UDK 533.9:661.666:542.428.8
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 45(3)233(2011)

MODIFICATION OF SURFACE MORPHOLOGY OF GRAPHITE BY OXYGEN PLASMA TREATMENT

SPREMEMBA MORFOLOGIJE GRAFITA MED OBDELAVO S KISIKOVO PLAZMO

Kristina Eleršič[1], Ita Junkar[1], Martina Modic[1], Rok Zaplotnik[1], Alenka Vesel[2], Uroš Cvelbar[2]

[1]Institut "Jožef Stefan", Jamova cesta 39, 1000 Ljubljana, Slovenia
[2]Center of Excellence for Polymer Materials and Technologies, Tehnološki park 24, 1000 Ljubljana, Slovenia
kristina.elersic@ijs.si

Prejem rokopisa – received: 2011-02-13; sprejem za objavo – accepted for publication: 2011-03-07

Samples of highly oriented pyrolitic graphite (HOPG) were exposed to fully dissociated oxygen plasma created by a radiofrequency discharge in pure oxygen. The discharge was powered with a radiofrequency generator operating at the standard industrial frequency of 13.56 MHz and the output power of 1000 W. Samples of pyrolitic graphite were in pieces with dimensions of 10 mm × 10 mm × (≈1.7) mm in high and exposed to plasma for different periods up to 90 s. The morphology of originally perfectly flat samples was monitored with a high resolution scanning electron microscope (SEM). Oxygen plasma caused non-homogeneous etching of samples. The first visible effect of plasma treatment was an appearance of rather spherical features of sub-micrometer dimensions as well as randomly oriented channel - like structures. Increasing the treatment time caused transformation of the spherical features into cones. The size of cones increased until about 40 s of plasma treatment. Large cones of few micrometers in size were observed at spots with surface dust particles. Prolonged treatment caused destruction of the cones and formation of sub-micrometer large holes. The effects were explained by interaction of highly excited oxygen Particles with surface carbon atoms.

Keywords: graphite, oxygen plasma, scanning electron microscopy, morphology, nanocones

Vzorce visoko orientiranega pirolitskega grafita smo izpostavili delovanju popolnoma disociirane kisikove plazme, ki smo jo vzbujali z radiofrekvenčnim generatorjem. Generator deluje pri industrijski frekvenci 13,56 MHz in izhodni moči 1000 W. Grafitne vzorce, narezane na kose z merami 10 mm × 10 mm × (≈1,7) mm v višino in jih obdelovali s plazmo v različnem času do 90 s. Morfologijo prvotno povsem ravnih vzorcev smo opazovali z vrstičnim elektronskim mikroskopom visoke ločljivosti. Opazili smo, da plazemska obdelava vodi k nehomogenemu jedkanju. Sprva se na površini grafita tvorijo kroglasti skupki dimenzije pod 1 μm, ki kaj kmalu prerastejo v stožce. Velikost stožcev narašča s časom plazemske obdelave do okoli 40 s, z nadaljnjo obdelavo pa postopoma izginjajo. Po dolgem času obdelave stožci povsem izginejo, namesto njih pa nastanejo okrogle vdolbine. Pri krajših časih obdelave smo opazili tudi nepravilno orientirane kanale. Na mestih, kjer so se nahajali prašni drobci, smo opazili tudi večje stožce dimenzije več mikrometrov. Opažene pojave smo razložili z interakcijo visoko vzbujenih kisikovih delcev s površinskimi atomi ogljika.

Ključne besede: grafit, kisikova plazma, vrstični elektronski mikroskop, morfologija, nanodelci

1 INTRODUCTION

Treatment of materials by oxygen plasma is a popular technique for modification of surface morphology. The development of high resolution scanning electron microscopes allow for monitoring the surface features at almost nanometer scale. It has been found that oxygen plasma treatment causes oxidation of metals.[1–6] The oxidation is never uniform, but interesting nanofeatures appear on the surface of samples exposed to plasma with right parameters.[3,7,8] Interaction of aggressive plasma with polymer materials usually results in burning of samples. Mild oxygen plasma treatment, however, causes both functionalization of polymers with polar functional groups [9–11] and modification of surface morphology. Quite often it happens that extremely rough surface is obtained with well-defined and dense nanocones and similar structures on the surface of polymer exposed to highly reactive but cold oxygen plasma.[12,13] Quite interesting as well, plasma treatment also causes modification of organic cells and tissues and represents an interesting method for modification of bacterial cell wall during plasma sterilization of delicate materials.[14–16] Plasma treatment of different materials therefore results in modification of surface properties of practically all materials.[17]

