Surface characterization and orientation interaction between diamond-like carbon layer structure and dimeric liquid crystals

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Abstract. Diamond-like carbon (DLC) and amorphous carbon films are very promising type of semiconductor materials. Depending on the hybridization sp²/sp³ ratio, the material’s band gap varies between 0.8 and 3 eV. Moreover carbon films possess different interesting for practice properties: comparable to the Silicon, Diamond like structure has 22-time better thermal conductivity etc. Here we present one type of implementation of such type nanostructure. That is one attempt for orientation of dimeric LC by using of pre-deposited DLC layer with different ratio of sp²/sp³ hybridized carbon content. It could be expected a pronounced π-π interaction between s and p orbital levels on the surface and the dimeric ring of LC. We present comparison of surface anchoring strengths of both orientation inter-surfaces DLC/dimeric LC and single wall carbon nanotubes (SWCNT)/dimeric LC. The mechanism of interaction of dimeric LC and activated surfaces with DLC or SWCNT will be discussed. In both cases we have π-π interaction, which in combination with hydrogen bonding, typical for the dimeric LCs, influence the LC alignment. The Raman spectroscopy data evidenced the presence of charge transfer between contacting hexagonal rings of DLC and the C = O groups.

1. Introduction

The alignment process of liquid crystal (LCs) is of significant importance for fundamental researchers aiming to understand the variety of phenomena observed at the interface liquid crystal (LC) – aligning surfaces. Generally, thentatic (NLC) director \( \mathbf{n} \) (the average direction of the longer axis of the LC molecules) can be collinear with the LC cell boundary surfacenormal (z axis) or perpendicular to it, thus determining the two typical surface symmetries, homeotropic and planar respectively [1].

In the case \( n \perp z \), \( n \) follows all possible directions over the boundary \( xy \) surface plane. However, because of the anisotropic surface properties, practically an “easy” axis appears. It defines a special direction \( \mathbf{n}_e \), determined by an unit vector at the interface plane, which minimizes the interface free energy. The “easy” direction can be created in many ways. It exhibits the “anchoring” of \( \mathbf{n}_e \) on the interface. The most popular one is the rubbing of the polymer (e.g. polyimide) surface with special cloths or SiOx oblique evaporation, thus creating an orienting surface which causes \( \mathbf{n}_e \) to align along the rubbing direction. Recently we applied a new method for surface orientation of LCs, by imposing unidirectional oriented single wall carbon nanotubes (SWCNTs) and found that such deposited carbon nanostructures significantly increase both the strength of the surface “anchoring” and the surface memory effects [2, 3]. As an important result we indicated that the carbon structures, mainly due to the electronic π–π interaction, induce in the vicinity of the orienting surface a double electric layer (selective electric ion adsorption), which strongly influenced the surface forces. Thus, the surface orientation of the LC system can be modified using the carbon structures, such as,
SWCNTs, amorphous carbon (a-C) or diamond-like carbons (DLC), which provoke a selective ion adsorption and trapping of LC bulk charges, thus leading to surface charge density increase.

The goal of the present work is to estimate efficiency of the a-C and DLC layers deposition on the alignment of the nematic (N) dimeric liquid crystals. The $\pi-\pi$ impact ability of a-C and DLC material on formation of an N LC monocrystals will be indicated. Using the liquid crystal anchoring strength estimated at orienting substrates treated with a-C and DLC/ITO we will present a comparison with that of SWCNT/ITO treated surfaces [3]. We analyze the influence of the dimeric LC structure on the growth of oriented N domains at different a-C and DLC coatings.

Diamond-like carbon (DLC) and amorphous carbon films are very promising type of semiconductor materials. Depending on the hybridization $sp^2/sp^3$ ratio, the material’s band gap varies between 0.8 and 3 eV. The primary desirable qualities of DLC are hardness, wear resistance, and slickness [4]. DLC is usually applied as coatings to other materials that could adopt some of those properties. The more common carbon atoms in DLC are in $sp^3$ hybridized state predominantly and they possess very high hardness and electrical resistivity. The hardness as well as the resistivity decreases with increasing of the $sp^2$ content of the carbon film [5]. By mixing these types in various ways at the nanoscale level of structure, DLC and a-C films can be made that at the same time are amorphous, flexible, thus presenting interesting material characteristics. The hardest, strongest, and slickest is such a mixture, known as tetrahedral amorphous carbon (ta-C). Such type of carbon structure can be considered to be the "pure" form of DLC, since it consists only of $sp^3$ bonded carbon atoms. The amorphous graphite films consists of predominantly $sp^2$ hybridized carbon without long-range ordering.

