

INFLUENCE OF THE OPERATIONAL PARAMETERS ON THE WETTABILITY OF THE DLC FILMS DEPOSITED BY TVA METHOD

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1. Introduction

Wetting of solid substrates by liquids is a fundamental phenomenon with relevance to both the technological and natural worlds. Applications include the spreading behaviour of liquids on coatings, as well as flows in oil reservoirs and chemical reactors.

For solid surfaces, the concept of wettability is defined by mean of surface energy. The surface free energy is the extra energy needed to form a material surface exposed to gas or vacuum. The surface energy of the films is an important factor due to the fact that it can give some clues to the surface properties of the thin film could be crucial for applications of various branches of industry.

Surface modification can change surface chemical composition and structure and the surface free energy. The exact knowledge of the surface free energy of films is essential for optimizing deposition parameters and coatings processes.

A common way of estimating solid surface energies is to measure the contact angle that a liquid makes with its surface. The contact angle measurements can be performed by establishing the tangent angle of a liquid drop with a solid surface. An imaging system (SEE SYSTEM) was used to measure contact angle of testing liquids droplets on the deposited films.

This measurement is considered to be a relatively simple, useful and sensitive tool for assessing hydrophobicity or hydrophilicity of a surface¹.

This technique is generally applied only to low energy solid surfaces, as most available liquids as water and ethylene glycol have relatively low surface tensions and wet solids with higher surface energy. In the contact angle measurement process, the selection of appropriate test liquids is sometimes sophisticated².

If the energy required to create the solid-liquid (γ_{sl}) interface is greater than that required for creation of a solid-vapour (γ_{sv}) interface, then the critical angle will be greater than 90° . In other words, the liquid will bead up on the surface to minimize the solid-liquid interfacial area.

For DLC films deposited on different substrates the evaluation of the surface energy with contact angle measurement using different liquids represents an optimum method³. The diversity of methods used for the deposition of diamond-like carbon films provides the flexibility to tailor their properties according to specific needs and potential applications.

The aim of this paper is to analyse the surface free en-

ergy by meaning of the contact angle of the nanostructured carbon thin films deposited by an original method: Thermionic Vacuum Arc (TVA). By variations of plasma treatment conditions it is possible either to increase or decrease the wettability of the surface

2. Experimental set-up

The deposition of the DLC thin films was carried out by the Thermionic Vacuum Arc (TVA) method. Because this system can heat any material at relevant temperature it is one of the most adequate deposition technologies for evaporate and condensate on a substrate high melting point materials. Moreover, it has been already reported to be a very suitable method for deposition of high purity carbon thin films with compact structure and extremely smooth, just convenient for nanostructured film synthesis⁴.

Thermionic Vacuum Arc (TVA) deposition method consists from an externally heated cathode surrounded by a Wehnelt cylinder. The vapors are obtained by heating the material with thermo electrons generated by the externally heated filament of a circular form placed above the anode. The anode used was a graphite rod⁵.

The cathode and the vacuum chamber are grounded, so the carbon plasma has a potential against the chamber wall equal with the cathode potential fall. On the substrate are deposited, with the evaporated neutral atoms, the incident energetic ions.

The cathode can be mounted in various positions against the anode. The highest density of plasma vapors is obtained above the anode. Due to the potential differences between the plasma potential and the walls, the ions are accelerated to the chamber walls.

Practically, the deposition takes part in the vapors of the anode materials, the deposited film containing only the ions of this material and therefore the energy of ions could achieve values up to 500 V. In this way the carbon film is bombarded during its deposition by carbon ions with established value of energy.