Different discharges were applied for generation of oxygen plasma but it seems that the majority of authors like high frequency electrode-less discharges such as radiofrequency [18–21] and microwave one.[22–24] The properties of plasma created in such discharges vary enormously and depend on the size of the discharge chamber, the type of materials facing plasma, the discharge power, frequency and coupling, the pressure and flow of oxygen through a vacuum system, the concentration of impurities in the discharge vessel, and (usually neglected but often very important) the properties of samples treated by plasma. The major reactants in such plasma are neutral oxygen atoms in the ground state,[25–29] although other excited particles may play a certain role in modification of materials as well. The density of oxygen

atoms depends on many discharge parameters including the discharge power, but in highly concentrated plasma the dissociation fraction is practically 100 % as long as the materials facing plasma exhibit a low coefficient for heterogeneous surface recombination. Although graphite samples have been exposed to oxygen plasma by several authors,[30–34] the evolution of surface morphology during plasma treatment is still far from being well understood. The current paper presents recent results obtained in our laboratories using extremely aggressive oxygen plasma for treatment of highly oriented pyrolitic graphite samples.

2 EXPERIMENTAL

Commercially available graphite samples were used. Samples were supplied by NT-MDT,HOPG marked as ZYH, with piece thickness of 1,7 mm. Samples have special properties as they are prepared layer by layer. After exposure to plasma we can renew upper working layer with simply removing it with scotch tape. Graphite molecular layers have a spalling angle in relation to the surface layer, at which the layers are easily removed and the sample can be exposed to plasma modification more then once.

Samples were exposed to extremely reactive oxygen plasma created in a discharge chamber of a vacuum system. The system was pumped with a two stage rotary pump with a pumping speed of 80 $m^3\ h^{-1}$ and commercially available oxygen was leaked into the chamber during continuous pumping. The pressure of oxygen inside the chamber was 75 Pa. Plasma was generated with a radiofrequency generator operating at the standard industrial frequency of 13.56 MHz and the output power of 1000 W. The plasma volume was pretty small (less than 1 L) so plasma was pretty energetic. Any attempt to measure plasma parameters by an electrical or a catalytic probe resulted in a rapid melting of the probe so we were unable to obtain a meaningful result. Only optical emission spectroscopy was used for estimation of plasma parameters. The measurements showed that oxygen molecules are almost fully dissociated. Taking into account the measured pressure in the system before turning on the discharge it was possible to calculate the density of oxygen atoms using the standard vacuum equation

$$p = n_M\, k\, T \tag{1}$$

where p is the measured pressure, n the density of molecules, k Boltzmann constant and T the absolute gas temperature before turning on the discharge. Assuming 100 % dissociation as suggested by optical emission spectroscopy measurements, the density of O atoms in plasma is twice the density of molecules before turning on the discharge, i.e.

$$n_A = 2\, p\, /\, (k\, T) \tag{2}$$

Taking into account numerical values the density of oxygen atoms in our plasma is $3.7 \times 10^{22}\ m^{-3}$.

The morphology of samples was monitored by scanning electron microscopy. We used the high-resolution scanning electron microscopy FEG-SEM7600F from JEOL. Images were taken by angle of 45° and magnitudes of 1 000-times and 10 000-times at low accelerating voltage 2 kV. Lower secondary electron images (LEI) are presented in this paper.

3 RESULTS

Samples of pyrolitic graphite were cut to pieces with dimensions of (10 × 10) mm with thickness of working layer (1.7 ± 0.2) mm and exposed to plasma for different periods up to 90 s. After the plasma treatment they were mounted in the electron microscope and imaged at different magnifications. In this paper we present only results obtained at two different magnifications: 1 000-times and 10 000-times. The surface of an untreated sample was almost perfectly flat so we do not show a corresponding SEM image. Interesting modification of surface morphology starts after about 15 s of plasma treatment. **Figure 1** represents a couple of SEM images of the samples exposed to oxygen plasma for 18 s. The original image is obtained at magnification of 1 000-times, while the insert was obtained 10 000-times. The same applies for all other Figures. The SEM image pre-