2. Experimental
The experiments have been carried out with $4-n$-alkoxybenzoic acids, nOBAs, which are widely used as components in supramolecular hydrogen bonded LCs. Two of them with alkyl chain lengths of $n = 7$ and 8 have been exploited, which have the following phase transitions:

**7OBA:** $Cr \leftrightarrow 92^\circ C SC \leftrightarrow 98^\circ C N \leftrightarrow 146^\circ C I$;

**8OBA:** $Cr \leftrightarrow 101^\circ C SC \leftrightarrow 108^\circ C N \leftrightarrow 147^\circ C I$;

Its chemical structure in dimeric form is demonstrated below:

![Chemical Structure](image)

The LC material in its isotropic phase was filled in the cell using the capillary force action. The gap between the glass plates, defining a cell thickness of 12 μm, was maintained with Mylar spacers. The temperature of the sample was varied with a rate of 0.2 °C min$^{-1}$ by a hotstage temperature controller Linkam TMS 90, and the chosen experimental temperature was stabilized with an accuracy of ±0.1 °C. Monitoring the optical textures, in the liquid crystal cell (LCC) $xy$ plane was carried out using a video camera Hitachi on a microscope Zeiss NU2. In turn, the optical signal was studied by video capturing equipment.

We deposited carbon thin films applying the plasma enhanced chemical vapor deposition (PECVD) method, which is widely used for coating of thin carbon films due to its high reliability. By this method the $sp^2/sp^3$ hybridized carbon ratio in the films can be varied with the plasma voltage. We deposited thin films on indium-thin oxide (ITO) coated glass substrates aiming of obtaining layers with different phase composition and thickness. It was also expected that the increased number of $\pi$-bonds in $sp^2$-dominated carbon films will enhance additionally the orientation of liquid crystals inserted on the carbon films. Several specimens were also nitrogen doped during the deposition in order to decrease the resistance of the carbon layer.

For the experiments we used four types of carbon films designated as follows: C_02, TCH_03, TC_04 and TCH_05 (the specimens TCH_03 and TCH_05 are doped with about 0.2-0.4 at% nitrogen). The thickness and phase composition of carbon films were determined by ellipsometric and X-ray photoelectron spectroscopy measurements carried on control samples. The XPS study enables
distinguishing of sp² and sp³ fractions [6, 7]. The ellipsometry measurements were performed using J.A. Woollam Co., Inc. M2000D rotating compensator spectroscopic ellipsometer with a CCD spectrometer with wavelength range from 193 to 1000 nm. Experimental data for \( \Psi \) and \( \Delta \) were acquired at angles of incidence of 55, 60, 65, 70 and 75 degrees and were modelled using the CompleteEASE Woollam Co., Inc. software. The thickness of C_02, TCH_03, TC_04 and TCH_05 specimens according to the ellipsometry studies is 12-14, 140, 70 and 20 nm, respectively. The X-ray photoelectron spectra were obtained using non-monochromatized Al Kα (1486.6 eV) radiation in a VG ESCALAB MK II electron spectrometer under base pressure of 1x10⁻⁸ Pa. The spectrometer resolution was calculated from the Ag3d₅/₂ line with the analyzer transmission energy of 20 eV. The full width at half maximum (FWHM) of this line is 1 eV. The spectrometer was calibrated against the Au4f₇/₂ line (84.0 eV) and the samples’ charging was estimated from C1s (285 eV) spectra from natural hydrocarbon contaminations on the surface. The accuracy of the binding energy (BE) measured was 0.2 eV. The photoelectron spectra of C1s, O1s and N1s lines of carbon films deposited on different substrates were recorded and corrected by subtracting a Shirley-type background and quantified using the peak area and Scofield’s photoionization cross-sections. The sp²/sp³ ratio in different specimens is about 90% in C_02 and about 60% in TCH_03, TC_04 and TCH_05 specimens according to XPS results. The results of XPS and ellipsometry measurements are summarized in Table 1 and the carbon films can be classified as amorphous carbon (a-C): C_02 specimen as well as tetrahedral carbon (ta-C): specimen TC_04 and hydrogenated ta-C (ta-C:H): specimens TCH_03, TCH_05. The Raman spectroscopy and especially the dispersion and the intensity ratio of D and G bands are established to enable the determination of sp²/sp³ ratio in the films [8]. Our Raman measurements were carried out in the micro-Raman spectrometer HORIBA Jobin Yvon Labram HR 800 Visible with a He-Ne (633 nm) laser. The laser beam with 0.5 mW power was focused on a spot of about 1 μm in diameter on the studied surfaces, the spectral resolution being 0.5 cm⁻¹ or better. The Raman spectroscopy measurements were performed directly on the thin films deposited on ITO/glass substrates. The observed features in figure 1 strictly correlate with the results of XPS and confirm the phase composition of the specimens according to [8,9].

