Nanocrystalline carbon film electrodes generated and patterned by UV-laser ablation of polystyrene

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A carbon conductive film consisting of nanometer sized domains has been patterned by scanning photoablation of polystyrene. The film formation involves the photoablation of a highly insulating polymer, and the redeposition of conductive carbon fragments. This film has been investigated by scanning electron microscopy, atomic force microscopy, microRaman spectroscopy, electrical conductivity and standard electrochemical measurements. Film deposition under different gas flow conditions has revealed major differences in the electrical and electrochemical properties of the material. Cyclic voltammetry and double layer capacitance measurements have indicated the formation of a conductive layer with a high specific area when generated in ambient atmosphere. Inert atmospheres like nitrogen and argon lead to conducting films with low double layer capacitance values ($10 \mu\text{F cm}^{-2}$), whereas an air atmosphere leads to conducting films with supercapacitance values (5 mF cm^{-2}). This large difference in capacitances is discussed in terms of the photochemical effects of the ambient atmosphere during the polymer treatment.

Introduction

Polymer photoablation is a laser etching technique developed in the early eighties,^{1,2} which rapidly led to various applications such as human tissues surgery^{3,4} or electrical circuit fabrications.⁵ Recent developments have extended the application range to the fabrication of analytical tools like microelectrodes,^{6,7} microfluidic devices⁸ or to the patterning of biomolecules.⁹ Besides these application oriented developments, the photoablation mechanism still remains a subject of fundamental research.¹⁰ Even though several physical models describing this mechanism have appeared in the literature¹¹ with some clear correlation with measurements,¹² it is still difficult to predict the actual phenomena occurring during the interaction of the laser light with the polymer, especially at higher fluences. However, it is generally admitted that, above the threshold fluence value, the ablation process follows from the high pressure induced by the photons impinging on the polymer surface, which produces mini-explosions leading to the ejection of the material at velocities of about 500 to 1500 m s^{-1} (ref. 13). Several phenomenological studies have been undertaken to study the changes of the physical properties of the surface after the photoablation^{14–16} and to characterise the debris ejected during the process.^{17,18} The surface characterisation of ablated surfaces has been extensively studied by different techniques like atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and microconfocal Raman spectroscopy. General comments about the surface state include an increase of the surface roughness^{8,14,19–21} as well as changes in the surface oxidation state⁸ and crystallinity¹⁶ of the ablated polymer. XPS studies pointed out the chemical changes of the functionalised carbon in the polymer. It is generally observed that no oxidation occurs on the surface during the UV-laser irradiation. For instance, during the photoablation of poly(ethylene terephthalate), an important change is the decrease of the O/C ratio^{22,23} leading to carbonisation of the surface.²⁴ This carbonisation is even larger with increasing

fluence and highly dependent on the laser wavelength, building a graphite network on the surface of the organic polymer.²⁵ Mass spectrometry analysis provided the identification of the debris in the plume during the ablation. The presence of small fragments like C_nH_n ($n = 2, 3, \dots, 8$) and their corresponding oligomers has been observed during the ablation of polystyrene.²⁶ The nature of the ejected particles strongly depends on the fluence of the laser beam on the surface. Close to the threshold value, the ablation products of polystyrene are mainly composed of monomers,²⁷ but, with increasing fluence, different degradation processes lead to the formation of carbon.²⁸ However, discrepancies between the morphology of the ejected carbon occurred between different studies. Actually, some authors mentioned the presence of the C_2 ion in the plume of ablated poly(methyl methacrylate),²⁹ the ion precursor of fullerene type carbon. However, this conclusion was discussed in a study where no such m/e 24 could be detected by mass spectrometry.³⁰ Several studies identified the presence of C_3 during the ablation of polycarbonate,³¹ while products similar to those of the pyrolysis reaction were observed after the ablation at 193 nm.^{31,32} The mechanism of carbon formation, hereafter named carbonisation, is probably induced by the degradation of the ejected fragments in the plume where the temperature reaches more than 10 000 K.³¹ With long enough laser pulse durations ($> 10 \text{ ns}$), the plasma is also heated by multiphoton absorption of the ejected debris in the plume. Indeed, the time scale of fragment ejection has been measured to lie below 10 ns by nanosecond interferometry, and it is even shorter at high fluences.³³

