN) technique onto $\mathrm{Si}(100)$ at room temperature under varying ratio of flow rates of $\mathrm{H}_{2}$ and $\mathrm{CH}_{4}$ is described elsewhere [1,2]. Thus the as-prepared HDLC samples are named as S44, S42, S40, S38, S36, S34, and S32. In this paper we have measured the hybridization $\left(\mathrm{sp}^{2} / \mathrm{sp}^{3}\right)$ of the HDLC samples quantitatively by Raman spectra and correlate with Hamaker Constant (A) and Surface Energy (E) which are measured by AFM and Contact angle (CA) Goniometry.


Key word: Diamond, Raman, AFM, Hamaker Constant, Surface Energy, Hybridization

## 1. Introduction

Hamaker constant (A) can be defined as a convenient quantity with which the Van der Waals (VdW) bodybody 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 surface of the body [3]. The formula for ' A ' is given by

$$
\begin{equation*}
\mathrm{A}=\pi^{2} \times \mathrm{C} \times \rho_{1} \times \rho_{2} . \tag{1}
\end{equation*}
$$

where $\rho_{1}$ and $\rho_{2}$ are the number of atoms per unit volume in two interacting bodies and $C$ is the coefficient in the particle-particle pair interaction [4]. Since Hamaker constant is system specific physical constant whose value is independent $[3,5]$ of method of measurement, the value of ' A ' measured by any accurate technique will agree well with that from 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. Hamaker constant can be obtained from AFM by force-distance measurements using AFM and from surface energy using CA goniometer. Comparison of the result of ' $A$ ' by all methods for HDLC samples can be correlated with $\mathrm{sp}^{2} / \mathrm{sp}^{3}$ ratio, surface energy and wettability of the samples.

## 2. Experimental

Measurement of Hamaker constant by AFM
2. 1. Using parametric tip model

When the tip-sample separation i.e. actual cantilever deflection height ( $h_{j}$ ) (Fig.2.15.a.) for attraction is not negligible compare to spherical tip radius $(\mathrm{R})$, the van der Waals force $\left(F_{V}^{S}\right)$ between a sphere and a neutral surface is given by [6]

$$
\begin{equation*}
F_{V}^{S}=-\frac{2 A R^{3}}{3 h_{j}^{2}\left(h_{j}+2 R\right)^{2}} \tag{2}
\end{equation*}
$$

And when $R \gg h_{j}$ this equation reduce to

$$
\begin{equation*}
F_{V}^{S}=-\frac{A R}{6 h_{j}^{2}} \tag{3}
\end{equation*}
$$

This assumsion is not valid for our experimental case where $\mathrm{R} \approx 10 \mathrm{~nm}$ and $h_{j}$ around 2 nm again Eq. (2) is not valid here because it assumes that the sphere "floats" in space, by which we mean that its radius is large enough so that all the "nonspherical" parts of the probe are away from the region of the strong interaction [7,

8]. C.Argento (1996) and then Achintya Singha (2007) elaborately discussed about 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 Fig.2.15.b. The model is completely defined by two parameters: the tip radius $R$ and the cone angle $\gamma$. According to this parametric tip-model, the total van der Waals force on the probe due to a flat surface is [9]

$$
\begin{equation*}
F_{V}\left(\mathrm{~h}_{\mathrm{j}}\right)=\frac{A R^{2}(1-\sin \gamma) *\left(R \sin \gamma-h_{j} \sin \gamma-R-h_{j}\right)}{6 h_{j}^{2}\left(R-h_{j}-R \sin \gamma\right)^{2}}+\frac{-A \tan \gamma\left(h_{j} \sin \gamma+R \sin \gamma+R \cos 2 \gamma\right)}{6 \cos \gamma\left(h_{j}+R-R \sin \gamma\right)^{2}} . \tag{4}
\end{equation*}
$$

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 $\mathrm{Si}_{3} \mathrm{~N}_{4}$ cantilever measured force constant about ( $0.765 \mathrm{~N} / \mathrm{m}$ ), tip radius $\approx 10 \mathrm{~nm}$ and cone angle $\approx 0.365$ radians .The Hamaker constant values obtained from Eq.(4) for samples S44 to S32 are given in Table 1.