**Figure 1.** Raman spectra of C_02, TCH_03, TC_04 and TCH_05 specimens. The Raman spectrum of TCH_03, TC_04 and TCH_05 specimens is dominated by the G-band (that appears at about 1490-1500 cm⁻¹) (green, red and blue traces) while D and G bands (at 1332 and 1580 cm⁻¹, respectively) appear in the Raman spectrum of C_02 specimen- the black trace.
Table 1. Summarized results for the layers configuration and thickness as well as for their phase composition obtained by XPS and ellipsometry studies.

| Experiment | Fraction sp²/sp³ C | C, at% | O, at% | N, at% | Layer Thickness, nm |
|------------|---------------------|--------|--------|--------|---------------------|
| C_02       | 0.90                | 95.56  | 2.01   | 0.00   | 12-14               |
| TC_04      | 0.55                | 92.19  | 4.48   | 0.33   | 70                  |
| TCH_03     | 0.60                | 92.65  | 5.03   | 0.23   | 140                 |
| TCH_05     | 0.62                | 93.01  | 4.01   | 0.40   | 20                  |

3. Results and discussion

Choosing these specimens and by micro texture polarization analyze, we obtained the corresponding micro textures necessary for the anchoring energy calculation. In figure 2, the texture of C_02 specimen with 7OBA is indicated. We present the polarization analysis of the π-inversion walls obtained by cooling from the isotropic phase at a cooling rate of 1 °C min⁻¹, used for the measurement of the wall's width l. The walls in crossed polarizers (P₂A), where P denotes the polarizer and A the analyzer are seen. As is seen in figure 2, the π inversion walls, due to their meta-stability, can form irregularly shaped loops. Depending on the cooling rate elliptical wall loop also can be formed. Following the microtextural polarization analysis one observes in the figure the walls as bright lines. Basing on the polarization micro-textural analysis we assume the observed wall to be Neel type. Hence we can use the formula \[ W_s = \pi^2 K d^2 / 2l^2, \] where d is the cell thickness and \( K \) is the elastic constant (10⁻¹¹ J m⁻¹) considered in the one-constant approximation. Here we assume \( K \) to represent the trace of the elasticity tensor \( K_{ii} \) which is relevant for the Neel type wall, i.e. accounts for the director's deviations along polar and azimuthal coordinates, leading to splay and bend shape of the wall. The wall thickness \( l \) was derived from a study of normally incident monochromatic light on micrometric etalon. Using the measured \( l \) values for C_02 specimen and the Rapini-Papoular formula \[ W_s = K(n \cdot n_o)^2 L^{-1}, \] we determine the extrapolation length \( L \) which is a measure for the anchoring strength [1].