The present work describes the degradation of polystyrene into carbon by high fluence laser ablation and its redeposition into nanometer sized domains. The aim of this work is to pattern polymer substrates for the generation of carbon electrodes and to characterise the type of carbon redeposited during the photoablation of polystyrene under high power conditions. The machining under different atmospheres indicates dramatic changes in the electrochemical behaviour of this conductive layer depending on the presence or the

absence of oxygen in the ambient gas. A first characterisation by Raman spectroscopy and electrochemistry provides some information about the morphology of the patterned carbon. This nanocrystalline electrode exhibits a very high surface area that can provide supercapacitance when placed in an electrolyte solution.

Material and methods

Generation of the UV-laser ablated carbon films

The laser scanning ablation procedure was performed following a method described previously.¹⁶ This scanning technique has been developed for the laser irradiation of large surface areas (in the range of a few cm²) used for micropatterning hydrophilic channels¹⁶ or microfluidic systems driven by capillary and electroosmotic flow.⁸ Briefly, to open a channel, a polystyrene sheet (Goodfellow, UK) was rinsed with distilled water and mounted on an X,Y machining stage; then UV-laser pulses (193 nm) (Lambda Physik LPX 205 i, Germany) were fired onto the polystyrene target through a photomask and a 10:1 telescope objective at various fluences ranged between 800 and 3200 mJ cm⁻² at the image points. The distance between the image plane and the focal plane was changed in order to maximise the carbonisation of the polymer. The focal length of 56 mm was chosen in order to promote a small but very hot plasma at the focal point.³⁴ During the pulsed ablation process, the substrate was moved horizontally with the X,Y stepping motor at a velocity between 0.05 and 0.2 mm s⁻¹ in order to generate ablated lines with final dimension of 7 mm × 2 mm as presented in Fig. 1. This lateral displacement allowed the redeposition of the ejected fragments over a large surface area. The ablation process was carried out under different atmospheres (air, argon or nitrogen) to follow the effect of the plasma during the photoablation process.

Microscopic characterisation

Characterisation of the produced film was achieved by scanning electron microscopy (SEM, JEOL JSM-6300F, USA). The volume of the film was investigated by studying the film thickness in the redeposition area. For this reason, the polystyrene substrate was cut with a microtome and the cross section observed by SEM.

Atomic force microscopy (AFM) measurements were also carried out for the determination of the size of the redeposited fragments on the surface of the polymer. The film treated by the laser ablation was scanned by AFM (Nanoscope, Digital

Instrument, USA) and images of the redeposited fragment were captured by tapping mode and by phase imaging, which provides nanometer scale information about surface structures. The analysis of these samples was performed 200 µm and 500 µm away from the laser treated surface in order to analyse the redeposited debris.

Spectroscopic characterisation

Information on the morphology of the carbon films was obtained by Raman spectroscopy. Graphitic carbon and other sp² bonded amorphous carbon are strong Raman scatterers despite their intense optical absorption. This technique is commonly used in the analysis of carbon films since it provides information not only about the structure of the carbon but also about its degree of order.³⁵ The confocal arrangement used in this work presents the advantage of a high three-dimensional resolution, which is particularly suited for the analysis of microstructures.¹⁶ The morphology of the conductive carbon film was obtained with an XY Dilor Raman spectrometer (UK). The 514.53 nm exciting line of an argon laser was focused on the samples through the objective of a microscope such that the diameter of the analysed area was about 1 µm. The laser beam power was limited to 0.5 mW in order to prevent heating of the sample. Several spectra were collected at different spots on the surface of the treated and non-treated areas.

Electrochemical characterisation

Film resistance measurements were performed using a 1 mm collinear four-point probe (Jandel Engineering Ltd, UK). Resistance values of the films were determined along the film and are therefore expressed in units of Ω mm⁻¹. Film capacitance measurements were performed with a conventional three electrode potentiostat with a calomel reference electrode and a platinum counter electrode (AEW1, Sycopel Scientific Ltd, UK). Cyclic voltammetry measurements were carried out at room temperature (23 ± 0.5 °C) in 1 M H₂SO₄ (titrisol, Merck, Darmstadt, Germany) as electrolyte, with scan rates ranging from 5 to 300 mV s⁻¹. The working electrode was defined by masking an area of approx. 1 mm² of the carbon film using a dielectric adhesive tape.

