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Structural, chemical and biological properties of carbon layers sputtered on polyethyleneterephtalate

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Abstract Carbon layers on polyethyleneterephtalate (PET) backing were prepared by sputtering from graphite target. UV-VIS, Raman spectroscopy, RBS (Rutherford backscattering) and ERDA (Elastic Recoil Detection Analysis) techniques were used for the characterization of the layers. Surface morphology of the layers was determined by AFM technique and the adhesion of 3T3 mouse fibroblasts on the layers was studied *in vitro*. It was found that the properties of the deposited carbon layer depend on the sputtering time. The concentration of conjugated double bonds, fraction of amorphous hydrogenated carbon (a-C:H) containing oxygen and surface roughness are increasing functions of the sputtering time. The changes of the layer surface morphology with increasing sputtering time were also observed. For the sputtering times up to 30' the number of adhering 3T3 cells increases with increasing sputtering time. For longer sputtering times, however, the cell adhesion becomes lower probably due to unfavorable changes in roughness and morphology of the layer.

1. Introduction

It has been shown that the biocompatibility of polymers is favorably affected by the presence of carbonaceous structures, since the carbon materials are generally well tolerated by living cells [1]. Different procedures have been used to prepare carbon-polymer composites for biological experiments. Biocompatibility of polymer doped with carbon black [2] or carbon fibres [3] was recently studied. It was found that the cell adhesion and proliferation can be affected by carbonization of polymer surface layer by pyrolysis [4], by ion implantation [5, 6], irradiation with UV-excimer lamp [7] or by exposure to plasma discharge [1].

Another possibility how to prepare a polymer-carbon structure is the deposition of carbon layers onto polymer surface. Different carbon forms have been identified in such layers, namely (i) diamond like carbon (DLC), (ii) amorphous hydrogenated carbon (a-C:H), amorphous carbon (a-C), (iv) pyrolitic graphite and (v) fullerene (C_{60}) [4, 8–10].

DLC films can be deposited using d.c. plasma chemical vapor deposition, radio frequency magnetron sputtering or ion beam-based methods [1]. DLC (polycrystalline diamond) needs high temperatures to be deposited [11]. Amorphous carbon can be prepared at low temperatures by different techniques but its physical, chemical and mechanical properties depend on the deposition conditions, mainly on the temperature and hydrogen content [12]. Hydrogenated amorphous carbon (a-C:H) is usually prepared by plasma-assisted CVD of hydrocarbons (i.e. methane or ethylene [13]). Amorphous carbon (a-C) is prepared by PVD techniques such as sputtering, arc discharge, pulsed laser deposition [14]. Amorphous hydrogenated carbon is unstable under thermal treatment since it tends to eliminate hydrogen and transform in to a more stable graphitic structure [12].

In this study carbon layers on polyethyleneterephtalate (PET) backing were prepared by sputtering from graphite target. The deposited layers were characterized by different techniques (UV-VIS, Raman spectroscopy, RBS, ERDA, AFM, electromagnetic wave reflection). The

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biocompatibility of the layers was studied by cultivation of 3T3 mouse fibroblasts.

2. Experimental

2.1. Materials and treatment

Oriented polyethyleneterephtalate (PET, [-OOC-C_6H_4-COO-$(CH_2)_2$-]$_n$, density 1.41 g cm^{-3}, supplied by Goodfellow Ltd., Cambridge, UK) in the form of 50 μm thick foils was used in the present experiments. For preparation of carbon layers RF magnetron sputtering system (Balzers Pfeiffer PLS 160) was used. We used 5 cm diameter graphite target (99.99 %, target to substrate distance 3.7 cm) and the depositions proceeded in argon (pure 99.999%). Typical growth parameters were: deposition temperature 300 K, deposition time from 0 to 90 min, total argon pressure 2 Pa and power 50 Watts.

