Characterization of carbon nanolayers flash evaporated on PET and PTFE

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ABSTRACT

Carbon nanolayers were prepared by flash evaporation of carbon filaments onto polyethylene terephthalate and polytetrafluoroethylene substrates. The chemical composition of the deposited layers was determined using Raman, XPS, RBS and ERDA. Also the concentration of free radicals in the deposited layer was determined by EPR method. The thickness of the deposited carbon layer as a function of the deposition distance was determined by a scratch technique and AFM. Surface morphology of the samples was examined by AFM and nanointendation was used to determine microhardness and elasticity modulus and to perform scratch tests. The thickness of the deposited carbon layer decreases with increasing distance between the substrate and the filament. In addition to the dominant amorphous carbon fraction (a-C), various oxidized structures and hydrogen admixture in the deposited material were observed. The deposition of carbon leads to a significant decline of surface electrical resistance in comparison with pristine polymer, the change being a function of the deposition distance. The deposited carbon layer has semicrystalline character and it exhibits higher microhardness and elastic modulus than pristine polymer.

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1. Introduction

Thin carbon layers are considered as a prospective material for a wide range of biomedical application [1–5], e.g. tissue regeneration [6], controlled drug delivery [7], surface coating for bone-related implants [8], increase of resistance to microbial adherence [9], blood interfacing implants applications [10] or neuronal growth [11]. Ultrathin carbon films can also be used for electronic and analytical applications, e.g. carbon micro-arrays for transmission electron microscopy [12], high resolution microscopy [13], micro-electromechanical systems [14] or electrodes for corrosion sensor applications at high temperatures [15]. Carbon monolayer (graphene) has a great potential in development of FET transistors [16].

Carbon layers with different structure (from amorphous carbon (a-C) to diamond or diamond-like (DLC) layers) are prepared by various techniques such as evaporation [17,18], flash evaporation [19], sputtering [20], plasma-assisted chemical vapor deposition [21] or ion beam deposition [22]. Depending on deposition conditions these layers possess many outstanding properties (e.g. hardness, chemical structure, optical band gap) [18]. The structure and properties of carbon layers prepared by various deposition techniques have been studied extensively using different experimental and
theoretical methods [23–25]. However, little attention has been devoted to the study of carbon layers prepared by the simplest deposition technique – flash evaporation. By flash evaporation carbon layers of different thickness can be produced for routine SEM and TEM electron microscopy. In general, there is a need for these layers to be fine grain, even coating, with uniform and controllable layer thickness. Flash deposition is distinguished from other techniques (e.g. vacuum evaporation, ion beam) by short deposition time and low total power input [19]. The thickness of flash prepared carbon layer should be controlled, but at present none of the conventional methods in general use allows precise and reproducible deposition and layer thickness control [26].

Flash deposition can be accomplished either by rapid vaporization of a carbon filament [27] or by pulsed laser vaporization of a carbon target [28]. The former technique is based on rapid vaporization of carbon filament caused by an electric discharge. The majority of the vaporized material is believed to be in the form of molten globules.

In this work the carbon layers are deposited by flash evaporation onto PET and PTFE substrates. Their properties are of interest for many potential applications mentioned above and, in our case, for their usage in the study of interaction of living cells with carbonaceous materials and carbon based structures with potential applications in medicine. Physical, chemical and electronic properties of the deposited carbon layer are studied as a function of the distance between the substrate and the carbon source.

2. Experimental

2.1. Materials and carbon layer deposition

Oriented polyethyleneterephthalate (PET, supplied by Goodfellow Ltd., Cambridge, UK) and polytetrafluoroethylene (PTFE, Goodfellow, UK) in the form of 50 μm sheets, were used in the present experiments. Carbon layers were prepared using the SCD 050 Carbon Thread Evaporation Device by flash evaporation process from carbon filaments (BAL-TEC). The filaments, 15 mm in length, were kept to standard clamps. The filament degassing was performed for 10 s (pressure 4 Pa, room temperature) and with the current of 2.5 A. During degassing process the substrate was shielded by a shutter to avoid substrate heating. Subsequent flash evaporation (after shutter removal) was performed with the current of about 16 A (pressure 4 Pa). Deposition from one or two filaments is possible in the present experimental arrangement. Polymer substrates, 2 cm in diameter, were situated in the centre of the device at the distances from 2-7 cm from the filaments. For the measurement of the layer thickness the deposition onto a glass substrate was performed under the same deposition conditions. The term flash evaporation evolved from the fact that the carbon filament burns very quickly, in the order of 1 s or less.