Assuming that \( (n \cdot n_o) = 1 \), we estimated the anchoring energy for the basic surface treatments and found the extrapolation length of the specimen to be 1.68 µm. The corresponding extrapolation lengths for the specimens TCH_03/8OBA, TC_04/8OBA are 6.75 µm and for TCH_05/7OBA is 4.3 µm. The value of the anchoring energy for C_02 /7OBA is \( W_s = 0.59\times10^{-5} \text{ J m}^{-2} \), while for the TCH_03/8OBA, TC_04/8OBA it is 0.148 \( \times10^{-5} \text{ J m}^{-2} \), and for TCH_05/7OBA it is...
0.23×10−5 J m−2. As an example of the lower anchoring we present that of TCH_03/8OBA, TC_04/8OBA indicated in figure 3. As is seen on the Table 2, the surface anchoring is biggest for C_02 /7OBA and lowest for both TCH_03/8OBA, TC_04/8OBA specimens. At the same time, interesting is that the surface anchoring of TCH_05/7OBA specimen range between those of the C_02 /7OBA and TCH_03/8OBA, TC_04/8OBA.

Table 2. Represent the calculated values of anchoring energy and extrapolation length for different type of orientation interfaces.

| Orienting surface/LC | Anchoring energy - Ws, Jm−2 | Extrapolation Length-L µm |
|---------------------|-----------------------------|---------------------------|
| C_02 /7OBA          | 0.59×10−5                   | 1.68                      |
| TCH_03/8OBA, TC_04/8OBA | 0.148×10−5          | 6.75                      |
| TCH_05/7OBA         | 0.23×10−5                   | 4.3                       |
| SWCNT/7OBA          | 16×10−5                     | 0.06                      |

Figure 3. The micro texture of TCH_03 specimen filled with 8OBA. The π-inversion walls at T=169 °C in the N phase obtained at cooling rate 1 °C min−1 and cell thickness d=12 µm for P.LA.

4. Conclusions
We test the favorable effect of the molecular structure on the N domain growth, and found that the p,n alkylxybenzoic acids (nOBA) LCs, constituted by dimer rings, containing two parallel linear hydrogen bonds-cyclic dimer, are the most effective in this surface interaction. It is found that the dimeric LC/ta-C, LC/ta-C:H and LC/a-C anchoring energy is significantly less than that one of the dimeric LC/SWCNTs [3], and is approximately comparable with that of the conventional physical adsorption, meaning that the LC/ta-C, LC/ta-C:H and LC/a-C coatings rather prefers the homeothropic than planar orientation. Thus, the main contribution to the surface energy anchoring strength is due to the combination of π-π/hydrogen bonds, both acting within the double electric surface layer, in direction perpendicular to the substrate’s surface plane. The result also indicated that the decisive influence of the anchoring strength is that of the linear hydrogen bond energy which in 7OBA is rather bigger than that of 8OBA, i.e. 20kJ/mol and 5kJ/mol respectively [3]. We can
generalized that the direct dimeric LC/ta-C, LC/ta-C: H and LC/a-C interaction can be controlled by π-π electronic bonding, strongly expressed in the sp² hybridization (the ratio sp² / sp³), as the Raman spectra indicated. This investigation provokes the surface action of a-C to be considered as a full picture and optimization of the influence of carbon nanostructures, SWCNT, DLC and a-Con the orientation of the LC.

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References
[1] de Gennes P G and Prost J 1993 *The Physics of Liquid Crystals* 2nd edition (New York: Oxford University Press)
[2] Rapini A, Papoular M 1969 *J. Phys. Colloq.* 30 54
[3] Petrov M, Katranchev B, Rafailov P M, Naradikian H, Dettlaff-Weglikowska U and Keskinova E, 2013 *J. Mol. Liq.* 180, 215
[4] Robertson J 2002 *Mater. Sci. Engineer.* R37 129
[5] Ferrari A and Robertson J 2004 *Phil. Trans. R. Soc. Lond.* A 362 2477
[6] Lascovich J, Giorgi R and Scaglione S 1991 *Appl. Surf. Sci.* 47 17
[7] Diaz J Paolicelli, G Ferrer S and Comin F 1996 *Phys. Rev.* B54 8064
[8] Casiraghi C, Ferrari A and Robertson J 2005 *Phys. Rev.* B 72 085401
[9] Tinchev S, Nikolova R, Dylgerska J, Danev G and Babeva Tz 2005 *Solar Energy Materials Solar Cells* 86 421