2.2. Layer characterization

Some of the relevant properties of the deposited layers were determined using standard techniques. The concentration of conjugated double bonds was determined by UV-visible spectroscopy in 200–900 nm wave length interval using a Perkin-Elmer device [15]. Raman spectra were collected using the LabRam HR system (Jobin Yvon). The 532.2 nm laser line was used for excitation. An objective ($\times$100) was used to focus the laser beam on the sample placed on an X-Y motorized sample stage. The surface morphology and roughness of films was characterized using an extended multimode nanoscope atomic force microscope (AFM) MultiMode Digital Instruments NanoScope™ Dimension IIIa set-up (contact mode technique). Reflection of electromagnetic waves was used for the characterization of continuous and discontinuous carbon layers on the PET surface. The technique was described earlier in ref. [16]. Simultaneous RBS and ERDA analyses were performed on NPI Van de Graaff accelerator with 2.72 MeV alpha particles incident at the angle of 75° measured from the surface normal. The samples were irradiated in a vacuum target chamber equipped with RBS semiconductor detector for registration of alpha particles scattered under the laboratory angle of 105° and ERDA detector for registration of hydrogen ions recoiled under the angle of 30°. The ERDA detector was covered with 12 μm thick mylar range foil to stop scattered alpha particles. The RBS and ERDA spectra were evaluated by the GISA3 [17] and the SIMNRA5.0 [18] codes respectively. The element concentrations were determined with 10–15% error. The depth profiles were determined up to the depth of a few μm with the typical surface depth resolution of 10 and 50 nm for RBS and ERDA respectively.

2.3. Cell culture and adhesion

The adhesion of mouse embryonic fibroblasts (line 3T3, ATCC CCL — 92 Rockville, MD, USA) in culture on PET/carbon substrate was investigated *in vitro* [15]. For evaluation of initial adhesion (measured by the number of adhered cells 24 hours after seending), the 3T3 cells were seeded onto the samples at a density of about 2.6×10^4 cells per cm^2 (1×10^5 cells per pit). The number of cells after seeding was determined using Burker haemocytometer and presented as mean $\pm$ SD from 4 independent measurements. Optical micrographs of adhered cells were taken in a phase-contrast microscope (Axioplan, Opton, Germany).

3. Results and discussion

Absorption spectra of pristine PET and PET with deposited carbon layers (sputtering times up to 90 min) are shown in Fig. 1. For the sake of clarity only some typical spectra are depicted. UV-VIS spectrometry is used frequently to follow the changes in chemical structure of polymers. Absorbance increase indicates an increase of the concentration of structures with certain length (number) of conjugated double bonds. Longer structures absorb on longer wave lengths [15, 19]. The amount of π bonds (sp^2 hybridization) and the length

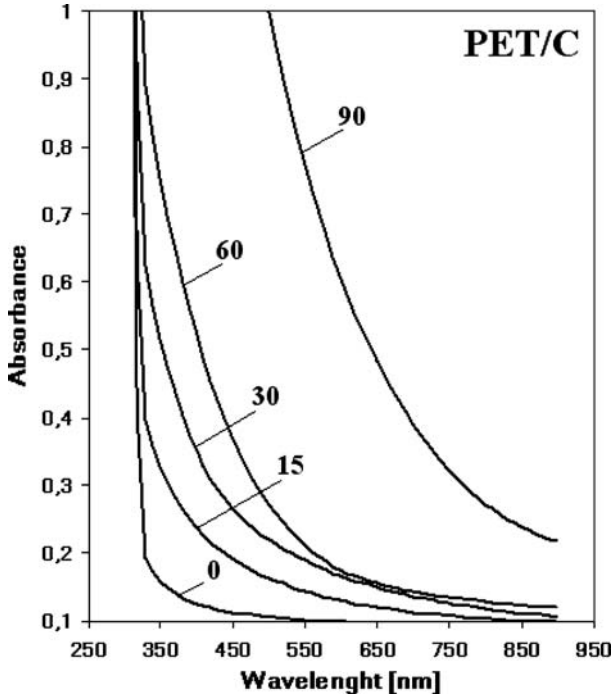

Fig. 1 UV-VIS spectra from pristine PET and PET samples with carbon layers deposited for different sputtering times (min) as indicated in the figure.