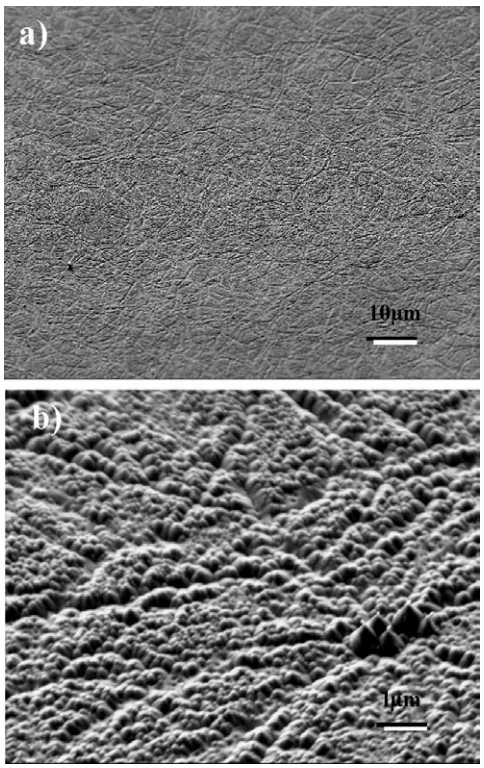

Figure 1: SEM image of a sample exposed to plasma for 18 s; a) at magnification of 1 000-times, b) at magnification of 10 000 times

Slika 1: Površina vzorca po obdelavi s kisikovo plazmo za 18 s; a) pri povečavi 1 000-krat, b) pri povečavi 10 000-krat

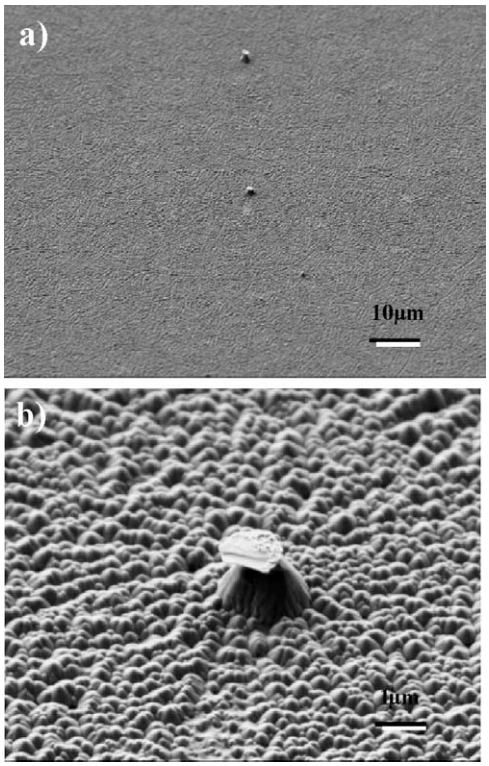

Figure 2: SEM image of a sample exposed to plasma for 20 s; a) at magnification of 1 000-times, b) at magnification of 10 000-times

Slika 2: Površina vzorca po obdelavi s kisikovo plazmo za 20 s; a) pri povečavi 1 000-krat, b) pri povečavi 10 000-krat

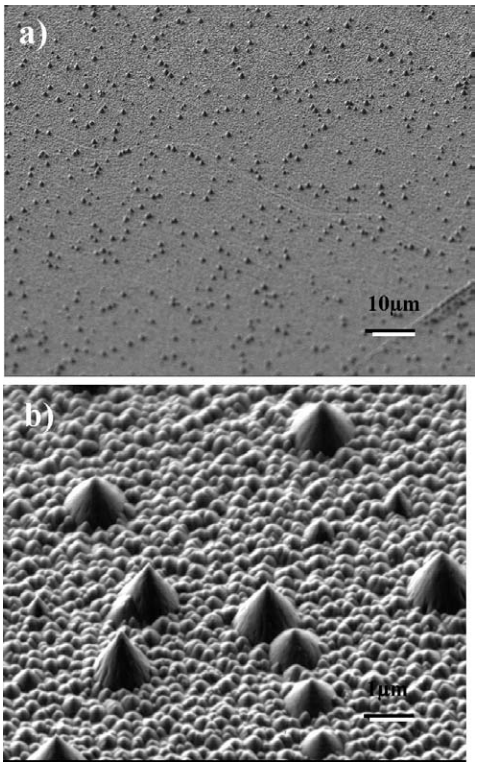

Figure 4: SEM image of a sample exposed to plasma for 31 s: a) at magnification of 1 000-times, b) at magnification of 10 000-times

Slika 4: Površina vzorca po obdelavi s kisikovo plazmo za 31 s; a) pri povečavi 1 000-krat, b) pri povečavi 10 000-krat

