SURFACE MODIFICATION OF GRAPHITE BY OXYGEN PLASMA

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Key words: plasma, oxygen, etching, graphite, nanostructure, cone

Abstract: The technology of plasma etching of graphite by highly reactive oxygen plasma is presented. Etching was performed with low pressure cold weakly ionised oxygen plasma created in a glass plasma reactor by an inductively coupled RF generator. The density of charged particles, density of neutral oxygen atoms and the electron temperature was about 2×10^{16} m^{-3}, 6×10^{21} m^{-3}, and 4 eV, respectively. The effects of etching were observed by scanning electron microscopy. It was found that the surface roughness was increased dramatically after plasma treatment. The roughness increased with increasing plasma exposure time. The technology allows for pretty good control of the surface morphology of the samples and thus improved adhesion of different coatings.

Modifikacija površine grafita s kisikovo plazmo

Kjučne besede: plazma, kisik, jedkanje, grafit, nanostructure, stožec

Izvleček: Prikazujemo tehnološki postopek za jedkanje grafita z visoko reaktivno kisikovo plazmo. Za jedkanje uporabimo nizkotlačno hladno kisikovo plazmo, ki jo ustvarimo v steklenem plazemskem reaktorju z induktivno sklopljeno radiofrekvenčno razelektritvijo. Gostota nabitih delcev v naši plazmi je 2×10^{16} m^{-3}, gostota nevtralnih kisikovih atomov 6×10^{21} m^{-3}, temperature elektronov pa okoli 4 eV. Vpliv jedkanja smo spremljali z vrstičnim elektronskim mikroskopom. Ugotovili smo, da kisikova plazmo povzroči zelo močan porast hrapavosti grafita. Hrapavost narašča z naraščajočim časom obdelave. Opisani tehnološki postopek omogoča precej natančno določeno hrapavost materiala, ki je potrebna za izboljšanje adhezivnosti različnih prevlek.

1 Introduction

Advanced methods for the modification of surface properties of different materials often include treatment by gaseous plasma. Gaseous plasma is created in a suitable discharge. It can be created at atmospheric pressure or under vacuum conditions. Atmospheric pressure plasma is often characterized by a pretty high density of charged particles and a moderate, if not high kinetic temperature of neutral gas. /1-7/ Electron temperature is rather low: the typical electron temperature in atmospheric plasma is close to 1eV. Atmospheric plasma is usually limited to a rather small volume inside the discharge chamber. This is due to a high collision frequency of gaseous particles as the mean free path is extremely low. The high collision frequency allows for rapid de-excitation of plasma particles. On the other hand, low pressure plasma can spread far from the discharge region due to a rather small collision frequency./8-12/ Rather homogeneous plasma can be created in large chambers, often of the order of a m^3, if not more. This unique property makes low pressure plasma particularly suitable for treatment of materials and components on the industrial scale. Not surprisingly, low pressure plasma is nowadays widely used in various technologies from the synthesis of nanoparticles to automotive industry. /13-22/ Such plasma if created in oxygen or a mixture of oxygen, is extremely suitable for treatment of organic materials. /23-29/. The plasma parameters vary enormously depending on particular conditions, but as a general rule, the gas usually remains close to the room temperature, the electron temperature easily reaches several eV, while the density of charged particles can be anywhere between about 10^{15} and 10^{18} m^3 /30-33/. Low pressure oxygen plasma is often characterized by a huge density of neutral oxygen atoms /34-37/.

A modern technology based on interaction of oxygen plasma with carbon containing materials is selective etching. /38,39/ Plasma radicals that interact with the surface of materials can cause a surface functionalization with polar functional groups as well as slow etching. /40-42/ Although the flux of plasma radicals onto the surface is usually pretty uniform, the etching is often anisotropic and sometimes also not homogeneous. /43,44/ Plasma treatment often also causes increased surface roughness or even new structures. /38,45-50/ The features formed spontaneously on the surface of carbon containing material depend on the characteristics of specific material as well as on plasma parameters. /51,52/ In the current paper we address the possibility of increasing roughness of pure highly oriented electrolytic graphite.