Results and discussion

The photoablation procedure is first optimised in order to produce microstructures at the image point. When the film is placed at the image plane, the photoablated surface does not exhibit any measurable conductivity and produces clear patterns as already published elsewhere.¹⁶ By changing the distance between the target and the objective, the formation of a dark film is observed around the ablated area. The presence of this film takes place only on the border of the laser treated surface within a radius of approx. 500 µm as schematically represented in Fig. 1. By moving the table during the ablation, it is possible to produce line patterns of this dark film (see Fig. 1). Two films generated with this technique are presented in Fig. 2, which clearly shows that the surface exposed to the laser beam at the end of the scan is not covered by dark particles (see "ablated area" at the left end of the dark pattern). This is due to the fact that each pulse always cleans the surface defined by the laser beam from the redeposited debris of the precedent pulse. Outside the surface defined by the laser beam, the debris can accumulate to form a continuous layer of debris, shown in Fig. 2.

The distance between the image point and the objective has been varied in order to determine how the energy density of the laser beam affects the carbonisation of the ablated material. Resistance measurements of the film generated at different distances from the image plane are reported in Fig. 3. It

Fig. 1 Laser ablation and patterning mechanism. The redeposited debris forms a layer around the ablated surface. By scanning the substrate, the debris can be patterned over a larger surface in order to generate a conductive film.

Fig. 2 Top picture of the patterned carbon electrodes. The laser ablation has been performed from the right to the left. The clear square area on the left is the place of the latest pulses. (Ablation conditions: position of the sample at the focal point; mask size, $1\text{ cm} \times 1\text{ cm}$; laser fluence at the image point, 2000 mJ cm^{-2} , 50 Hz; table displacement, 0.1 mm s^{-1} .)

is obvious that the resistance of the film is minimal at a distance of about 5.5 mm before the image plane. This point placed at a tenth of the distance between the image plane and the objective corresponds to the focal plane, where the fluence is at its maximum. This point of maximal fluence is the place for which the carbonisation of the ejected fragments is maximum. The microstructured pattern obtained on the substrate is about 40% smaller than that obtained at the image point, and it exhibits a lower aspect ratio. As a consequence, the optical arrangement leading to the maximal carbonisation (*i.e.* at 5.5 mm before the image plane) has been chosen for all other characterisations of the redeposited debris formed during photoablation.

Significant changes in the resistance occur by varying the pulse numbers per unit area. Fig. 4 presents a semi-logarithmic plot of the polymer surface resistance as a function of the number of laser pulses fired per mm on the polystyrene. The decrease in the resistance is dramatic from 0 to 300 pulses mm^{-1} and a lower decrease is observed in the range of 300 to 800 pulses mm^{-1} . Polystyrene fragments carbonised in the plume are redeposited on the surface. Below 100 pulses mm^{-1} , however, the carbon film is discontinuous: only a few domains in contact with each other are responsible for the low value of the measured conductivity. By increasing the number of pulses mm^{-1} , a higher number of carbon particles are redeposited on the surface, forming a continuous layer of conductive material.

The effect of the fluence on the film resistance has also been measured. At low fluences ($<1000\text{ mJ cm}^{-2}$), the film is ten times more resistant than at higher fluences. It is generally observed that polymer photoablation is less efficient at lower

Fig. 3 Electrical resistance of the carbon film as a function of the distance from the image point (2000 mJ cm^{-2} at the image point, 50 Hz, 300 pulses mm^{-1}).