2.2. Analytical methods

The thickness of the deposited layer was determined on a microscopy glass exposed under the same conditions as polymer substrates by a scratch technique which can not be applied to polymers. The scratches were done at ten different specimen positions by nanotentation tip and the layer thickness was determined by AFM in contact mode [29]. In this manner the mean thickness and layer homogeneity were determined. We examined the surface morphology of the samples by AFM using VEESCO CP II setup (tapping mode). Silicon probe RTESPA-CP with the spring constant 20–80 N/m was used. By repeated measurements of the same region (1×1 μm) we certified that the surface morphology did not change after five consecutive scans. The mean roughness value (R_a) represents the arithmetic average of the deviations from the centre plane of the sample.

Contact angles of distilled water, characterizing the surface wettability, were measured at RT at 6 positions (3 rows each 2 measuring positions situated at a 5 mm distance) using a Surface Energy Evaluation System (SEES, Masaryk University, Czech Republic). The static contact angle was measured for pristine [30] and carbon evaporated samples immediately after flash deposition (with <10 min delay). Drops with 8.0 ± 0.2 μl volume were deposited using an automatic pipette (Transferpette electronic, Brand, Germany) and their images were taken after 5 s delay. Then the contact angles were evaluated using SEES software.

The continuity of the carbon layer was examined by measuring electrical sheet resistance (R_s). R_s was determined by a standard two-point technique using KEITHLEY 487 picoamperimeter. For the measurement two Au contacts about 50 nm thick were deposited on the layer surface by sputtering (Balzers SCD 050 device). The measurements were performed at a pressure of about 10 kPa. Typical error of the sheet resistance measurement was ±5%.

The chemical structure of carbon layers was determined from X-ray photoelectron spectra (XPS), measured on Omicron Nanotechnology ESCAProbeP spectrometer. X-ray source was monochromated at 1486.7 eV and area 2×3 mm^2 was exposed and analyzed. Spectra were measured stepwise with a step in binding energy 0.05 eV. The spectra evaluation was carried out by CasaXPS program. Before the measurement the samples were stored under standard laboratory conditions.

The deposited carbon layers were characterized by near-infrared excited surface-enhanced Raman scattering (NIR SERS), too. The spectra of the layers were measured on SERS-active golded platinum substrate [31]. NIR Raman spectra were collected using a Fourier-transform near-infrared (FT-NIR) spectrometer Equinox 55/S (Bruker, Germany) equipped with an FT Raman module FRA 106/S [4].

The Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) were performed in a vacuum target chamber with 2.72 MeV He ions. Using RBS and ERDA techniques elemental depth profiles are determined non-destructively with the typical depth resolution of 10 nm and 20 nm, respectively. The RBS and ERDA spectra were evaluated by the GISA3 [32] and the SIMNRA5.0 codes [33], respectively. The accuracy of RBS and ERDA concentration determination is about 2 at.%.

The concentration of free radicals was determined using an electron paramagnetic resonance spectroscopy (EPR) using an X-band spectrometer Elexsys E-540, Bruker-Biospin with a relative error of 10%. The experimental conditions were as...
follows: the magnetic field range 600 mT, sweep time 180 s, magnetic modulation 0.4 mT, field modulation 100 kHz. The standards Mn/ZnS and Cr/MgO were used for the g-factor calibration and for quantitative evaluation of the spectra.

Measurements of mechanical properties (hardness, elastic modulus) were carried out using a NanoIndenter XP MTS instrument with a CSM additional module at loadings up to 20 mN and displacement into the surface up to 2 μm. The results were obtained as a mean of 20 different indentations (4 rows each with 5 points at the distance of 100 μm). Scratch tests were performed over a distance of 500 μm with the tip being gradually loaded from 0 to 20 mN.

3. Results and discussion

3.1. Homogeneity and thickness of deposited carbon layer

3.1.1. Layer homogeneity

In first experiment the carbon layer was deposited at the distance of 2 cm from the filament on the glass sample, 5 cm in diameter. Homogeneity of the deposited layer was examined by thickness measurement of carbon layer at positions situated along two perpendicular directions in 0.5 cm steps starting from the sample centre. As expected, the layer thickness depends on the distance from the sample centre. The layer thickness measured at 10 positions varies within ±10% over the distance of ±1.5 cm from the sample centre.