2 Experimental

Samples were used as received from the NT-MDT producer. No cleaning (degreasing) was performed since oxygen

plasma effectively removes any possible organic impurities from surfaces of materials. The samples were pieces of highly oriented electrolytic graphite (HOPG-ZYH). Samples with the thickness of 1.7 mm were in quadratic pieces with the surface of 1x1 cm^2. Samples were mounted into the discharge chamber of a vacuum system schematically presented in Figure 1. The discharge vessel was a cylindrical tube with inner diameter of 36 mm and the length of 600 mm. The tube was made of a borosilicate glass (Schott 8250) with the recombination coefficient for oxygen atoms at the room temperature of less than $2x10^{-3}$. At both ends it was joined to kovar rings, which were welded to standard KF 40 flanges. The glass-to-metal joint was bakeble up to 400°C. On one side, the tube was connected to the vacuum system. The system was pumped with a two-stage oil rotary pump with the pumping speed of 4.4 l s^{-1} and the base pressure of 0.1 Pa. All connections between the pump and the discharge vessel were made of components with the conductance of approximately two orders of magnitude higher than the pumping speed of the pump, so the effective pumping speed in the discharge vessel was nearly as high as that of the pump. The pressure in the system was measured with a Pirani gauge. Prior to experiments the gauge was calibrated for oxygen with a precise baratron. A recombinator for O atoms was placed in front of the gauge in order to prevent its degradation

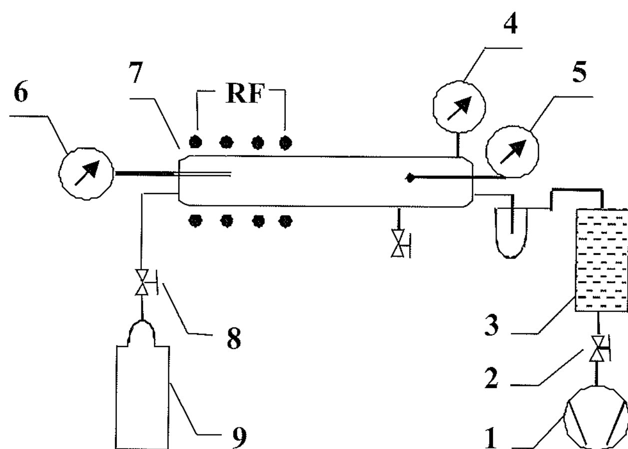
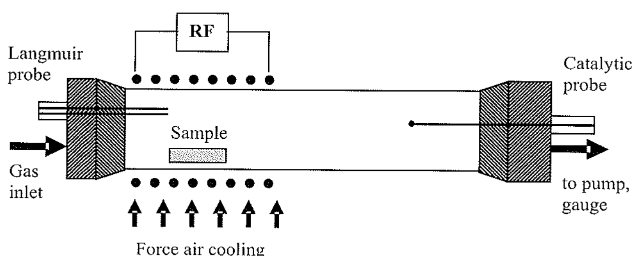


Fig. 1. Schematic of the experimental system. 1 - rotary pump, 2 - valve, 3 – trap with molecular sieves, 4 - vacuum gauge, 5 - catalytic probe, 6 – Langmuir probe, 7 – optical fibre catalytic probe, 8 - discharge chamber, 9 - leak valve, 10 - oxygen flask



Fg. 2. The plasma reactor.

during plasma experiments. The discharge vessel was placed in a coil connected to a RF generator as shown in Figure 2. The frequency of the generator was 27.12 MHz and the output power approximately 250 W. The other side of the discharge vessel was connected to a gas inlet system. Commercially available oxygen was leaked to the system trough a leak valve. The discharge vessel was forced air-cooled.

The parameters of plasma in the discharge vessel were measured with a double Langmuir probe and a nickel catalytic probe. Measurements with Langmuir and catalytic probes were performed prior to experiments with samples. The position of the two probes is shown in Figure 2. The Langmuir probe is placed in the plasma region (to allow for proper reading of the electron temperature and plasma density) while the catalytic probe was mounted into afterglow, about 20 cm away from the glowing plasma region. The reasons for that were explained to details in /35,53,54/. Due to the completeness of this paper let us briefly repeat them here. Catalytic probes are based on measuring power released on the catalyst surface due to heterogeneous surface recombination of oxygen atoms. While they make give accurate results in afterglows, they are less accurate in plasma itself where other heating mechanisms have to be taken into account. Since other mechanisms (relaxation of metastables, recombination of charged particles, bombardment by positive ions, absorption of light quanta) are generally difficult to estimate, the probes are better placed in the afterglow, where they give accurate atom density in their vicinity. The oxygen atom density in the plasma itself is then calculated by taking into account the known oxygen atom decay along a continuously pumped glass tube (as explained in /35,53,55/). The density of charged particles was about $2x10^{16}$ m^{-3} and the electron temperature about 4 eV. The density of neutral oxygen atoms was $6x10^{21}$ m^{-3}.