Fig. 4 Semi-logarithmic plot of the resistance of the film *vs.* the number of pulses drilled per unit area (2000 mJ cm^{-2} at the image point).

than at higher fluences,¹⁶ leading to a lower source of carbon in the plume. The plasma is also cooler due to the lower photon density reabsorbed in the plume. This leads to a less effective carbonisation process. At higher fluences ($>1000\text{ mJ cm}^{-2}$), the ablation and plume carbonisation reach saturation, and the resistance becomes smaller and comparable for all fluences. On the other hand, the film formation depends only weakly on the repetition rate of the laser on the surface, indicating that this factor does not affect the carbonisation. Indeed, no significant conductivity differences are measured between films generated in the range of 2 to 40 Hz. This result means that the carbonisation process is mainly a one pulse process and that the cooling time of the substrate surface at 40 Hz between two consecutive pulses is long enough.

The laser treated substrate is cut with a microtome and the section is investigated by SEM. Fig. 5(a) shows the cross section of the laser treated polymer. The photoablation process has led to the generation of structures in the substrate, in the present case, a $50\text{ }\mu\text{m}$ deep and $600\text{ }\mu\text{m}$ wide open channel. The removed polymer acts as a carbon source in the porous layer weakly bound to the surface. A more precise view of the surface layer is presented in Fig. 5(b). A homogeneous coating 1 to $1.5\text{ }\mu\text{m}$ thick can be observed on the ablated surface. Considering that the conductivity of the photoablated layer is due to this layer, it is possible to calculate its volume resistivity. This material exhibits a remarkably low resistivity of $2 \times 10^{-2}\text{ }\Omega\text{ m}$, a value slightly higher than that of graphite, $3.9 \times 10^{-3}\text{ }\Omega\text{ m}$ (ref. 36). The resistivity, in particular, is two orders of magnitude lower than that of pyrolytic carbon ($1\text{--}1.8\text{ }\Omega\text{ m}$).³⁶

The AFM image presented in Fig. 6(a) shows the polymer morphology at $200\text{ }\mu\text{m}$ from the border of the laser treated area. The redeposited fragments build a continuous film with a mean roughness of 24.9 nm instead of the 1.4 nm for the native polymer surface. The mean dimension of the deposited fragments is also found to lie in the range of 10 to 100 nm . The total specific area of the scanned surface has been calculated to be 85% larger than the theoretical surface. This increased surface area is however underestimated. Indeed, the AFM technique only measures over the part of the structures with a maximal angle of 60° from the vertical because of the tip profile. The cavities in the redeposited fragments can therefore not be examined and calculated as the real surface area. The morphology of the fragments redeposited on the surface has also been measured $500\text{ }\mu\text{m}$ away from the photoablated channel and is reported in Fig. 6(b). Far from the ablated line, the film is discontinuous and the native polymer can be observed. The fragments are less numerous and randomly redeposited on the surface, with sizes of about 50 to 100 nm , which is comparable to the size of spots deposited by pulsed laser deposition.³⁷

Spectroscopic information has been obtained by the analysis of the film with microconfocal Raman spectroscopy.

Fig. 5 (a) Cross section of the laser treated polystyrene. The cavity shown on the surface is created by the photoablation of the polymer. (b) Detailed view of the channel cross section at the surface of the ablated structure. An about 1 μm layer of weakly bound material can be observed on the surface.

The Raman spectrum of the black film presented in Fig. 7 exhibits two bands at 1582 and 1355 cm⁻¹, which are typical in graphite samples. Indeed, the Raman spectrum of large single-crystal graphite domains consists of a sharp band at 1580 cm⁻¹ (the G peak), attributable to the in-plane symmetric C–C stretch. In polycrystalline graphite, a second peak appears at about 1355 cm⁻¹ (the so-called disorder or D peak), which is activated by disorder associated with finite crystallite sizes. An analysis of both band intensities gives information about the crystallinity degree and the particle size of the sp² carbon.³⁵ The graphite particle size can be estimated with eqn. (1) as reported by Knight and White:³⁸

$$P = 44(I_D/I_G)^{-1} \quad (1)$$

where P is the particle size and I_D/I_G the ratio of the D peak *vs.* the G peak intensities. The in-plane microcrystallite size is of the order of 60 Å. It is worth noticing that no other Raman band is present in the spectrum, meaning that polystyrene redeposited on the surface is quantitatively converted into graphitised carbon. The film is thus composed of microporous carbon exhibiting a high specific surface area.³⁹

The electrochemical activity of the laser formed carbon films was studied in a sulfuric acid electrolyte solution by cyclic voltammetry. The voltammograms (–100 to 400 mV)