In Fig. 1 is presented the experimental setup. The symmetry of the cathode – anode arrangement allows

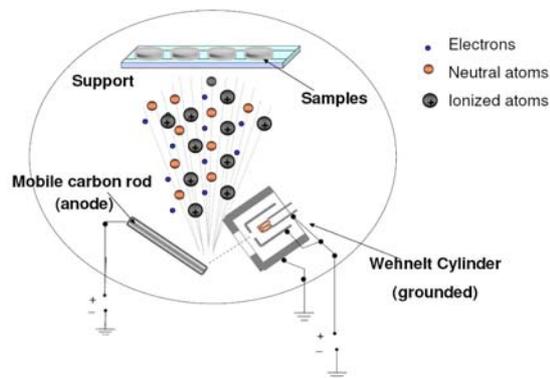


Fig. 1. Experimental setup of the Thermionic Vacuum Arc (TVA) system

Table I
Experimental parameters for the deposition of the DLC films on samples

Sample no.	B3	B5	B7	B8	B10	B11	B12
d [cm]	20	29	28	30	31	35	35
I _f [A]	50	50	51	50	45	53	45

a perpendicular bombardment of the electron beam on the anode surface.

Due to the high energy dissipated in the unit volume plasma, the material is strongly dispersed and completely droplets free. The obtained thin film was very smooth and in some experimental conditions had a nano-scale structure.

In Table 1 are presented the main experimental parameters involved in this study: the distance between samples and the point of the ignition of the discharge (**d**) and the intensity of the heating current of the filament (**I_f**). The voltage applied ranged between 2 kV to 4 kV.

The variation of the contact angle measurements with ion energy is believed to be correlated to the topography of the films^{7–9}.

An imaging system (SEE SYSTEM) was used to measure contact angle and shape of testing liquids droplets for the prepared samples. This system mainly consist of a device with a adjustable view-station sample support and a CCD camera, which observe a liquid drop on the studied surface and a computer software that calculates the contact angle, the total free surface energy and her components¹⁰.

For making the measurements, samples were placed on the top of a miniature height adjustable view-station in front of the CCD camera. Static contact angles were measured in the horizontal direction.

The drops of 0.5 µl volumes was released on the thin film surface in 10–15 locations and the data were averaged. Small droplets of constant volume were used for the measurements in order to minimize gravitational effects.

During the measurements the room temperature was 22–25 °C and the contact angle for spread liquid droplets was determined from the side view.

For determination of the free surface energy some mathematical formulas were used, for equations of states models (Kwok-Neumann model, Li-Neumann model, Wu model) and for OWENS-WENDT method.

Because plenty of samples have to be analyzed for determination of the surface energy the results can differ from sample to sample and in consequence the statistical free energy distributions could be undesirably distorted by the non-uniformity of the samples. Therefore we snapped the drops of various liquids on one sample only and we determinate the contact angle from these snaps.

The operator selects the points of the interface with a normal error distribution, being discredited due to the finite resolution of the analyzed bitmap. The generated values of contact angles were analyzed with the two-liquid equations of states models and with OWENS-WENDT method and compared¹¹.

The accuracy of the values obtained is essentially influenced by the test liquids selected. On the one hand an in-

fluence on the surface by the test liquid by partial etching or dissolving must be ruled out. On the other hand, the surface tension of the test liquid must not be changed by soluble substances possibly existing on the solid surface. If one or both of the described processes take place, this manifests itself by a strong variation of the measured contact angles in spite of a visually homogeneous surface, and by a poor reproducibility of the results.

3. Results and discussions

The contact angle method uses the ability of a liquid to flow in response to the tension generated by the differences in surface energies at the solid – liquid contact line.

Typical images frames acquired by the image analysis system described above are displayed in Fig. 2. The figure shows a printout of the sample of experimental measurement for ethylene glycol and water spreading on polycarbonate substrate. Selection of several points of solid–liquid and liquid–vapor interface makes possible to fit the drop profile and to calculate the tangent angle of the drop with the solid surface. The contact angle for spreading of liquid droplets was determined from the side view. These data were digitalised and measured using the SEE SYSTEM software.

The equilibrium contact angle was given by Young when a drop of liquid lies on a solid surface. Young's equation is^{12,13}:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (1)$$

where γ_{SL} , γ_{SV} , and γ_{LV} are solid-liquid, solid-vapour and respectively liquid-vapour interfacial tensions which measure the free energy, θ is the equilibrium contact angle.