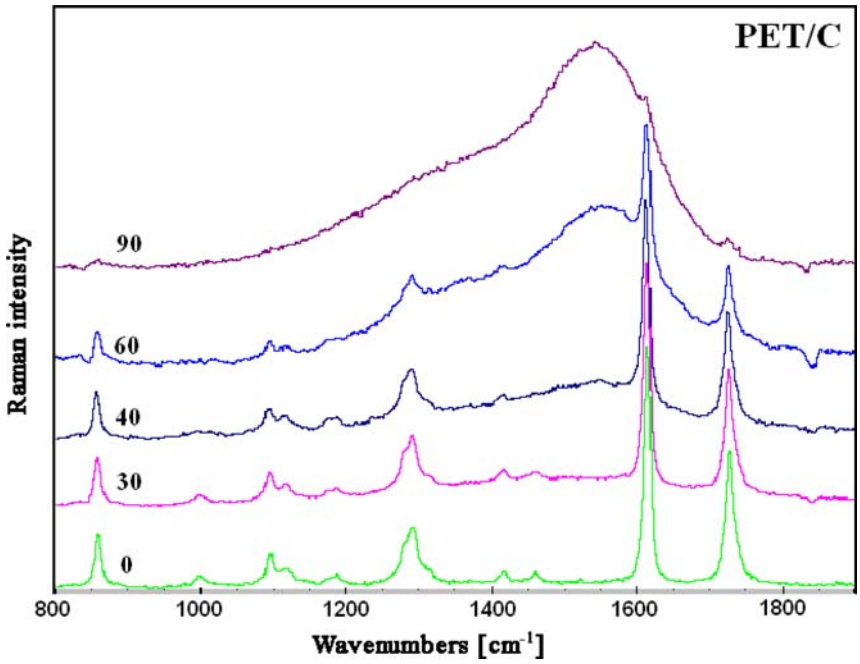

Fig. 2 Raman spectra from pristine PET and PET samples with carbon layers deposited for different sputtering times (min) as indicated in the figure.

of conjugated double bonds are increasing functions of the sputtering time (see Fig. 1). The result from Fig. 1 indicates that the thickness of the deposited carbon layer increases with increasing sputtering time as could be expected.

The structure of the carbon layers can be characterized by Raman spectroscopy [12, 19, 20]. Raman peak at 1360 cm^{-1} is attributed to disordered mode of graphite and that at 1500–1550 cm^{-1} corresponds to an amorphous-like structure with $sp^3 + sp^2$ bonding [19, 20]. Figure 2 shows the Raman spectra from pristine PET and PET with carbon layer deposited for 30–90 min. The carbon deposition for the times up to 30 min does not result in any observable changes in the spectra. The deposition for longer times leads to appearance of a signal in 1100–1700 cm^{-1} region, the intensity of the signal being an increasing function of the deposition time. All spectra exhibit a broad peak at 1530 cm^{-1} indicating that the deposited layers are composed mostly of amorphous carbon with sp^3 and sp^2 bonds [19]. Small peak at 1360 cm^{-1}, which is also present in all spectra, is due to the presence of disordered graphite [19]. More detailed discussion of the Raman spectroscopy results, especially the relation between graphite and amorphous carbon components, will be published elsewhere [21]. The results of Raman and UV-VIS spectroscopy show that the thickness of the deposited layers increases with increasing sputtering time.

The results of the ERDA and RBS analysis of pristine PET and PET with deposited carbon layers are presented in Table 1. From ERDA spectra an information on hydrogen concentration and its depth profile in the deposited layers is obtained. RBS spectra provide information on carbon and oxygen concentration and on the layer total thickness. The

Table 1 Composition of deposited carbon layers and their thickness measured by RBS and ERDA methods as a function of the sputtering time

Sputtering time (min)	Composition of layer (at. %)			Thickness of layer (at 10^{15} cm^{-2})
	C	O	H	
0 (pristine PET)	45	18	37	–
45	65 ± 6	9 ± 2	26 ± 5	1000 ± 50
60	66 ± 6	8 ± 2	26 ± 5	1300 ± 50
90	77 ± 7	7 ± 2	16 ± 4	2200 ± 50

concentrations are given in at. % and the layer thickness in at. cm^{-2}. The RBS and ERDA signals from carbon layers deposited for sputtering times below 30 min can not be reliably separated from that of PET substrate. For the sputtering times above 45 min the composition of the deposited layers does not depend, within RBS and ERDA experimental errors, on the deposition time. The measured concentrations vary from 7–9 at. % for oxygen and from 16–26 at.% for hydrogen. These concentrations are significantly lower than those in pristine PET (see Table 1). The layer thickness increases roughly linearly with increasing deposition time.