Fig. 1.(a) Force vs. distance curve by AFM and schematic cantilever deflection (inset), (b) Parametric tip model: R is the tip radius, $\mathrm{r}_{\text {max }}$ is the radius of the cylindrical part of the probe, $\boldsymbol{\gamma}$ is the cone angle, $\boldsymbol{\alpha}=\frac{\pi}{2}-\boldsymbol{\gamma}$ is the angle included in the spherical cap, $\mathrm{h}_{\mathrm{j}}$ is the probe-sample separation, $r$ is the radius at any point on the surface, $x$ is the distance from the cone apex, and $x, y$ and $z$ define the spherical cap section and the conical section of the probe [7, 9].

### 2.2. Using jump-into-contact method

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 (5) [10]

$$
\begin{equation*}
A=\frac{24 k_{c} h_{j}^{3}}{27 R_{t}} \tag{5}
\end{equation*}
$$

Where we have used actual cantilever deflection height for attraction $=\left(h_{j}\right) \mathrm{R}_{\mathrm{t}}=$ tip radius $\approx 10 \mathrm{~nm}, \mathrm{k}_{\mathrm{c}}=$ measured force constant about ( $0.765 \mathrm{~N} / \mathrm{m}$ ) and the Hamaker constant values were obtained from Eq. (5) [7] for HDLCs sample.

## 2. 3. Surface energy method

Nancy A.Burnham et al. [11] explained the Hamaker constant (A) A=24 $=D_{0}^{2}\left(\gamma_{1} \gamma_{2}\right)^{1 / 2}$
through equation (6) that when surface energy of tip $\left(\gamma_{1}\right)$ and surface energy $\left(\gamma_{2}\right)$ of the sample. Here we have taken $\gamma_{2}$ from our calculated value by 3L method [12] and $\gamma_{1}$ was taken from literature [13] $\mathrm{D}_{0}=0.2 \mathrm{~nm}$ and Hamaker constant values were calculated for HDLCs sample.

### 2.4. Measurement of $\mathbf{s p}^{2} /$ sp $^{3}$ ratio by Micro Raman

Raman spectrum was used to estimate the ratio of $\mathrm{sp}^{2}$ and $\mathrm{sp}^{3} \mathrm{C}$ in a typical bulk HDLC sample [14]. From the position of G band in the Raman spectrum of HDLC film we can estimate, using an empirical relation $\mathrm{sp}^{3}$ content $=0.24-48.9\left(\omega_{\mathrm{G}}-0.1580\right)$, approximately $45 \% \mathrm{sp}^{3}$ and $55 \% \mathrm{sp}^{2}$ carbons in the film [1]. Our result is similar to the $40: 60$ ratio observed in amorphous hydrogenated carbon films having hexagonal graphite and diamond as coherent domains [15]


Fig. 2. Comparatives Raman spectrum of S44 to S32 HDLC films onto Si (100) substrate; Excitation wavelength 488 nm , laser power 7.5 mW , grating $1800 \mathrm{gr} / \mathrm{mm}$, objective 100 x , aperture $100 \mu \mathrm{~m}$.

Estimation of the ratio of $\mathrm{sp}^{2}: \mathrm{sp}^{3}$ for the samples S 44 to S 32 is made using the formula $\mathrm{sp}^{3}$ content $=0.24-48.9$ ( $\omega_{\mathrm{G}}-0.1580$ ) [1] from the knowledge of G peak position $\left(\omega_{\mathrm{G}}\right)$ of Raman spectra ( Fig.2.) and the values are shown in table 1.

## 3. Result and discussion

Summary of the results is shown in the table 1 and from the results we may decide as prepared HDLC synthesized by BEN process under various ratio of flow rates of $\mathrm{H}_{2}$ and $\mathrm{CH}_{4}(\sim 44,42,40,38,36,34,32)$ have a great influence of 'Hamaker constant (A) on the parameters ' $\mathrm{sp}^{2} / \mathrm{sp}^{3}$ ratio', 'Surface Energy(E)' and 'van der waals force of attraction (F)' of HDLC samples.