Fig. 6 AFM pictures of the redeposited fragments taken (a) 500 μm and (b) 200 μm away from the laser treated surface.

for films deposited under ambient atmosphere or under argon gas flow are presented in the insert of Fig. 8. It is obvious that the film generated under argon gas flow displays significantly lower capacitive currents compared to films formed under ambient air atmosphere. The high capacitive current observed in the case of the film formed under air indicates that the real surface area of the electrode in contact with the electrolyte is large and highly activated, whereas the lower residual current in the case of argon gas flow reveals a non-activated surface. This effect has also been observed for carbon films formed under nitrogen flow. Nevertheless, a remarkable effect is observed after the cathodic and anodic activation of the film generated under argon or nitrogen. Indeed, when the potential is scanned out of the potential window (–0.5 to 1 V), where oxidation of the carbon occurs,^{40,41} the double layer capacitance of the film increases and reaches the same value as that obtained for the film formed under air environment. The activation process that usually leads to the formation of oxidised functionalities in the carbon film considerably changes the

Fig. 7 Confocal Raman spectroscopy study of the carbon film generated by the laser ablation of polystyrene. The two bands at 1582 and 1355 cm⁻¹ reveal the graphitisation and the high disorganisation of the carbon particles.

Fig. 8 The dc capacitance measurement of an electrode fabricated under air atmosphere (1 M H₂SO₄, scan rates from 10 to 300 mV s⁻¹, electrode area 0.8 mm²). Insert: Comparison between the dc charging current of two freshly laser fabricated carbon electrodes under air (---) and Ar (—) atmospheres (1 M H₂SO₄, scan rate 10 mV s⁻¹).

dielectric constant and the wettability of the electrode. This observation suggests that electrodes fabricated in air contain oxygen functionalities, whereas those fabricated in argon or nitrogen are free from them. The mechanism is therefore a reduction of the polymer fragments to carbon with surface reoxidation in air. The origin of the charging current can be explained by two different and probably complementary phenomena. The first one is a quasi-continuous sequence of redox potential due to the successive charging of mutually interacting redox groups similarly to chargeable polymeric layers.⁴² In this case, the charge capacity results in the charging of individual functional groups. On the other hand, this charging current may be attributed to the “common” double layer with mobile charge carriers on either side of the interface.⁴³ It should be noted that the Raman detection of functional groups on the electrode surface has been impossible due to the large absorption of the excitation light by the carbon.

The electrolytic capacity of the carbon film can be estimated from the *I*-*E* plots with eqn. (2):

$$I_c = vC_d \quad (2)$$

where *v* is the potential scan rate, *C_d* the double layer capacitance and *I_c* the capacitive current. As shown in Fig. 8, the capacitive current values obtained at -0.2 V vs. a calomel reference electrode are proportional to the scan rate, which allows one to estimate the film capacitance. Capacitance values in the order of 0.5 to 5 mF cm⁻² are calculated for the films generated in ambient atmosphere. These values are much larger than those obtained for a non-activated carbon fiber electrode (2 to 8 μF cm⁻²).⁴⁴ Indeed, our data are similar to those obtained with fractured fibers (1 to 5 mF cm⁻²)⁴⁴ or with activated planar glassy carbon (10 mF cm⁻²).⁴⁵ Differences that are measured from one film to another probably originate from the weak adhesion of the conducting layer and the weak control of the ablation conditions, which leads to irreproducible carbon coverage on the surface of the polymer.

Conclusion

This work shows the patterning and the characterisation of a nanocrystalline graphite produced by photoablation of polystyrene. The carbon film exhibits either large or small double layer capacitance depending on the oxidative properties of the atmosphere used during the laser process. This work shows the importance of the redeposited debris generated during the photoablation of polymer. If the photoablation is considered as a clean technique for microfabrication, it should be noted that, under particular conditions, the redeposited debris considerably affects the surface properties of the surrounding surface. This phenomenon is even enhanced by the use of

scanning photoablation due to the systematic redeposition of photoablated debris behind the treated area. This work also shows how a conductive and/or capacitive layer can be patterned on a highly isolating matrix.

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