The surface of the samples was imaged after the plasma treatment with a Scanning Electron Microscope (SEM) The SEM images obtained using a field emission microscope Carl Zeiss Supra 35 VP at accelerating voltage of 1 keV.

3 Results and discussion

The SEM images of plasma treated samples are presented in Figures 3 - 12. The original material is extremely flat so the SEM image does not reveal any measurable feature and is therefore not presented in this paper. After 10s of plasma treatment the surface of graphite remains practically intact as demonstrated by Fig. 3. The dose of oxygen atoms is calculated using equation (1)

$$D = 1/4\, n\, v\, t \qquad (1)$$

Where n is the atom density, v the average thermal velocity of oxygen atoms and t the treatment time. In 10s, the dose is $9x10^{24}$ m^{-2}. From this calculation it is possible to conclude that doses below $10^{25} m^{-2}$ are pretty benign to highly oriented graphite.

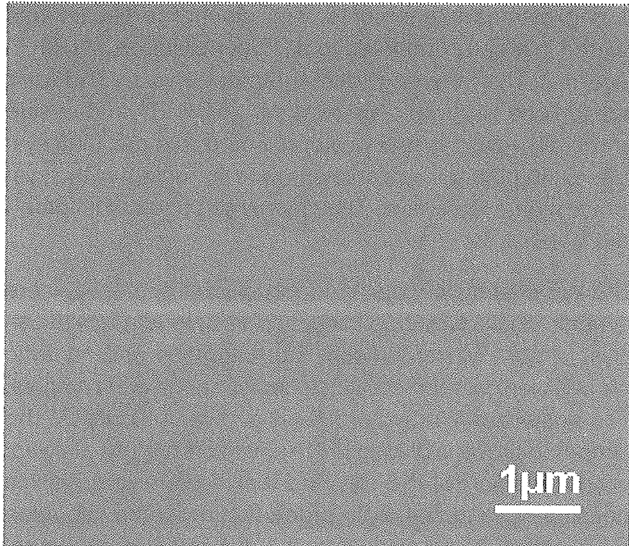


Fig. 3. SEM image of a sample exposed to plasma for 10s.

Interesting features are observed after 90s of plasma treatment. The corresponding SEM images are presented in Figures 4-6. The surface is far from being smooth. It is rather covered with small and almost spherical features with the typical diameter of few micrometers. The appearance of these features is definitely due to etching of graphite by oxygen atoms. Namely, positively charged oxygen ions that are other possible plasma particles capable of etching graphite are found at minor concentrations. Since the ion density in our plasma is more than 5 orders of magnitude smaller than the neutral atom density, they cannot cause such intensive etching even if all ions would remove a carbon atom from the surface of the samples. The flux of oxygen atoms onto the surface of graphite is homogeneous and isotropic so the formation of such structures is rather surprising. The anisotropic etching can be explained by localized inhomogeneity of the samples. Namely, any defect, even at atomic