The technique based on the reflection of electromagnetic waves has been successfully used for the characterisation of the continuity and homogeneity of thin metallic layers [16]. The same technique was applied on the present samples but no difference in the reflection of electromagnetic waves was observed between pristine PET and PET with deposited carbon layers. This finding indicates that the deposited carbon layers behave as insulator. To verify this conclusion

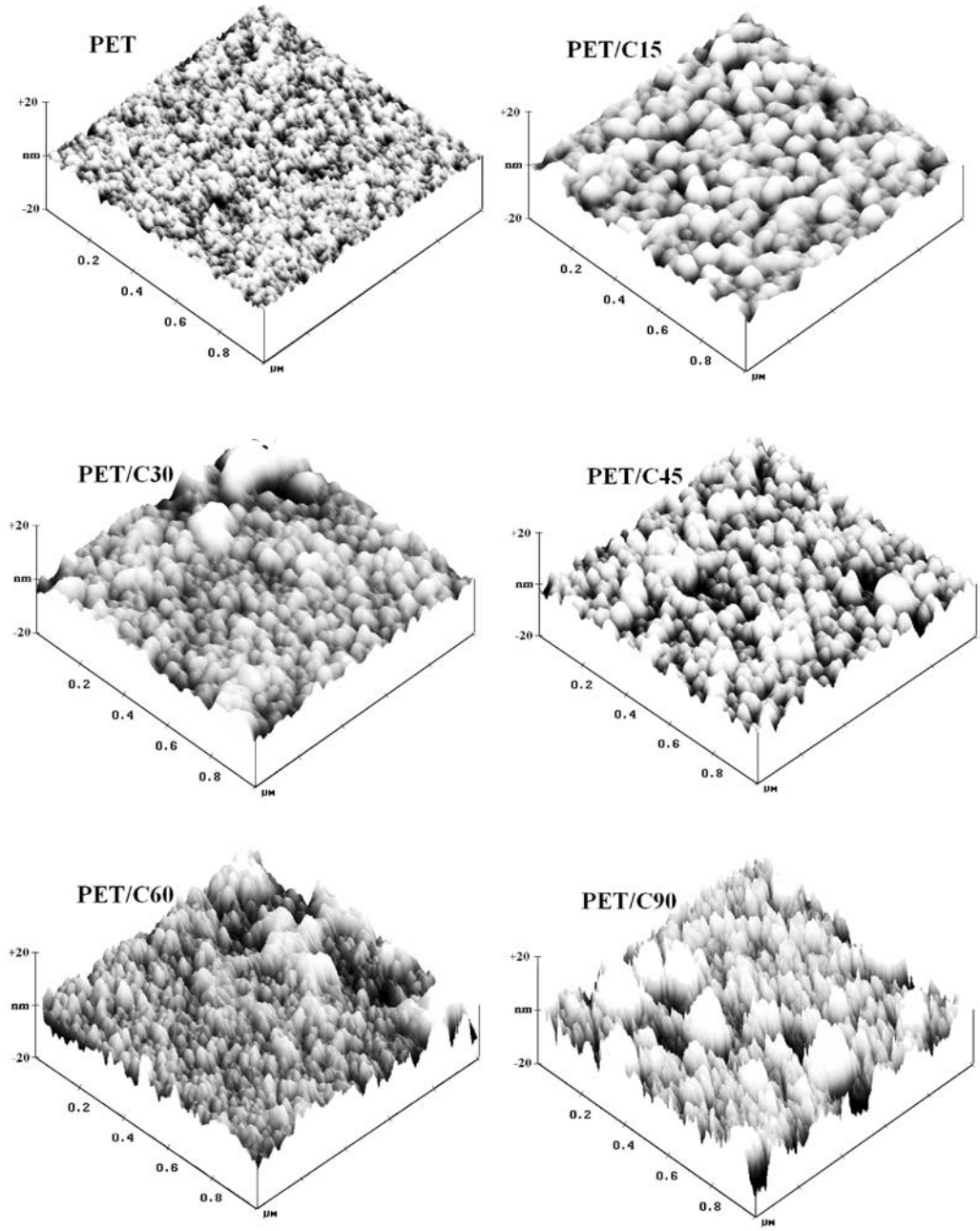

Fig. 3 AFM images of surface morphology of PET and carbon sputtered on PET for the times from 15–90 min.