The OWENS-WENDT method requires the use of at least two test liquids with known surface tension and its polar and dispersive contributions. Each additional liquid will increase the accuracy of the estimation¹⁴.

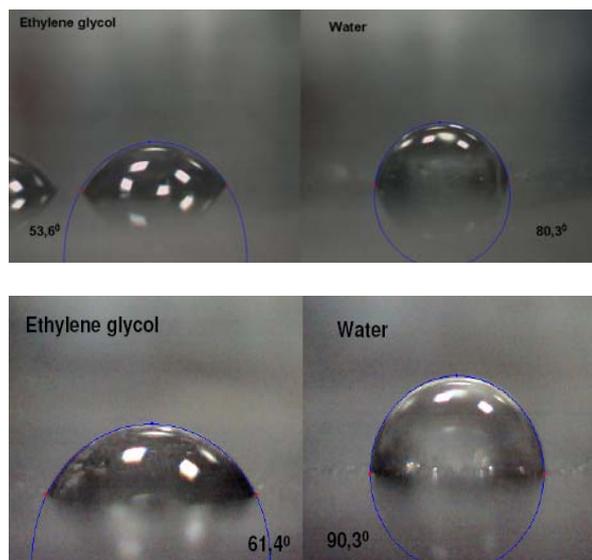


Fig. 2. Pictures of the droplets on sample B3 (up) and samples B12 (down)

The formula for equation of states proposed by Kwok-Neumann in combination with the Young's equation gives:

$$\cos\theta = -1 + 2 (\gamma_{sv}/\gamma_{lv})^{1/2} [1 - 0,0001057(\gamma_{lv} - \gamma_{sl})^2] \quad (2)$$

The equation derived by Li and Neumann combined with Young's equation yields:

$$\cos\theta = -1 + 2 (\gamma_{sv}/\gamma_{lv})^{1/2} \exp(-0,0001057(\gamma_{lv} - \gamma_{sl})^2) \quad (3)$$

Wu suggested for equation of state the following expression:

$$\gamma_c = \frac{\gamma_l(1 + \cos\theta)^2}{4} \quad (4)$$

where γ_c is function of interaction parameter on the surface free energy.

The equation proposed by Owens and Wendt is an extension of the equation give by Fowkes and propose a division of the total surface energy in two components: the dispersive force component γ^d and hydrogen bonding component γ^p .

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p}\right) \quad (5)$$

Combining this equation with Dupre's formula the following term is obtained⁹:

$$(1 + \cos\theta)\gamma_l = 2\left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p}\right) \quad (6)$$

In Table II are presented the values obtained for the contact angle in the case of the two liquids used for measurements: water and ethylene glycol.

The data in the table shows clearly that there are differences in the contact angles between the treated films that were closer of the ignition of plasma and the films obtained at a bigger distance from the plasma.

The obtained values of the contact angle, in the case of water as testing liquid, vary from 77.44° to 90.34° and a constant increase is observed for samples B8, B10, B11 and B12.

Using ethylene glycol as liquid test the obtained values are between 51.27° and 61.42° and the samples B11 and B12 present 5 respectively 6 degrees visible increased compared with the previous samples.

In Fig. 3 the total film surface energy calculated with the

Table II
Contact angle values for DLC films

Sample no.	Contact angle water [°]	Error	Contact angle ethylene glycol [°]	Error
B3	80.67	0.40	53.93	1.46
B5	77.68	0.28	55.28	0.39
B7	79.46	0.34	51.53	0.32
B8	77.44	0.36	51.27	0.32
B10	83.25	0.20	54.62	0.18
B11	85.37	0.52	60.39	0.41
B12	90.34	0.27	61.42	0.33