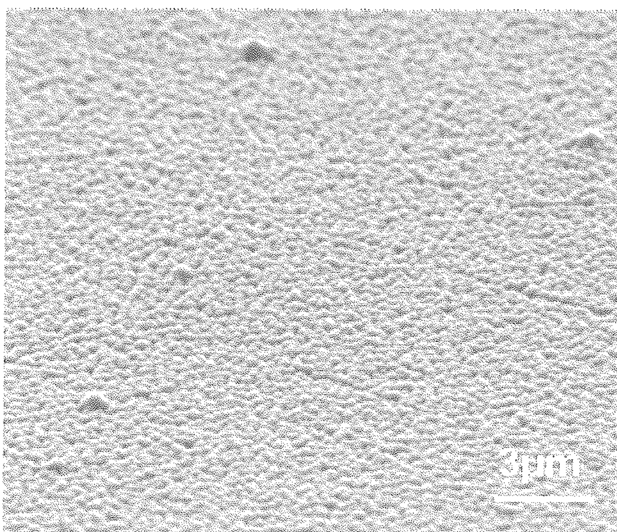


Fig. 4. SEM image of a sample exposed to plasma for 90s at low magnification

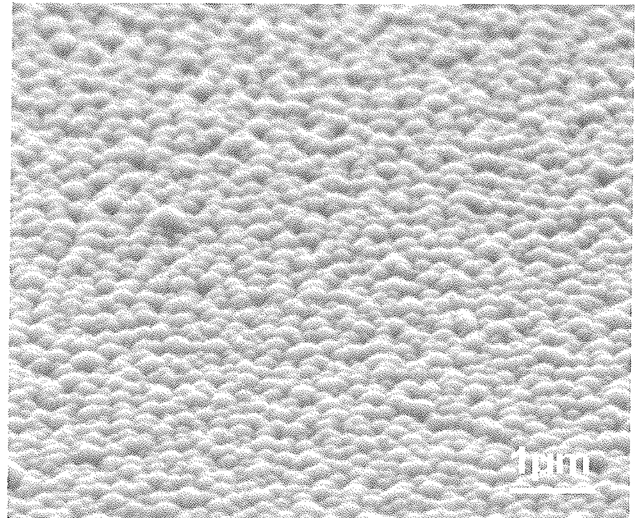


Fig. 5. SEM image of a sample exposed to plasma for 90s at medium magnification

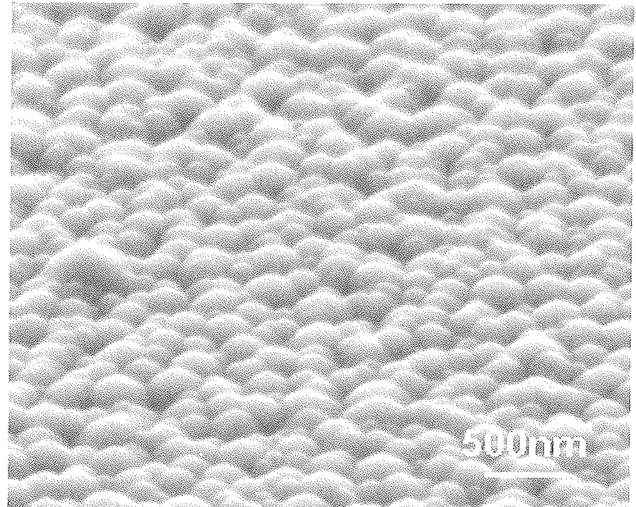


Fig. 6. SEM image of a sample exposed to plasma for 90s at high magnification.

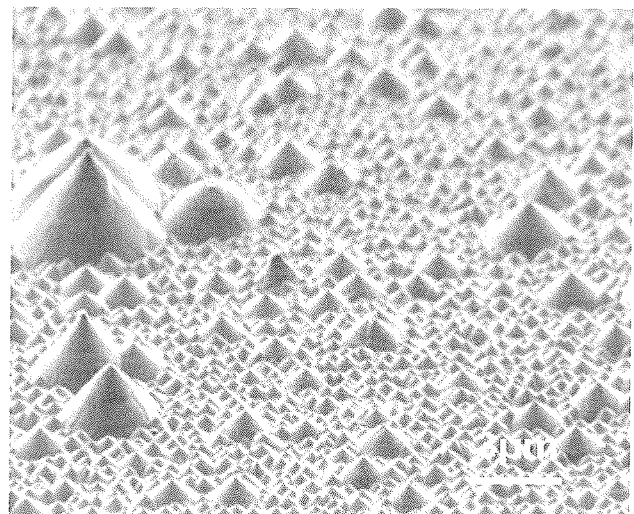


Fig. 7. SEM image of a sample exposed to plasma for 180s at low magnification.

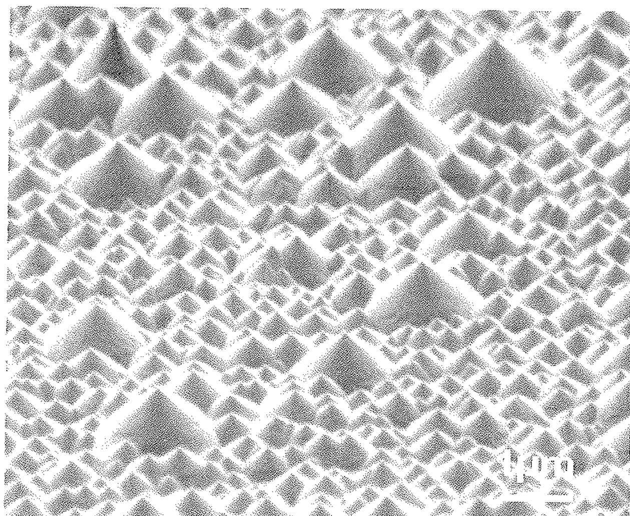


Fig. 8. SEM image of a sample exposed to plasma for 180s at medium magnification.