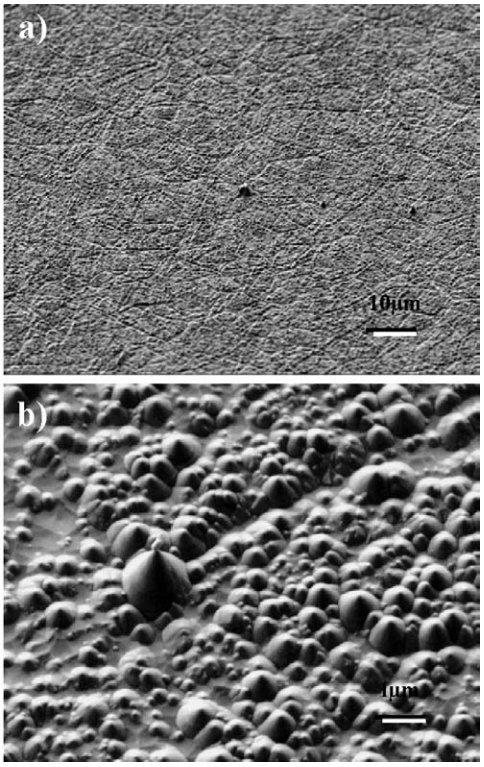

Figure 3: SEM image of a sample exposed to plasma for 25 s; a) at magnification of 1 000-times, b) at magnification of 10 000-times

Slika 3: Površina vzorca po obdelavi s kisikovo plazmo za 25 s; a) pri povečavi 1 000-krat, b) pri povečavi 10 000-krat

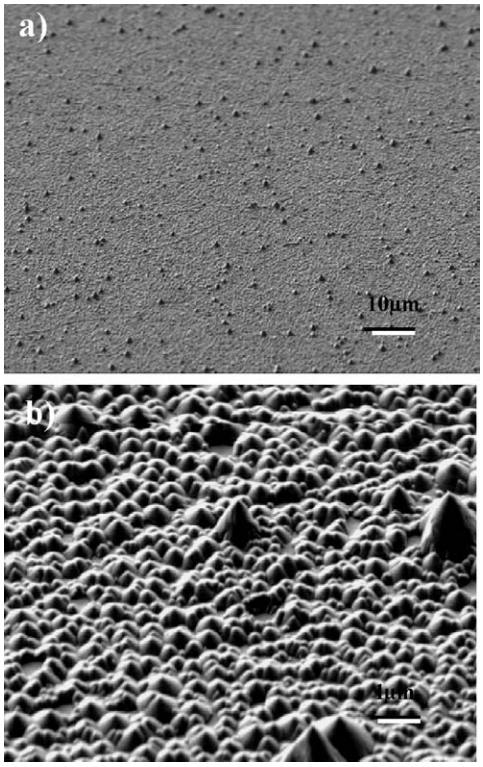

Figure 5: SEM image of a sample exposed to plasma for 35 s; a) at magnification of 1 000-times, b) at magnification of 10 000-times

Slika 5: Površina vzorca po obdelavi s kisikovo plazmo za 35 s; a) pri povečavi 1 000-krat , b) pri povečavi 10 000-krat

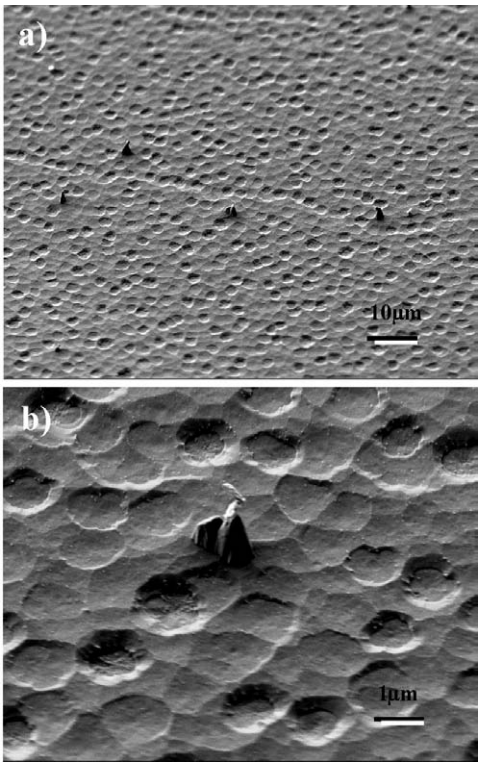

Figure 6: SEM image of a sample exposed to plasma for 52 s; a) at magnification of 1 000-times, b) at magnification of 10 000-times
Slika 6: Površina vzorca po obdelavi s kisikovo plazmo za 52 s; a) pri povečavi 1 000-krat, b) pri povečavi 10 000-krat