Table 1. A comparative study table of 'A' on the parameters ' $\mathrm{sp}^{2} / \mathrm{sp}^{3}$ ratio', ' E ' and ' F ' of HDLC samples

| Sample | $\begin{gathered} E \\ \begin{array}{c} \text { (3Liquid } \\ \text { method) } \\ \left(\mathrm{mj} / \mathrm{m}^{2}\right) \end{array} \end{gathered}$ | $\begin{gathered} \mathbf{F} \\ (\mathrm{nN}) \end{gathered}$ | A $\begin{gathered}\text { by Jump } \\ \text { into }\end{gathered}$ <br> Contact method ( $10^{-19} \mathrm{~J}$ ) <br> (Eq.5) | A <br> by Sphere Flat <br> method <br> ( $10^{-19} \mathrm{~J}$ ) <br> (Eq.4) | A Estimated from E ( $10^{-19} \mathrm{~J}$ ) ( Eq.6) | $\begin{gathered} \mathrm{sp}^{3} \\ \% \end{gathered}$ | $\begin{gathered} \mathrm{sp}^{2} \\ \% \end{gathered}$ | $\begin{aligned} & \hline \mathrm{sp}^{2} / \\ & \mathrm{sp}^{3} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| S-44 | $\begin{aligned} & 40.83 \\ & \pm 0.10 \end{aligned}$ | $1.38 \pm 0.25$ | $\begin{gathered} 4.21 \\ \pm 0.38 \end{gathered}$ | $2.50 \pm 0.46$ | $\begin{gathered} 4.36 \\ \pm 0.15 \end{gathered}$ | 37.70 | 62.30 | 1.65 |
| S-42 | $\begin{gathered} 41.90 \\ \pm 0.06 \end{gathered}$ | $1.47 \pm 0.30$ | $\begin{gathered} 5.02 \\ \pm 0.42 \end{gathered}$ | $2.67 \pm 0.51$ | $\begin{gathered} 4.42 \\ \pm 0.45 \end{gathered}$ | 38.67 | 61.33 | 1.59 |
| S-40 | $\begin{gathered} 41.67 \\ \pm 0.20 \end{gathered}$ | $1.64 \pm 0.17$ | $\begin{gathered} 6.37 \\ \pm 0.31 \end{gathered}$ | $2.79 \pm 0.31$ | $\begin{gathered} 4.41 \\ \pm 0.30 \end{gathered}$ | 39.65 | 60.35 | 1.52 |
| S-38 | $\begin{array}{r} 42.73 \\ \pm 0.15 \end{array}$ | $1.73 \pm 0.30$ | $\begin{gathered} 7.13 \\ \pm 0.41 \end{gathered}$ | $3.13 \pm 0.52$ | $\begin{gathered} 4.46 \\ \pm 0.32 \end{gathered}$ | 41.11 | 58.89 | 1.43 |
| S-36 | $\begin{gathered} 42.87 \\ \pm 0.40 \end{gathered}$ | $1.74 \pm 0.26$ | $\begin{gathered} 8.02 \\ \pm 0.34 \end{gathered}$ | $3.16 \pm 0.48$ | $\begin{gathered} 4.47 \\ \pm 0.44 \end{gathered}$ | 42.58 | 57.42 | 1.35 |
| S-34 | $\begin{array}{r} 43.35 \\ \pm 0.35 \end{array}$ | $2.41 \pm 0.32$ | $\begin{gathered} 20.09 \\ \pm 0.44 \end{gathered}$ | $4.37 \pm 0.51$ | $\begin{gathered} 4.49 \\ \pm 0.12 \end{gathered}$ | 45.03 | 54.97 | 1.18 |
| S-32 | $\begin{gathered} 44.20 \\ \pm 0.20 \end{gathered}$ | $\begin{gathered} 1.92 \\ \pm 0.18 \end{gathered}$ | $\begin{gathered} 6.13 \\ \pm 0.31 \end{gathered}$ | $3.64 \pm 0.32$ | $\begin{gathered} 4.54 \\ \pm 0.20 \end{gathered}$ | 46.00 | 54.00 | 1.22 |

## 4. Conclusion:

It is seen from table 1 with the decrease of $\mathrm{sp}^{2} / \mathrm{sp}^{3}$ ratio surface energy as well as Hamaker constant gradually increases irrespective of methods used due to increase of number density increases for hydrogen incorporation. Hence, measuring the $\mathrm{sp}^{2} / \mathrm{sp}^{3}$ ratio we can predict the surface energy as well as Hamaker constant of HDLC surface.

## Acknowledgements

One of the authors (HSB) thanks University Grant Commission Reference No..F.PSW-140/15-16 (dated 15 Nov-2016), Govt. of India for funding during XII plan period for carrying out the present work. We thank Dr.S. Chatterjee, Dr. L. Das for technical help and Dr. S Chattopadhyay and Dr. S Bhuia for fruitful scientific discussions

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