3.1.2. Layer thickness

The dependence of the layer thickness, measured by the scratch technique, on the distance between the substrate and the carbon filaments is shown in Fig. 1 for arrangements with one and two filaments. The thickness of thinner layers prepared at the deposition distances above 6 cm (or 5 cm for 1 filament) can not be determined by the scratch technique. One can see from Fig. 1 that the layer thickness decreases with deposition distance monotonically, as expected. The observed dependence of the layer thickness (t) on the distance between carbon source and substrate (d) can be described by the equation 

\[ t = \frac{a}{d^b} \]  

[34,35]. From least-squares fit of the experimental data the following values of adjustable parameters were obtained:

- For deposition from one filament: 
  - \( a = 158 \pm 13 \) and \( b = 1.7 \pm 0.1 \)
- For two filament case: 
  - \( a = 189 \pm 18 \) and \( b = 1.4 \pm 0.1 \)

Good coincidence between measured and calculated curves is seen from Fig. 1. It should be noted that the deposition process is affected by several phenomena. The filament does not represent a point-like carbon source [34,35] and during the evaporation process it breaks without fully evaporating along its complete length. The flash evaporation proceeds in rather low vacuum and evaporated carbon particles under a large number of inelastic scattering events with molecules of residual gas on the way from the filament to the substrate, by which their energy is reduced and flight direction is changed randomly. Moreover, the excited carbon atoms may recombine with molecules of residual gas and create molecular fragments, e.g. different oxidized structures which were observed in deposited layers. Both processes become more significant for larger deposition distances. A complete quantitative model of this process is beyond the scope of this study.

3.2. Chemical composition and structure of deposited layers

3.2.1. Surface composition

Fig. 2 shows a typical XPS spectrum from carbon layer deposited onto PTFE. PTFE was chosen for the sake of simplicity

![Graph](image-url)

**Fig. 1** – Dependence of the thickness of the flash-evaporated carbon layer on the distance of glass substrate from 1 (●) and 2 (■) filaments (exp.), determined by AFM technique. The values calculated according to formulae presented in the text are also shown (1 (○) and 2 (△) filaments (calc.)).
since it does not contain oxygen. One can see (Fig. 2) that besides of carbon oxygen is also observed. The presence of oxygen is explained by oxygen absorption from residual atmosphere during deposition process. C1s and O1s peaks correspond to about 94.1 and 5.8 at.%, of carbon and oxygen concentration, respectively. Structure of O1s band is also shown in the inset of Fig. 2 with positions of groups –C– (284.7), –C–O– (286.5), –C=O (288.0) and –O–C=O (289.2 eV) marked [36,37]. The presence of –C–O–, –C=O and –O–C=O structures in the carbon layer is evident.

3.2.2. Chemical composition of the layer
RBS study did not confirm the presence of oxygen, probably because of its too low concentration in surface layer interior. Hydrogen depth profile was determined by ERDA (Fig. 3). One can see that the concentration of carbon and hydrogen

Fig. 2 – XPS spectrum of the carbon layer deposited from 2 cm distance on PTFE; decomposition of the O1s band is shown too.

Fig. 3 – Depth concentration profiles of C and F, determined by RBS method and H, determined by ERDA method on the PTFE sample carbon coated from the deposition distance of 2 cm.
decreases with increasing depth while the concentration of fluorine increases. No hydrogen is detected beyond 75 nm and at deeper regions concentration ratio of C and F is close to 1. These observations may indicate that the thickness of deposited carbon layer is about 75 nm (in accordance with measurements performed on glass samples, see Fig. 1) and at larger depths the composition approaches pristine PTFE.

The structure of the carbon layer was further characterized by Raman spectroscopy. Because of too low layer thickness the technique described in [31] was applied instead of classical one. The Raman spectrum of the sample deposited at the distance of 2 cm is shown in Fig. 4. Main band observed at 1392 cm\(^{-1}\) corresponds to amorphous carbon (a-C) and it could be assigned to D (disorder)-band of carbon materials [4,38]. The band at 712 cm\(^{-1}\) is typical for non-flat deformation of carbon layers. Band at 1604 cm\(^{-1}\), corresponding to graphitic carbon, is not present.

3.2.3. Radical concentration

Radical concentrations (R) as a function of the deposition distance and the time from the deposition end are given in Table 1. As expected, the concentration decreases with increasing time elapsed from the end of deposition because of radical recombination. The R is lower for thinner layers (i.e. layers deposited from larger distances) but the concentration ratio is not directly correlated with the layer thickness.