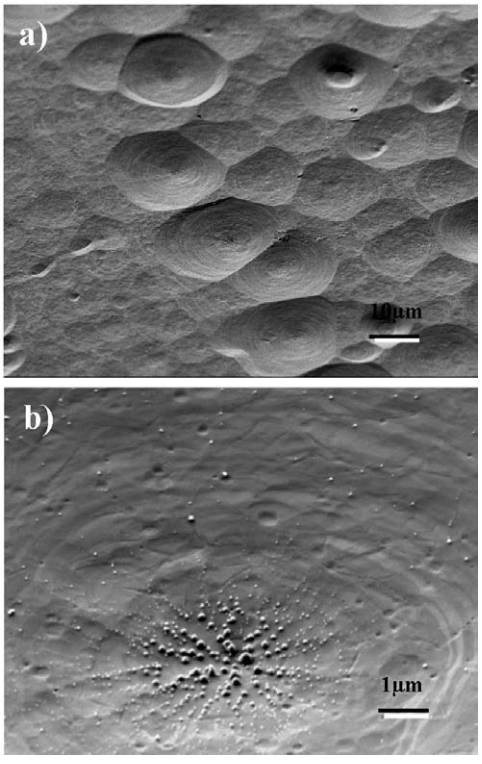

Figure 7: SEM image of a sample exposed to plasma for 90 s; a) at magnification of 1 000-times, b) at magnification of 10 000-times
Slika 7: Površina vzorca po obdelavi s kisikovo plazmo za 90 s; a) pri povečavi 1 000-krat, b) pri povečavi 10 000-krat

sented in **Figure 1** shows interesting surface morphology. Randomly oriented channels are observed already at 1 000-times, but the 10 000-times magnification reveals spherical features on the surface of (as mentioned above) originally flat surface. The features are transformed quickly to cone – like structures as shown in **Figure 2** which is the image after 20s of plasma treatment. The features become somewhat bigger since they may be visible even at the small magnification. **Figure 3** presents a couple of images obtained after 25 s of plasma treatment. Numerous small cones with randomly distributed large cones are observed in **Figure 4** which represents the images obtained after 31 s. The features remain rather unchanged for 35 s (**Figure 5**). After 52 s of plasma treatment, however, they almost vanished as demonstrated in **Figure 6**. Also, small craters become visible. Further increase of treatment time causes an important increase of the crater diameters and disappearance of all surface cones. **Figure 7** represents the SEM images after 90 s. It is interesting that small cones are observed at the bottom of craters as revealed from **Figure 7**.

4 DISCUSSION

The SEM images presented in **Figures 1–7** are attractive if not all that un-expected and definitely deserve a discussion. As mentioned in Introduction, exposure of almost any material to oxygen plasma causes increased roughness. In the case of materials that form rather stable oxides, exposure to oxygen plasma leads to formation of a thin oxide film. The oxide film created at exposure of a metal to non-equilibrium oxygen plasma, however, may have different morphology than an oxide film obtained by thermal oxidation performed close to thermal equilibrium conditions. For instance, bundles of nanowires with an extremely favorite aspect ratio may grow on the surface of some metals. The first report on this phenomenon appeared in 1995,[35] but until recently, no solid hypothesis that would explain the phenomenon appeared. Much work has been performed on oxidation of iron and an appropriate hypothesis appeared recently.[36] The hypothesis may explain interaction of oxygen plasma with metals, but is inappropriate for the case of carbon containing materials. Namely, carbon does not form stable oxides but the interaction between reactive oxygen particles results in formation of CO radicals and perhaps also CO_2 molecules that desorb from the surface even at room temperature. Exposure of carbon containing materials to oxygen plasma therefore results in etching. Surprisingly enough, etching is far from being homogeneous. Numerous authors showed that exposure of many polymers to oxygen plasma yields to formation of cone – like structures. While no internationally accepted theory appeared, an appropriate hypothesis was launched recently by Junkar et al.[12] The authors proposed a hypothesis that the extremely non-homo-

geneous etching was due to non-homogeneity of the sample. Namely, polymers are often semi-crystalline and a hypothesis was that the crystalline part of polymer is etched at lower rate than the amorphous component. Unfortunately, the authors of that paper presented no solid confirmation in terms of the size of polymer crystallites. In any case, the hypothesis of Junkar is not applicable to the case of highly oriented graphite since it is almost mono-crystalline. The results observed in **Figures 1–7** therefore cannot be explained by inhomogeneity of the original material.

One possible explanation that seems obvious when monitoring **Figure 2** is an existence of surface dust particles. Namely, the insert in **Figure 2** reveals a dust particle above the large cone. The dust particle prevents reactive oxygen particles that abound in our plasma reaching the surface of graphite. The result is a side erosion of material. Such effects are known to exist in natural formations on a meter-scale practically in all cases where the uppermost layer of material is eroded at lower rate than the material beneath. This hypothesis therefore explains formation of large cones such as the one observed in **Figure 2**. The hypothesis, however, cannot explain formation of numerous small features observed in **Figures 1–5**.