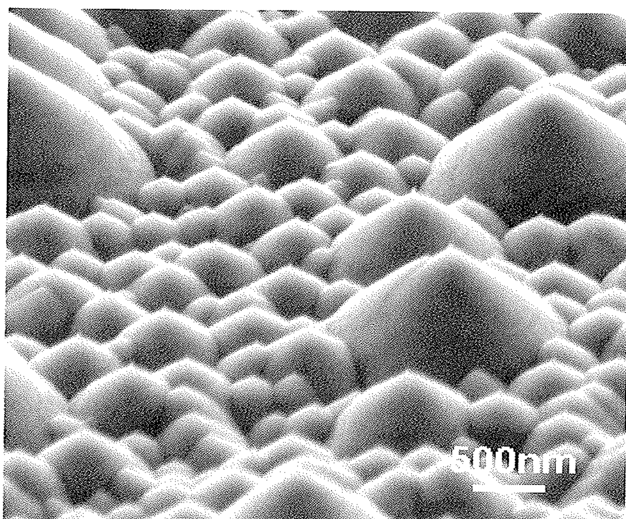


Fig. 9. SEM image of a sample exposed to plasma for 180s at high magnification.

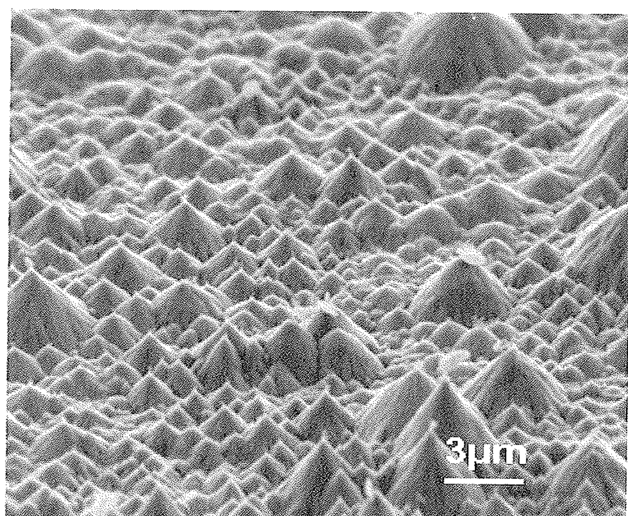


Fig. 10. SEM image of a sample exposed to plasma for 600s at low magnification

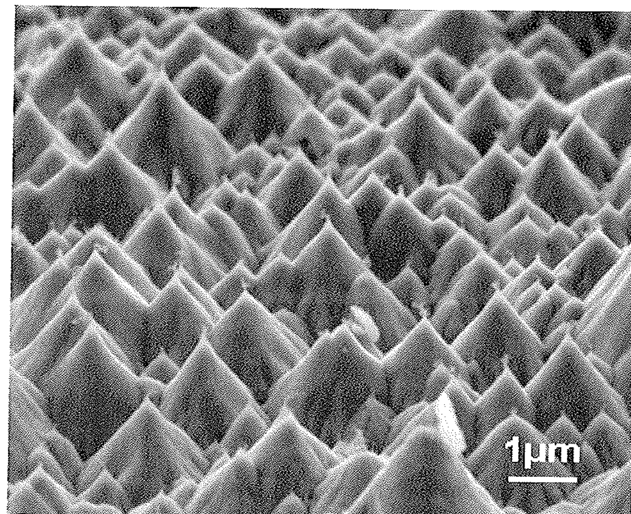


Fig. 11. SEM image of a sample exposed to plasma for 600s at medium magnification

scale, would lead to somewhat different reaction probability. Since the received dose is huge (after 90s of plasma treatment the dose is about $8x10^{25}m^{-2}$) the atoms can be extremely selective and still capable of removal carbon atoms. It is well known that any selectivity of etching causes the so-called orange skin effect: the etching un-isotropy keeps increasing with increasing dose of reactant.