two point resistance measurements with Keithley 487 device [16] were performed. No differences between resistance (10^{14}–10^{15} Ω) measured on the pristine PET and PET with carbon layers of different thickness was observed. It may be therefore concluded that the deposited carbon layer is non-conducting and this is typical for amorphous carbon.

The results obtained by different techniques (ERDA, RBS, Raman spectroscopy, resistance measurement and reflection of electromagnetic waves) indicate that the layers prepared by the present technique consist mostly of amorphous hydrogenated carbon (a-C:H) with an oxygen admixture.

The evolution of the surface morphology of the deposited carbon layers in dependence on the sputtering time is illustrated in Fig. 3 where some typical AFM scans are shown. For the sake of clarity only measurements for some deposition times were chosen. It is seen that the layer morphology changes as a function of the sputtering time and the layer thickness. After 15' deposition carbon creates rounded, regular grains the size of which is larger comparing to those observed for longer sputtering times. For the sputtering times above 30' the carbon grains become smaller but some irregularities arise. On the layers deposited for 60 and 90' some

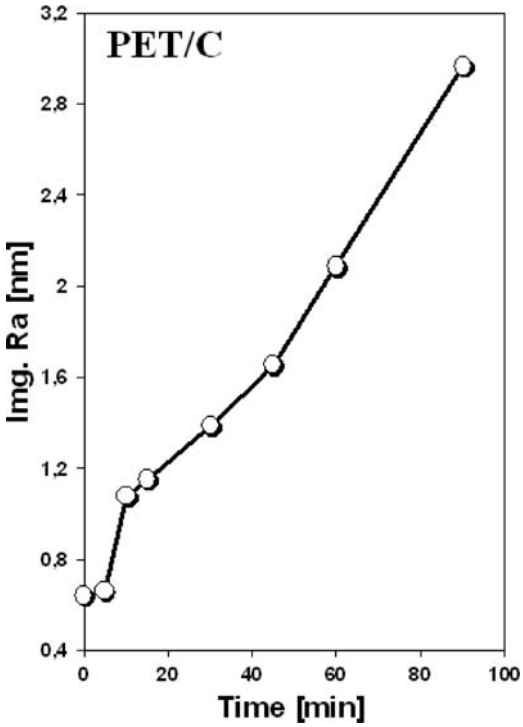

Fig. 4 Dependence of the surface roughness of the carbon layer, determined by AFM method, on the sputtering time.

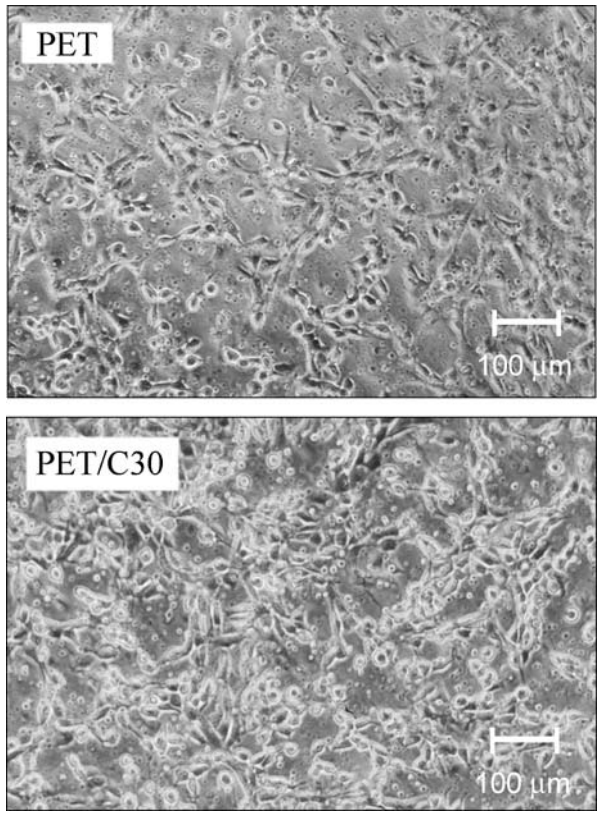

Fig. 6 Microscopic images of adhering 3T3 cells 24 hour after seeding on pristine PET and PET with carbon layer sputtered for 30 min.

sharp objects appear. The results s of AFM determination of the surface roughness are shown in Fig. 4. It is seen that the surface roughness is an increasing function of the deposition time.