The lack of appropriate hypothesis may lead to a speculation that an extremely thin, by SEM not visible film of impurities is presented on the surface of the graphite. The film may shrink to small islets upon plasma treatment either due to electrostatic forces (assuming the impurities are not conductive), or due to thermodynamic forces (heating of materials often leads to formation of droplets, or both. The speculation may be justified by careful examination of cone peaks, for instance the largest cone in the insert of **Figure 3**. It seems that this cone as well as many others is peaked with a foreign material. The EDX analysis, however, did not reveal any impurities so the speculation is questionable. Still, appearance of quite a few cones scattered randomly on the surface of the sample best observed in **Figure 4** keeps this speculation appropriate.

Scientists familiar with materials etching by ion beams would quickly find an explanation for appearance of the cones. Namely, it is well known that etching of organic as well as some other materials by ion beams (for instance in Auger electron depth profiling) leads to formation of nanostructured surface. The explanation, however, fails in our case since the samples are not exposed to ions with any kinetic energy worth speaking about. Namely, the samples were kept at floating potential during plasma treatment. The floating potential depends on the electron temperature in plasma as well as on the mass of ions. As mentioned earlier, the electron temperature has not been measured but it can be estimated to few electron volts. The ion mass is known since we have only two ions: O_2^+ and O^+. The concentration of other gases in the system is negligible. The voltage across the sheath between unperturbed plasma and the sample can be estimated to about 10 V so the ions gain kinetic energy of only 10 eV. This energy is definitely too low for any decent discussion of ballistic effects caused on the surface of samples due to exposure to oxygen ions.

The formation of the features observed in **Figures 1–5** therefore remains an unresolved problem. Instead of presenting any other speculation let us point to another observation – this one is rather unexpected. **Figure 6** reveals a disappearance of the nano-cones after prolonged plasma treatment. The Figure clearly indicates that only largest cones are visible if not preserved as those shown in **Figures 2–5**. Obviously, the mechanism that is responsible for formation of cones becomes less important than a destruction mechanism. Also, well defined holes appear on the surface of the graphite sample. While the destruction may be explained by thermal effects (very high temperature of features stretching away from the surface) the explanation of the hole formation is a difficult task. The hole size increases with further treatment as shown in **Figure 7**. This Figure represents SEM images obtained after plasma treatment for 90 s. The size and depth of the holes vary but it is clear that the size of holes increases with increasing plasma treatment time. Any speculation on the observed fact that at least some holes contain small features at the bottom is beyond the scope of this paper.

The fact that molecules in our oxygen plasma are fully dissociate allows for estimation of the oxygen atom flux onto the surface and speculations of the effects they may cause on the graphite surface. The density of atoms in plasma was calculated using equation (2). The flux of atoms onto the surface is calculated using the standard equation

$$j = ¼\, n\, v \tag{3}$$

where v is the average thermal velocity of oxygen atoms. This value is not known since the gas kinetic temperature could not be measured. Still, the order of magnitude is 1000 K so the velocity in equation (3) is of the order of 1 000 m/s. The resultant flux is then of the order of 10^{25} m^{-2} s^{-1}. This is a really huge flux. Taking into account the recombination probability of the order of 10^{-2} [38] the sample is heated due to heterogeneous surface recombination at the rate of

$$P = ½\, \mathrm{j}\, \gamma\, W\, A \tag{4}$$

Here, γ is the probability for surface recombination, W the dissociation energy of and oxygen molecule and A the total surface of the sample. Taking into account numerical values, the power is of the order of 1 W. The power is pretty low and definitely does not suggest extensive heating of the graphite sample. Obviously, if thermal effects are important for disappearance of cones on the surface of graphite samples after prolonged plasma treatment, they should be due to other effects. Such effects may include neutralization of charged

particles and relaxation of metastables. Unfortunately, any attempt for a decent characterization of plasma failed so any discussion of the heating mechanisms is beyond the scope of the paper.

5 CONCLUSION

Exposure of highly oriented pyrolitic graphite samples to aggressive oxygen plasma revealed formation of nanocones on the surface. The appearance of nanocones was explained by non-homogeneous etching of material upon exposure to reactive oxygen particles created in plasma. The nanocones were of similar size of few 100 nm apart from few that were several micrometers large. The formation of such large cones was explained by presence of dust particles on the sample surface. The dust particles prevented reactive oxygen atoms from reaching the surface so side erosion prevailed. At prolonged treatment of samples the cones disappeared and were slowly but graduate replaced by holes whose dimensions increased with increasing plasma treatment time. Several speculations about the observed phenomena were presented and discussed but the results did not allow for presenting a decent hypothesis. The results, however, are interesting and represent just another example of un-usual modification of a material upon exposure to non-equilibrium oxygen plasma.