The next step in etching is formation of conical features on the surface of our samples as demonstrated from Figures 7-9. The lateral size of the features remains the same as after treatment for 90s, but the shape is definitely more conical. This effect could be explained by taking into account original crystalline structure of our graphite. Our samples, however, are made from highly oriented graphite so it is not probable that the crystallites would be of observed shape. The formation of the cones is rather explained by another effect. One of them is self - organization of atoms on the surface of plasma - exposed samples. /44, 56-60/.

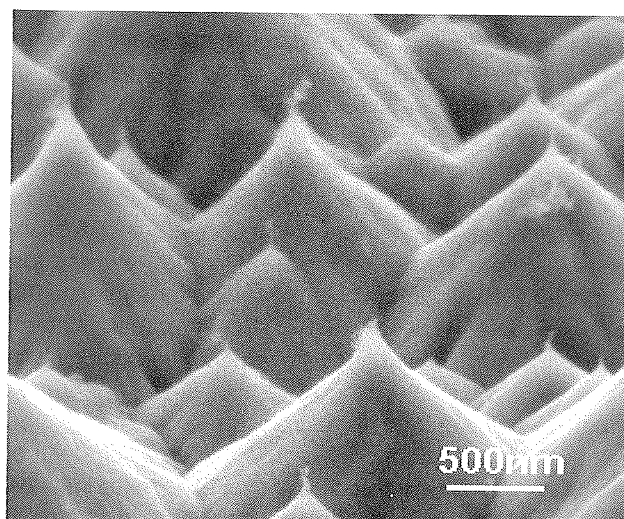


Fig. 12. SEM image of a sample exposed to plasma for 600s at high magnification

Namely, the surface mobility of atoms on the surface of samples under treatment with highly reactive plasma is huge comparing to the value calculated from the sample temperature assuming thermodynamic equilibrium. Our experiments may represent just another proof of the recent theory by Ostikov who predicted self-assembly and self-organization of material under extreme non-equilibrium conditions. Carbon atoms can have so high surface mobility that they move on the surface at the nanometer scale until they reach a thermodynamically more favourable position. /61, 62/ This position is definitely in the crystalline structure. The conical shape of the surface features may therefore be small crystals formed due to increased surface mobility of carbon atoms.

Prolonged plasma treatment does not influence the shape of surface features much, apart from the fact that the height of the features is much bigger. SEM images of samples treated for 600s are presented in Figures 10-12. Oxygen atoms obviously cause side etching of the features. The height of highest cones obtained after plasma treatment for 600s is several micrometers. This fact allows for (extremely rough) estimation of the etching rate. If the effective thickness of the removed layer is 3000 nm, then the etching rate will be

$$dx/dt = 3000\mathrm{nm}/600\mathrm{s} = 5\mathrm{nm/s} \quad (2)$$

Let us finally calculate the probability that an atom reaching the surface would remove a carbon atom. The probability is proportional to the etching rate and treatment time as well as the density of our material, and inversely proportional to the received dose of oxygen atoms:

$$\eta = dx/dt\, \rho\, t \,/\, 12u\, D \quad (3)$$

Taking into account numerical values, i.e. $dx/dt = 5\times10^{-9}$ m/s, $\rho = 2200$ kg/m^3, $t = 600$s, $u = 1.7\times10^{-27}$ kg and $D = 5\times10^{26}$ m^{-2} the probability is estimated to $\eta = 8\times10^{-3}$.

4 Conclusion

The change in morphology of graphite can result in better performance of graphite based devices like gas sensing, energy conversion and others./63,64/ Therefore, highly oriented graphite was exposed to highly reactive oxygen plasma with the atom density of 6×10^{21} m^{-3}. The samples were kept in plasma for different time up to 600s. After plasma treatment, the samples were characterized by scanning electron microscopy. The SEM images revealed formation of surface features whose shape depended on the received dose of oxygen atoms. Up to the dose of about 1×10^{25}m^{-2} no visible changes in surface morphology was observed. With increasing dose the surface becomes rough revealing orange-like skin morphology. The features were initially rather spherical and with increasing dose of atoms they became conical. The critical dose for transformation from the spherical to conical shape was almost 1×10^{26} m^{-2}. The transformation was explained by self-organization of atoms on the surface of the samples under extremely non-equilibrium conditions. Prolonged treatment of samples with oxygen plasma causes an extremely rough surface with well pronounced conical shape of surface features. The height of the highest cones allowed for estimation of the etching rate which was found to be about 5 nm/s. Since the oxygen atom density was measured it was possible to estimate also the reaction probability which was found to be almost 1%.

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