3.3. Surface properties of carbon layers

3.3.1. Surface electrical resistance

Typical sheet resistances of pristine PET and PTFE are \(R_s \approx 1 \times 10^{14} \Omega\) [39] and \(R_s \approx 1 \times 10^{17} \Omega\) [40], respectively. The results of the sheet resistance measurement are shown in Fig. 5. Carbon deposition results in a rapid resistance decrease (comparing to pristine polymers) indicating formation of continuous carbon layer on the polymer. The decrease of \(R_s\) is more pronounced on PET, probably due to lower surface roughness (it will be discussed later).

3.3.2. Surface wettability

Surface wettability dependent on surface chemical structure [41] and is commonly characterized by contact angle [41,42]. Contact angle as a function of the distance of PET and PTFE substrates from the filament is shown in Fig. 6. On PTFE the contact angle increases with an increasing deposition distance (thinner layer thickness), while on PET the contact angle does not change within experimental errors for deposition distances from 2 to 7 cm. According to XPS analyses chemical composition of the deposited carbon layer is the same for both polymers with low concentration of oxidized, polar structures. It is supposed that the wettability might also be affected by surface morphology and roughness of both polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time after deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 h</td>
</tr>
<tr>
<td>C2/PET</td>
<td>2.227</td>
</tr>
<tr>
<td>C6/PET</td>
<td>0.872</td>
</tr>
</tbody>
</table>

3.3.3. Other properties

Fig. 4 – Raman spectrum of carbon layer deposited onto Au/Pt backing form deposition distance of 2 cm.
Fig. 5 – Sheet resistance as a function of the deposition distance measured on PET and PTFE.

Fig. 6 – Contact angle determined by standard goniometry on carbon coated PET and PTFE in dependence on the deposition distance.

Fig. 7 – AFM images of pristine PET and PTFE and those coated with carbon from the deposition distance of 2 cm (C2/polymer). $R_a$ is surface roughness in nm.
3.3.3. Surface morphology and roughness

While the roughness of PET after carbon coating remains unchanged within experimental error, a dramatic change of the roughness is observed on PTFE. With increasing thickness of the carbon layer the PTFE roughness decreases from 13.3 nm for pristine PTFE to 2.9 nm for thickest layer (deposition from 2 cm).

Significant differences in the surface morphology are found between both polymers before and after carbon deposition. Surface morphology of PET and PTFE, before and after 2 cm deposition distance is shown in Fig. 7. For pristine PET the surface is composed of tiny, rounded formations, homogeneously distributed over the sample surface. Carbon deposition does not result in any significant change in the surface morphology and roughness. Surface of the pristine PTFE is markedly wrinkled and its roughness is higher comparing to PET. Carbon deposition results in a dramatic morphology change and roughness declines indicating a preferential carbon accumulation into holes.

3.3.4. Surface mechanical properties

Dependence of the surface hardness and elastic modulus on the tip displacement into the surface is shown in Fig. 8 for PET deposited from 2 cm. It is seen that hardness and elastic modulus decline with increasing depth, the decline being much slower at the depths of about 75–80 nm. This depth coincides with the carbon layer thickness (see Figs. 1 and 3). It may be therefore concluded that the carbon layer has higher hardness and elastic modulus than underlying, pristine PET.

A scratch test on carbon coated polymers was performed using Nanointender device. The result obtained for C2/PET sample (carbon evaporated from of 2 cm) is shown in Fig. 9 for illustration. The test shows a semicrystalline structure of the carbon layer. However, this result was not confirmed by Raman (missing 1604 cm$^{-1}$ band [4]) and XRD (too thin carbon layer).

4. Conclusions

The thickness of carbon layers prepared by flash evaporation was found to be a decreasing function of the distance between the carbon source and the substrate. In addition to the main carbon component the layers contain about 6 at.% of oxygen at the layer surface, mostly bound in chemical groups –C–O, –C=O and –O=O. Presence of significant
fraction of amorphous carbon (a-C) and a hydrogen admixture in the carbon layer was also proved. The specimens prepared on PET and PTFE exhibit reduced sheet resistance but different wettability and surface morphology. Flash evaporation is an efficient and easy technique for preparation of thin carbon layers with great application potential. However, layer design now relies primarily on trial-and-error or experience. The authors believe that more thorough examination of the flash evaporation process by broad spectrum of analytical techniques may lead to better understanding of the role of various contributing processes and to an optimization of this deposition technique.

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