ACKNOWLEDGEMENT

The authors acknowledge the financial support from the Ministry of Higher Education, Science and Technology of the Republic of Slovenia through the contract No. 3211-10-000057 (Center of Excellence Polymer Materials and Technologies).

6 REFERENCES

[1] N. M. D. Brown, N. Cui, A. McKinley, Applied Surface Science, 134 (**1998**), 11
[2] G. Arnoult, R. P. Cardoso, T. Belmonte, G. Henrion Appl. Phys. Lett. 93 (**2008**), 191507
[3] I. Denysenko, K. Ostrikov, U. Cvelbar, M. Mozetic, N. A. Azarenkov, Journal of Applied Physics 108 (**2010**), 74901
[4] H-X. You, N. Brown, K. F. Al-Assadi, Surface Science, 284 (**1993**), 263
[5] J. I. Paredes, A. Martínez-Alonso, P. X. Hou, T. Kyotani, T. J. M. D. Tascón, Carbon, 44 (**2006**), 2469
[6] M. Mozetic, A. Zalar, M. Kveder, M. Drobnic, Vacuum, 45 (**1994**), 1017
[7] U. Cvelbar, K. Ostrikov, I. Levchenko, M. Mozetic, M. K. Sunkara, Appl. Phys. Lett , 94 (**2009**), 211502
[8] U. Cvelbar, K. Ken Ostrikov, M. Mozetic, Nanotechnology 19 (**2008**), 405605
[9] A. Vesel, M. Mozetič, J. Phys.: Conf. Ser., 100 (**2008**), 012027
[10] A. Vesel, M. Mozetič, J. Phys.: Conf. Ser., 162 (**2009**), 012015
[11] U. Cvelbar, M. Mozetič, I. Junkar, A. Vesel, J. Kovac, A. Drenik, T. Vrlinic, N. Hauptman, M. Klanjsek - Gunde, B. Markoli, N. Krstulovic, S. Milosevic, F. Gaboriau, T. Belmonte, Applied Surface Science, 253 (**2007**), 8669
[12] I. Junkar, A. Vesel, U. Cvelbar, M. Mozetic, S. Strnad Vacuum, (**2009**) 84, 83.
[13] M. Mozetic, Vacuum, (**2003**) 71, 237.
[14] K. Lee, K.-H. Paek, W-T Ju, Y. Lee, J Microbiol. ,44 (**2006**), 269
[15] U. Cvelbar, D. Vujošević, Z. Vratnica, M. Mozetič, J. Phys. D: Appl. Phys., 39 (**2006**), 487
[16] C. Canal, F. Gaboriau, S. Villeger, U. Cvelbar, A. Ricard, International Journal of Pharmaceutics, 367 (**2009**), 155
[17] A. Vesel, M. Mozetič, S. Strnad, Z. Persin, K. Stana-Kleinschek, N. Hauptman, Vacuum, 84 (**2009**), 79
[18] A. Brockhaus, G. F. Leu, V. Selenin, K. Tarnev, J. Engemann Plasma Sources Sci. Technol., 15 (**2006**), 171
[19] Z. Shpilman, I. Gouzman, G. Lempert, E. Grossman, A. Hoffman Review of Scientific Instruments, 79 (**2008**), 025106
[20] Z. Kregar, N. Krstulović, N. Glavan Vukelić, S. Milošević, J. Phys. D: Appl. Phys., 42 (**2009**), 145201
[21] M. Goujon, T. Belmonte, G. Henrion, , Thin Solid Films, 475 (**2005**), 118
[22] B. W. Muir, H. Thissen, G. P. Simon, P. J. Murphy, H. J. Griesser,, Thin Solid Films, 500 (**2006**), 34
[23] R. P. Cardoso, T. Belmonte, G. Henrion, N. Sadeghi, J. Phys. D: Appl. Phys., 39 (**2006**), 4178
[24] A. Vesel, M. Mozetic, M. Balat - Pichelin, Vacuum, 81(**2007**), 1088
[25] N. Krstulović, I. Levchenko, S. Milošević, U. Cvelbar, A. Vesel, M. Mozetič, J. Phys. D: Appl. Phys., 39 (**2006**),799
[26] Č. Donik, A. K., D. Mandrino, I. Paulin, M. Jenko, B. Pihlar, Applied Surface Science, 255 (**2009**), 7056
[27] I. Arcon, M. Mozetič, A. Kodre, Vacuum, 80 (**2005**), 178
[28] M. Mozetic, Surface and Coatings Technology, 201 (**2007**), 4837
[29] M. Mozetic, A. Vesel, V. Monna, A. Ricard, Vacuum, 71 (**2003**), 201
[30] E. Bourelle, H. Konno, M. Inagaki, Carbon, 37 (**1999**), 2041
[31] H. Fredriksson, D. Chakarov, B. Kasemo, Carbon, 47 (**2009**), 1335
[32] J. I. Paredes, A. Martinez-Alonso, J. M. D. Tascón, Carbon, 38 (**2000**), 1183
[33] U. Cvelbar, B. Markoli, I. Poberaj, A. Zalar, L. Kosec, S. Spai, Applied Surface Science, 253 (**2006**) 1861
[34] M. Mozetič, A. Zalar, Materials Science Forum 437–438 (online 2003), 81
[35] K. (Ken) Ostrikov, I. Levchenko, U. Cvelbar, M. Sunkara, M. Mozetic, Nanoscale 5 (**2010**) 2012
[36] M. Mozetic, A. Zalar, P. Panjan, M. Bele, S. Pejovnik, R. Grmek, Thin Solid Films, 376 (**2000**), 5
[37] A. Drenik, A. Vesel, A. Kreter, M. Mozetič, Applied Surface Science, (2011) In Press, Accepted Manuscript
[38] M. Wolter, I. Levchenko, H. Kersten, S. Kumar, K. Ostrikov, Journal of Applied Physics, 108 (**2010**), 053302
[39] S. Xu, I. Levchenko, S. Y. Huang, K. Ostrikov, Applied Physics Letters, 95 (**2009**), 111505
[40] R. P. Cardoso, T. Belmonte, C. Noël, F. Kosior, G. Henrion, Journal of Applied Physics,105 (**2009**), 93306
[41] R. P. Cardoso, T. Belmonte, G. Henrion, T. Gries, E. Tixhon, Journal of Applied Physics 107 (**2010**), 24909
[42] A. Vesel, M. Mozetič, P. Panjan, N. Hauptman, M. Klanjsek - Gunde, M. Balat - Pichelin, Surface and Coatings Technology, 204 (**2010**), 1503
[43] J. A. Ferreira, F. L. Tabares, Plasma Sources Science and Technology, 18 (**2009**) 3, 034019
[44] A. Drenik, M. Mozetič, A.Vesel, U.Cvelbar, Journal of Physics: Conference Series, 207 (**2010**), 012009
[45] S. Kumar, I. Levchenko, M. Keidar, K. Ostrikov, Appl. Phys. Lett., 97 (**2010**), 151503
[46] S. Y. Huang, Q. J. Cheng, S. Xu, K. Ostrikov, Appl. Phys. Lett., 97 (**2010**), 213103