The same carbon layers-PET structures were used as a substrates for cultivation of 3T3 mouse fibroblasts. Dependence of the number of adhering cells, measured 24 hour after seeding, on the layer deposition time is shown in Fig. 5. The number of adhering cells increases with increasing deposition time for deposition times up to 30 min. For longer deposition times on the contrary the cell number decreases with increasing deposition time. Possible explanation of the decline may be found in unfavourable surface morphology and roughness of the layers deposited for longer times (Figs. 3, 4). Possibly the adhering cells prefer smooth surface without sharp irregularities. An effect of the layer continuity or discontinuity can not be excluded too [21]. It should also be noted that in the present case an non-polar material (carbon) is deposited onto polar substrate

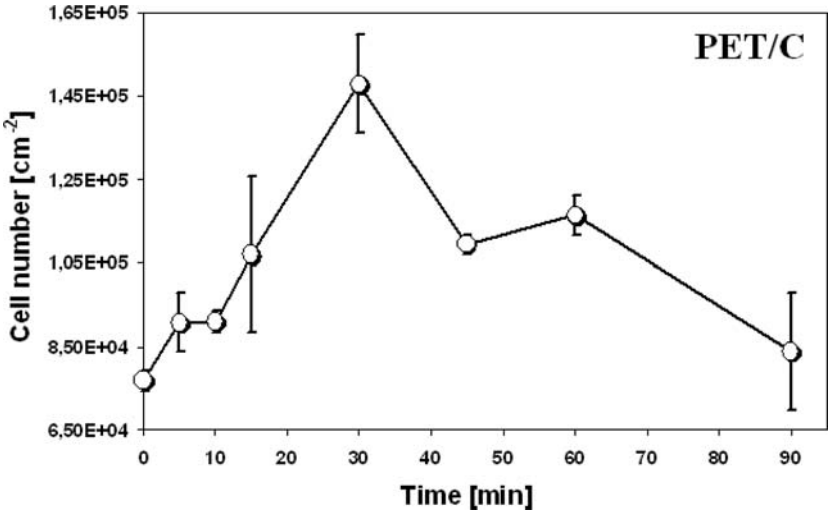

Fig. 5 Dependence of the number of adhering 3T3 cells, measured 24 hour after seeding, on the sputtering time.

(PET) and in this manner the surface polarity is changed significantly.

The results of 3T3 cell cultivation is illustrated in Fig. 6 where the microscopy images of adhering 3T3 cells on pristine PET and PET with carbon layer (30' sputtering time) are shown. For 30' sputtering time a maximum of adhering cells was achieved (see Fig. 5). It is seen that the carbon deposition leads to a significant increase of the number of adhering 3T3 cells. The positive effect of the carbon layer on the cell adhesion is manifested by lower fraction of spherical and higher fraction of polygonal cells observed on carbon coated sample in comparison with pristine PET.

4. Conclusion

The results of the present study can be summarized as follows:

- the number of conjugated double bonds in the deposited carbon layer is an increasing function of the deposition time, i.e. of the layer thickness,
- the results of RBS, ERDA analyses, Raman spectroscopy, measurements of electromagnetic wave reflection and electrical resistance show that the sputtered carbon layers consist of amorphous hydrogenated carbon (a-C:H) containing an oxygen admixture,
- the carbon layer roughness increases with increasing deposition time. Large, round carbon grains are observed after 30' deposition time by AFM technique. For longer deposition times the grains become smaller but sharp objects appear on the layer surface,
- the number of adhering 3T3 cells increases with increasing deposition time for the times up to 30 min. For longer deposition times the number of adhering cells decline probably due to surface morphology and roughness changes.

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