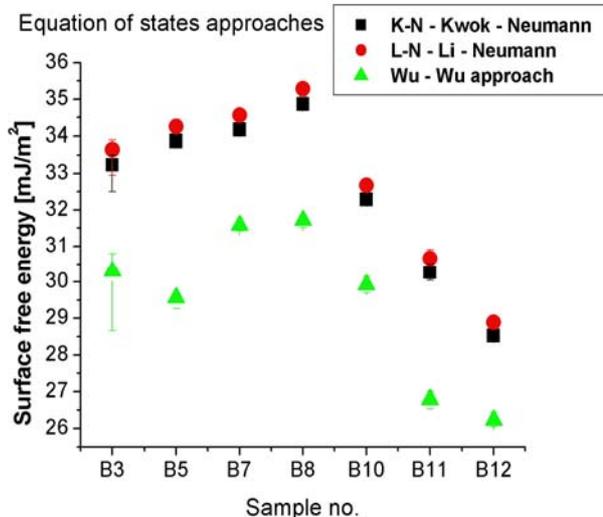


Fig. 3. Equations of states approaches

two liquids by mean of equations of states approaches are presented.

As can be noticed in Fig. 4 the total free surface energy of the thin film present, for Kwok-Neumann and Li-Neumann methods, have the same increased linear pattern for the first four samples with values of the surface energy from 33.23 to 34.86 mJ m^{-2} (K-N method) and 33.63 to 35.28 mJ m^{-2} (Li-N method).

For the last three samples a decreased is observed from 32.28 to 28.53 mJ m^{-2} (KN method) and 32.67 to 28.89 mJ m^{-2} (LiN method), the values of the surface energy for the two equation of state mentioned above are almost the same.

A similar distribution is observed for the Wu approach, with smaller values of the surface energy from 31.58 to 26.23 mJ m^{-2} .

In Fig. 4 are represented the variation of total surface energy g_{total} , of the dispersive component g_{LW} and the polar component g_{AB} obtained by mean of Owens Wendt model.

The total surface energy and LW component (g_{LW}) present the same variation of the surface energy and values are between 27.86 – 32.55 mJ m^{-2} for g_{total} and 17.85 – 27.99 mJ m^{-2} for LW component of the energy. The g_{AB} component describe a plot variation whit values from 26.23 to 31.71 mJ m^{-2} .

4. Conclusions

The SEE SYSTEM device and software offers an easy way to determine the surface energy of thin films deposited on different substrates.

The contact angle measurements of the samples deposited by TVA method have shown reproducible results ranging from 90.34 to 77.44 degrees for water and 51.27 to 61.42 degree for ethylene glycol which implies low ion energies of surface energy values. In this way, it was proved a hydrophobic character of these films.

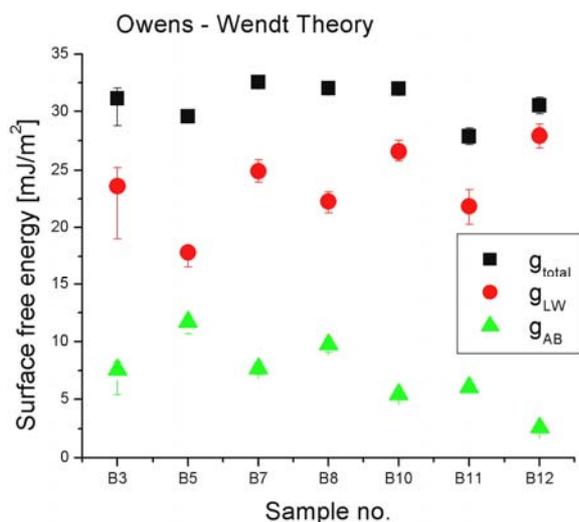


Fig. 4. Plot of the surface free energy obtained with Owens-Wendt method

The highest value of the surface free energy has been obtained in the case of sample B8 for Li-Neumann equation of states approaches. Contact angle can reflect the wettability of materials, and it is influenced by many aspects such as surface characters, roughness and temperature.

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