[47] A. Drenik, A. Vesel, M. Mozetič, Journal of Nuclear Materials, 386–388 (**2009**), 893
[48] M. Inagaki, E. Bourelle, V. Vignal, H. Konno, A. W. Morawski, Synthetic Metals, 125 (**2001**), 231
[49] A. Böttcher, M. Heil, N. Stürzl, S. S. Jester, S. Malik, F. Pérez-Willard, P. Brenner, M. M. Kappes, Nanotechnology, 17 (**2006**), 5889
[50] V. Chirila, G. Marginean, W. Brandl, Surface and Coatings Technology, 200 (**2005**), 548
[51] C-K. Liu, M.-W. Huang, H. C. Shih, Diamond and Related Materials, 19 (**2010**), 981
[52] I. Levchenko, K. Ostrikov, D. Mariotti, V. Švrček, Carbon, 47 (**2009**), 2379
[53] Z. Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, M. Radmilović-Rađenović Journal of Physics D: Applied Physics, 42 (**2009**), 194002
[54] C. Canal, F. Gaboriau, S. Villeger, U. Cvelbar, A. Ricard, S. Villeger, S. Cousty, B. Rouffet, J-P. Sarrette, P. Erra, A. Ricard, Applied Surface Science, 254 (**2008**), 5959
[55] D. Mariotti, R. Mohan Sankaran, Journal of Physics D: Applied Physics, 43 (**2010**), 23001
[56] I. Levchenko, O. Volotskova, A. Shashurin, Y. Raitses, K. Ostrikov, M. Keidar, Carbon, 48 (**2010**), 4570
[57] G. Gottardi, N. Laidani, R. Bartali, V. Micheli, M. Anderle, Thin Solid Films, 516 (**2008**), 3910
[58] A. Vesel, A. Drenik, M. Mozetic, M. Balat-Pichelin, Vacuum, 84 (**2010**), 969
[59] A. Ricard, F. Gaboriau, C. Canal Surface and Coatings Technology, 202 (**2008**), 5220